

Rudolf Clausius and the road to entropy

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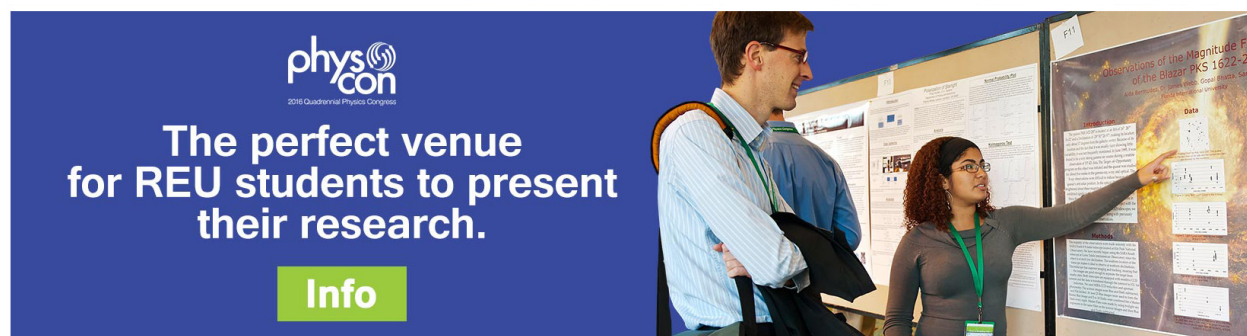
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Rudolf Clausius and the road to entropy

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That Rudolf Clausius invented the entropy concept is well known, but less familiar is the argument that served as his inspiration. This paper traces the development of Clausius' "transformation theory" of heat, which finally persuaded him to define the measure of transformation equivalence he called entropy.

Most of the fundamental concepts of classical thermodynamics were developed during the middle fifty years of the nineteenth century. The story begins with the work of Sadi Carnot on heat engines, published in 1824. Carnot showed theoretically, and in some rather rough calculations, that the efficiency (work output compared to heat input) of any heat engine operated in a reversible, cyclic mode had a maximum value and was dependent only on the engine's operating temperatures. Carnot died in 1832 when he was thirty-six, and for reasons which will probably never be more than half understood, his scientific work almost died with him. His memoir was first ignored and then nearly lost for almost twenty-five years.

Carnot's work was resurrected by two second-generation thermodynamicists, Rudolf Clausius and William Thomson (later Lord Kelvin), who were born (in 1822 and 1824) almost at the same time as Carnot's revolutionary memoir; they were, so to speak, Carnot's scientific progeny. Both Clausius and Thomson were profoundly influenced by Carnot's analysis. The Carnot heat-engine efficiency principle was Thomson's main inspiration in his lengthy search for an acceptable absolute temperature scale. First Clausius (in 1850), and then Thomson (independently, in 1851), modified Carnot's approach to permit the description of noncyclic processes, a crucial step in the history of thermodynamics because it necessitated the invention of a state variable to represent energy. Then, beginning with a simple extension of Carnot's fundamental cyclic device, Clausius developed his "transformation theory" which led finally to the entropy concept.

Clausius finally concluded in 1865 that thermodynamics should be based on two concepts, energy and entropy. This was just the clue needed by a third-generation thermodynamicist, Willard Gibbs, who developed the Clausius energy-entropy picture into an equilibrium theory of vast scope. Clausius' last words on the subject of thermodynamics, the famous energy and entropy rules,

The energy of the universe is constant,

The entropy of the universe tends to a maximum, were Gibbs' first words in his great 1875 monograph on the principles of equilibrium.

A full account of Clausius' role in the development of classical thermodynamics would require more space than we have in one paper. There is room for just one chapter from the Clausius book, the one that tells what is probably the most important, and at the same time least understood, part of the Clausius story, his development of the entropy concept.

Clausius initiated this work in a lengthy paper on heat theory published in 1854.¹ As before in his contributions to heat theory, he began his analysis with Carnot's heat-engine theory modified to assume that heat could undergo

two kinds of "transformations." With Carnot, he postulated that heat could drop from a high temperature to a low temperature in what we shall call a "transmission transformation" (this is not Clausius' terminology). Contrary to Carnot, however, he also assumed that heat could be converted to work in a "conversion transformation." Clausius was impressed by the fact that both kinds of transformations had two possible directions, one "natural" and the other "unnatural" (again, this is not Clausius' terminology). In the natural direction, a transformation could proceed by itself, spontaneously and unaided, while the unnatural direction was not possible at all unless forced by some outside influence.

The natural direction for the conversion transformation could be seen in James Joule's many observations of heat produced from work. Clausius saw the unnatural direction for the conversion transformation in the production of work from heat, a transformation which never took place by itself, but always had to be forced somehow in heat-engine operation. The natural direction for the transmission transformation was clearly the direct conduction of heat from a high temperature to a low temperature. The unnatural direction was the opposite transport from a low temperature to a high temperature, which was impossible as a spontaneous process; if such heat transport occurred at all, it had to be forced.

Clausius took this reasoning one very significant step further. He saw that in heat-engine operation the two kinds of heat transformations occurred at the same time. In each cycle of operation, the transmission transformation took place in its natural direction (heat dropped from a high to a low temperature), while the conversion transformation proceeded in its unnatural direction (heat converted to work). It was as if the transmission transformation was *driving* the conversion transformation in its unnatural direction. Moreover, if the heat engine was reversible, the conversion transformation could be run in its natural direction (work converted to heat) and made to drive the transmission transformation in its unnatural direction (heat raised from a low to a high temperature).

To formulate these ideas, Clausius pictured heat supplied from and to heat reservoirs and visualized some active medium or device, which we shall call the "system," communicating among the reservoirs and making possible the two kinds of transformations. In his various discussions of heat theory, Clausius sometimes took the viewpoint of the reservoirs, and other times he emphasized the system. These conceptual switches were a perennial source of confusion to Clausius' critics.

Clausius started his 1854 paper by introducing a special elaboration of the cyclic process Carnot had invented. Clausius' cycle was a six-stage, reversible, cyclic process

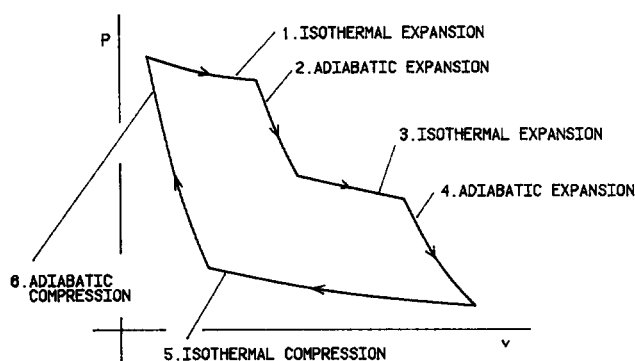


Fig. 1. The four expansion and two compression steps of the Clausius cycle, displayed in a pressure-volume plot. The diagram shows what happens to the system in one turn of the cycle.

involving four expansion steps and two compression steps in the following sequence:

Step 1, an isothermal expansion at the temperature t (expressed, say, on the centigrade scale) in which the heat Q was supplied to the system from the reservoir K .

Step 2, an adiabatic expansion in which the temperature decreased from t to t_2 .

Step 3, an isothermal expansion at t_2 in which the heat Q_2 was supplied to the system from the reservoir K_2 .

Step 4, an adiabatic expansion in which the temperature decreased further from t_2 to t_1 .

Step 5, an isothermal compression at t_1 in which heat Q_2 was supplied to a reservoir K_1 .

Step 6, an adiabatic compression in which the temperature increased from t_1 back to t .

Figure 1 shows how the cycle affects the pressure and volume of the system, and in Fig. 2 the heats Q and Q_2 are seen coming from, or going to, the reservoirs K , K_1 , and K_2 .

Clausius designed his cycle so it caused an amount of heat Q to undergo a conversion transformation, and at the same time it put the heat Q_2 through a transmission transformation between the temperatures t_2 and t_1 . Clausius demonstrated the conversion transformation by returning to an equation he had introduced in his 1850 paper,²

$$dQ = dU + APdv. \quad (1)$$

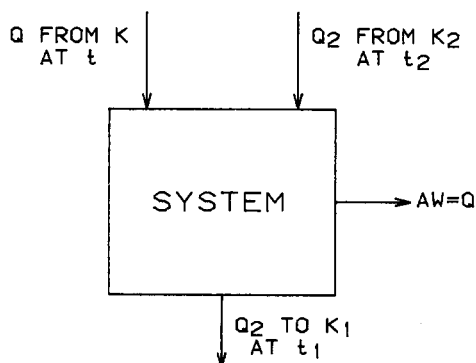


Fig. 2. The effect of one turn of the Clausius cycle displayed in a diagram which shows the heats Q and Q_2 coming from the reservoirs K and K_2 at the temperatures t and t_2 , and the heat Q_2 going to the reservoir K_1 at t_1 . The heat Q is converted to the work W .

The quantity dQ represented a small amount of heat supplied to, or lost from, the system; P and v were the system's pressure and specific volume; A was a factor which changed the mechanical units required by Pdv into the thermal units required by dQ (the value of A had been accurately determined by Joule in the 1840's).

In 1854, Clausius' understanding of the term dU in Eq. (1) was incomplete. He could prove that U was a state variable, dependent only on the state-determining variables v and t , but the physical meaning of the function was not entirely clear. He read Eq. (1) to mean that the heat dQ supplied to a system could either become "sensible heat" once it had entered the system, that is, its effect could be measured on a thermometer, or it could be converted into work. He recognized two kinds of work, that performed *internally* (against intramolecular or intermolecular forces in the modern interpretation) and that done *externally*, against an applied pressure. The term $APdv$ in Eq. (1) obviously evaluated the latter, so Clausius concluded that dU calculated two things, changes in the "sensible heat" and the amount of internal work done, if any.

At the same time Clausius was developing the interpretation of his function $U(v, t)$, Thomson was inventing a theory based on an identical function, which he labeled $e(v, t)$.³ Thomson had a name for his function—"mechanical energy"—and he understood it to be a measure of the mechanical effect remaining stored in a system after it exchanged heat and work with its surroundings. Thomson later used the term "intrinsic energy" for his function $e(v, t)$,⁴ and Helmholtz eventually called it "internal energy."⁵ It is an impressive measure of the subtlety of the energy concept—and of Thomson's insight—that Clausius was not willing to accept Thomson's energy theory for almost fifteen years. In 1865 he began calling his function U energy, and Eq. (1) written

$$dU = dQ - APdv$$

became the familiar statement of the First Law of Thermodynamics.⁶

When (in 1854) Clausius applied his Eq. (1) to his six-stage cycle, an integrated result was obtained,

$$\int dQ = \int dU + A \int Pdv, \quad (2)$$

in which the integration symbol meant adding contributions for the entire cycle. Taking the viewpoint of the system, he evaluated $\int dQ$ as the algebraic sum of the two heat inputs Q and Q_2 and the heat output Q_2 ,

$$\int dQ = Q + Q_2 - Q_2 = Q.$$

The net work W done in the cycle, a positive quantity in Clausius' scheme if done by the system, was obtained from the integral $\int Pdv$,

$$\int Pdv = W.$$

Since U was a state variable, dependent only on v and t , its integral around the cyclic path of Clausius' process was zero,

$$\int dU = 0.$$

Thus the integrated Eq. (2) became

$$Q = AW,$$

and this demonstrated the conclusion that Clausius' cycle caused the amount of heat Q to undergo a conversion transformation. Since this was a heat-to-work transformation, it had the unnatural direction.

At the same time, the Clausius cycle permitted the heat Q_2 to go through a transmission transformation between the temperature t_2 and t_1 . This was the natural direction for that transformation, and it was seemingly driving the conversion transformation in its unnatural direction. We shall represent the conversion transformation of the heat Q originating at the temperature t with the abbreviated notation (not used by Clausius),

$$Q[t] \rightarrow W,$$

and the transmission transformation of the heat Q_2 from the temperature t_2 to the temperature t_1 with

$$Q_2[t_2] \rightarrow Q_2[t_1].$$

The entire Clausius cycle is

$$\left\{ \begin{array}{l} Q[t] \rightarrow W \\ Q_2[t_2] \rightarrow Q_2[t_1] \end{array} \right\} \quad (3)$$

in this representation. Clausius always assumed that his cycle was reversible, so it could be completely turned around with no appreciable effects in the surroundings. It then became

$$\left\{ \begin{array}{l} W \rightarrow Q[t] \\ Q_2[t_1] \rightarrow Q_2[t_2] \end{array} \right\}$$

in our abbreviated notation. The conversion transformation, now proceeding in the natural direction, was driving the transmission transformation in its unnatural direction. In the first case, the transmission transformation dominated (just barely) and provided the driving force that made the conversion transformation go in its unnatural direction. In the second case, the conversion transformation dominated (just barely) and was driving the transmission transformation in its unnatural direction.

This theoretical picture suggested to Clausius that the two transformations were so nearly balanced in his reversible cycle that either could dominate the other. They were, in some sense, equivalent to each other. Clausius set out to construct a quantitative transformation theory which would follow this lead. His goal was to assess "equivalence values" for both transformations in his cycle and in other reversible processes. He hoped that the equivalence values could then be used to express in a new natural law the

condition of balance, or "compensation" as he called it. Although he could hardly have been aware of it at the time, Clausius had, in this simple theoretical expectation, started a line of reasoning as promising as any in the history of science. It would not be easy for him to appreciate fully the importance of what he was doing, but he now had all the theoretical clues he needed to reach the concept of entropy and its great principle, the Second Law of Thermodynamics.

Clausius began his transformation theory by assuming that equivalence values for either kind of transformation were proportional to the amount of heat transformed and also to some function of the temperature or temperatures involved. For his cycle, the assumptions were

$$\left. \begin{array}{l} \text{Equivalence value for the} \\ \text{conversion transformation} \end{array} \right\} = f(t)Q, \quad (4)$$

$$\left. \begin{array}{l} W \rightarrow Q[t] \\ \text{Equivalence value for the} \\ \text{transmission transformation} \end{array} \right\} = F(t_2, t_1)Q_2, \quad (5)$$

$$Q_2[t_2] \rightarrow Q_2[t_1]$$

in which $f(t)$ and $F(t_2, t_1)$ were functions of the temperatures indicated. These statements were both made for the transformations proceeding in their natural directions. For the unnatural directions of both transformations, Clausius assumed the equivalence values to have the same magnitudes but opposite signs,

$$\left. \begin{array}{l} \text{Equivalence value for the} \\ \text{conversion transformation} \end{array} \right\} = -f(t)Q, \quad (6)$$

$$\left. \begin{array}{l} Q[t] \rightarrow W \\ \text{Equivalence value for the} \\ \text{transmission transformation} \end{array} \right\} = -F(t_2, t_1)Q_2, \quad (7)$$

$$Q_2[t_1] \rightarrow Q_2[t_2]$$

For the Clausius cycle (3), the two appropriate equivalence values were given by Eqs. (5) and (6). Clausius wrote his fundamental condition of balance or compensation by simply setting the sum of these two equivalence values equal to zero,

$$F(t_2, t_1)Q_2 - f(t)Q = 0. \quad (8)$$

A similar analysis could be made for another Clausius cycle,

$$\left\{ \begin{array}{l} Q'[t'] \rightarrow W \\ Q_2[t_2] \rightarrow Q_2[t_1] \end{array} \right\},$$

in which a different amount of heat Q' , originating at a different temperature t' , was converted. The condition of compensation in this case was

$$F(t_2, t_1)Q_2 - f(t')Q' = 0.$$

Combination of this result with Eq. (8) led to an important property of the function $f(t)$, that its magnitude was inversely proportional to the amount of heat transformed, that is

$$f(t)Q = f(t')Q'. \quad (9)$$

A simple connection between the two functions of temperature f and F could be derived by applying the equivalence-value analysis to a reversible cycle whose effect is illustrated in Fig. 3. This was the cycle originally designed by Carnot to give maximum heat-engine efficiency. It had heat input at one temperature (rather than two temperatures, as in Clausius' cycle). Analysis of Carnot's cycle

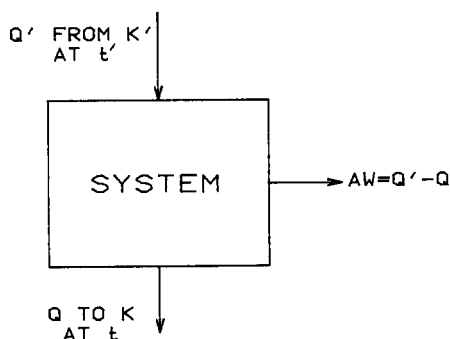


Fig. 3. The effect of one turn of the Carnot cycle displayed in a diagram which shows the heat Q' coming from the reservoir K' at the temperature t' , and the heat Q going to the reservoir K at t . The heat $Q' - Q$ is converted to work W .

with Clausius' Eq. (1) indicated that the work done for each turn of the cycle was determined by

$$AW = Q' - Q,$$

and therefore that the heat $Q' - Q$, originating at t' , was involved in a conversion transformation. At the same time, the heat Q went through a transmission transformation from t' to t . In this case, Clausius' equivalence-value calculation led to the condition of compensation,

$$F(t', t)Q - f(t')(Q' - Q) = 0. \quad (10)$$

Combined with Eq. (9), this became

$$F(t', t) = f(t) - f(t'). \quad (11)$$

This was another cornerstone of Clausius' transformation theory. It showed that a *single* function, the still undetermined $f(t)$, sufficed for equivalence-value determinations.

For Clausius' cycle, Eq. (11) was

$$F(t_2, t_1) = f(t_1) - f(t_2),$$

and this revised the condition of compensation (8) to

$$f(t_2)Q_2 - f(t_1)Q_2 + f(t)Q = 0.$$

The terms in this equation were all of the form $\pm f(t)Q$, with Q a heat input to, or output from, the system, and t the temperature at which the heat entered or left. The terms were positive for heat inputs and negative for outputs. (We are taking the viewpoint of the system.) Equation (10) for the Carnot cycle came out the same way when it was combined with Eq. (11),

$$f(t')Q' - f(t)Q = 0.$$

Again an equation was derived with terms of the kind $f(t)Q$ for heat inputs and outputs. Equivalence-value calculations for other reversible cycles reduced to equations of exactly the same form.

Clausius' original technique of requiring compensating equivalence values for reversible, cyclic processes had now revealed a simpler, and as it turned out, far more significant, pattern. Clausius was able to prove that *any* reversible cycle could be represented by a vanishing sum of $f(t)Q$ terms, with the Q s and t s interpreted as explained above. His general conclusion could be put

$$\sum f(t)Q = 0 \quad (\text{reversible, cyclic processes}),$$

for a process with a finite number of steps, or

$$\int f(t)dQ = 0 \quad (\text{reversible, cyclic processes}), \quad (12)$$

for a process consisting of an infinite number of steps, each one involving an infinitesimal heat transfer of amount dQ at the temperature t .

Clausius' proof of his general conclusion is too lengthy to fit into our limited space, but it is important to mention that the only assumption in the proof was the phenomenological "axiom" that heat cannot be transmitted from cold to hot. In his 1854 paper, Clausius stated his assumption: "Heat can never pass from a colder to a warmer body without some other change connected therewith, occurring at the same time."⁷ Later he simplified his axiom to: "Heat cannot of itself pass from a colder to a warmer body."⁸

Clausius must have quickly recognized that in making the seemingly formal change in his equivalence-value calculation that led to Eq. (12) he had actually taken a step of

considerable mathematical and physical significance. He was aware of the mathematical fact that vanishing of an integral $\int dF$, evaluated for a cyclic path determined by the independent variables x and y , guaranteed that dF was a differential of a function $F(x, y)$ of x and y . Applied to his conclusion (12), this theorem told him that the quantity $f(t)dQ$ was equal to the differential of some function of the state-determining variables used to define the reversible, cyclic process, perhaps v and t , or P and v . He had, in other words, discovered another state function, in addition to the function U defined and partially interpreted in his 1850 paper.

In this case, however, the interpretation was even more difficult. Just what the quantity $f(t)dQ$ meant in the physical problem was anything but clear. The integral $\int f(t)dQ$ performed in Clausius' theory as an assessment of transformation equivalence values, but its broader significance was still a mystery. As a skilled theoretician, Clausius was aware of the dangers of attaching too much physical meaning to quantities which might be found later to be mere figments of the mathematical argument. He did not offer a name for the new state function in 1854, nor did he even give it a symbol.

Sill Clausius felt he could trust his conclusion that $f(t)dQ$ was the differential of a state function, and from that mathematical fact he could determine the function $f(t)$. It will be easier to follow his argument here if we temporarily use the letter C (for Clausius) to represent his new state function (Clausius eventually, ten years later, decided on the letter S). Assuming with Clausius that the state-determining variables v and t are of interest, we write his new state function $C(v, t)$ and define its differential changes

$$dC = f(t)dQ \quad (\text{reversible processes}). \quad (13)$$

Notice the reversibility stipulation, without it the original integral statement (12) is not justified, so it must be included here.

Since $C(v, t)$ (as we are calling it) was a state function, Clausius reasoned in effect, its second derivatives with respect to v and t had to be equivalent:

$$\left[\frac{\partial}{\partial t} \left(\frac{\partial C}{\partial v} \right) \right]_v = \left[\frac{\partial}{\partial v} \left(\frac{\partial C}{\partial t} \right) \right]_t.$$

The two derivatives $(\partial C / \partial v)_t$ and $(\partial C / \partial t)_v$ could be evaluated by making use of a simple physical statement,⁹

$$dQ = Mdv + Ndt, \quad (14)$$

in which v and t were the specific volume and temperature of a system. As Truesdell remarks,¹⁰ equations like this had been in use for many years to represent the data of calorimetry. The equation pictured an amount of heat dQ added very slowly (in effect, reversibly) to a system, causing changes dv and dt in the system's volume and temperature. The factors M and N , determined by the particular material present in the system, represented the heat required to cause one-unit changes in the volume and temperature. The coefficient M was called the "latent heat of expansion," and N was the (constant-volume) heat capacity.

From the "calorimetry equation" (14) Clausius derived

$$dC = f(t)dQ = f(t)Mdv + f(t)Ndt,$$

and established that

$$\left(\frac{\partial C}{\partial v}\right)_t = f(t)M,$$

$$\left(\frac{\partial C}{\partial t}\right)_v = f(t)N.$$

Thus,

$$\left[\frac{\partial}{\partial t}\left(\frac{\partial C}{\partial v}\right)_t\right]_v = f'(t)M + f(t)\left(\frac{\partial M}{\partial t}\right)_v,$$

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial C}{\partial t}\right)_v\right]_t = f(t)\left(\frac{\partial N}{\partial v}\right)_t,$$

and equivalence of these expressions for the second derivatives led to a differential equation involving $f(t)$,

$$f'(t)M + f(t)\left(\frac{\partial M}{\partial t}\right)_v = f(t)\left(\frac{\partial N}{\partial v}\right)_t,$$

or

$$f'(t)M = f(t)\left[\left(\frac{\partial N}{\partial v}\right)_t - \left(\frac{\partial M}{\partial t}\right)_v\right].$$

In his 1850 paper, Clausius had proved that the expression on the right in the brackets was equivalent to $-A(\partial P/\partial t)_v$.¹¹ Thus the equation for $f(t)$ reduced to

$$f'(t)M = -Af\left(\frac{\partial P}{\partial t}\right)_v. \quad (15)$$

Clausius regarded $f(t)$ as a universal function which could be determined once and for all, most easily with M and $(\partial P/\partial t)_v$ in Eq. (15) evaluated for the ideal-gas case. He wrote the ideal gas law in the form

$$Pv = R(a + t),$$

with $a + t$ expressing the absolute temperature (Clausius assumed that the constant a had a value of about 273 °C), so

$$\left(\frac{\partial P}{\partial t}\right)_v = R/v. \quad (16)$$

He could evaluate the factor M for an ideal gas by writing the calorimetry equation (14) for an isothermal expansion,

$$dQ = Mdv \quad (\text{constant } T),$$

and then assuming, as Mayer and others had before him,¹² that when an ideal gas expanded isothermally all the heat it absorbed was converted to work, that is,

$$dQ = APdv \quad (\text{constant } T).$$

For an ideal gas, then,

$$M = AP. \quad (17)$$

When the two results (16) and (17) were substituted in Eq. (15) the $f(t)$ -determining equation became

$$Af'(t)P = -Af(t)R/v.$$

Substituting

$$P = R(a + t)/v$$

from the ideal-gas equation finally whittled the $f(t)$ equation to just

$$f'(t) = -f(t)/(a + t)$$

or

$$d \ln f = -d \ln(a + t).$$

Integration of the last equation produced a usable expres-

sion for $f(t)$:

$$f(t) = (\text{constant})/(a + t),$$

so Eq. (13) became

$$dC = (\text{constant})dQ/(a + t) \quad (\text{reversible processes}).$$

The constant factor, mathematically a constant of integration, simply determined the scale which measured C . The constant's value was arbitrary; Clausius chose a value of a unity and wrote

$$dC = dQ/(a + t) \quad (\text{reversible processes}).$$

Clausius represented the absolute temperature $a + t$ with T , and his final expression for the differential of his function was

$$dC = dQ/T \quad (\text{reversible processes}), \quad (18)$$

a familiar expression when our C is replaced by Clausius' S .

Even though the name and the symbol were missing in his 1854 memoir, Clausius had formulated in that paper rudiments of the theory of the concept he would eventually call entropy. Clausius was aware in 1854, however, that the theoretical picture he had created of the new concept was limited in several important ways. The differentials calculated according to the prescription (18) could so far be used *only* to set the condition (12), which was in turn rather severely limited to cyclic and reversible processes. The condition of reversibility had originally been invented by Carnot to define an ideal mode of heat-engine operation, ideal in the sense that it gave maximum efficiency. Reversibility was essential in Clausius' analysis because it permitted him to assert that his two kinds of heat transformation compensated each other. Carnot had also been the first to recognize the theoretical importance of cyclic processes; he had used his famous four-stage gas cycle in some of his most far-reaching arguments. Here, too, Clausius followed Carnot's lead; his theory began with a six-stage cycle, patterned after Carnot's, and was finally generalized in Eq. (12) to cyclic processes of any kind.

Clausius had done wonderful things with Carnot's theoretical style. One can imagine that if Carnot had lived longer (he would have been fifty-four in 1850), and if he had recognized the fact that heat could be transformed by conversion as well as by transmission, he might have reasoned much as Clausius did in 1850 and 1854. In the two papers, Clausius had done what Carnot demanded; and then in the 1854 paper he began to move beyond Carnot, into the more realistic realm of irreversible processes which were not of the ideal, reversible kind. Clausius showed, in a proof which is too lengthy to cover here, that the integral $\int dQ/T$, which vanished for cyclic, reversible processes, *always* had *negative* values for cyclic, irreversible processes¹³:

$$\int dQ/T = 0 \quad (\text{reversible, cyclic processes}),$$

$$\int dQ/T < 0 \quad (\text{irreversible, cyclic processes}).$$

Clausius used the letter N to represent the magnitude of his $\int dQ/T$ integral,

$$N = -\int dQ/T \quad (\text{cyclic processes}),$$

and expressed his conclusions

$$N = 0 \quad (\text{reversible, cyclic processes})$$

$$N > 0 \quad (\text{irreversible, cyclic processes}).$$

[Don't confuse this N with the N used as the temperature coefficient in the calorimetry Eq. (14).] In general, Clausius concluded, his integral $\oint dQ/T$, and therefore N , were measures of the equivalence values for all transformations occurring in a cycle. If the cycle was operated reversibly, all the transformations were balanced or compensated and N vanished. If the operation of the cycle was irreversible, some of the transformations were "uncompensated" (e.g., direct transmission of heat from hot to cold without a compensating conversion of heat to work) and N assessed the equivalence values of these uncompensated transformations.

Clausius had made another valuable addition to Carnot's theoretical repertoire in his 1850 and 1854 papers, his introduction of the state-function concept, embodied in the two functions U and (as we are still calling it) C . And it was the state functions, particularly the second one, which released Clausius' theory from its remaining restriction to the analysis of cyclic processes. The paper in which he made this final move toward generalization was published in 1865.¹⁴ By the time he wrote this paper, the last of his nine memoirs on thermodynamics, Clausius had decided that his theory must center, mathematically and physically, on the two state functions. He was now willing to accept the term energy for U , and at long last (as it seems to us, with all the benefits of hindsight) he had gained enough confidence in his " C function" to supply a letter and name for it. For no specified reason, he chose the letter S for the function and wrote its differential

$$dS = dQ/T \quad (\text{reversible processes}). \quad (19)$$

Since the quantity was used in dQ/T integrals to calculate transformation equivalence values, he derived his word for it from the Greek word "trope," meaning "transformation." The word he proposed was "entropy," with an "en-" prefix to make the word a fitting partner for "energy."

The entropy differential statement (19) could be applied to any process, cyclic or otherwise, as long as the process satisfied the reversibility stipulation. Since S was a state function, dS s could be integrated along some reversible path connecting any two states, call them 1 and 2, and the value of the integral determined entirely by S evaluated for the two states,

$$\int_1^2 dS = S(2) - S(1).$$

Thus the integrated version of Eq. (19) was

$$S(2) - S(1) = \int_1^2 dQ/T \quad (\text{reversible processes}). \quad (20)$$

How could the entropy calculation be made if the process connecting the two states was not reversible? This question was the final and crucial one answered by Clausius in his 1865 paper aimed at generalizing his theory. If it was to have practical importance, his theory again had to reach beyond the ideal, unrealistic province of reversible processes; all real physical and chemical processes were to some degree irreversible. The versatility and power of Clausius' theory permitted him to solve this problem, the most complicated and subtle he had faced, in the space of about one page.

He imagined a cyclic process in which two states, labeled say 1 and 2, were connected by two processes, one reversible and the other irreversible. The path of the cycle first

followed the irreversible path from state 1 to state 2, and then returned along the reversible path from state 2 back to state 1. Clausius' determination of N for this cycle was straightforward,

$$\begin{aligned} N &= - \int_1^2 dQ/T - \int_{2r}^1 dQ/T \\ &= - \int_1^2 dQ/T + \int_{1r}^2 dQ/T, \end{aligned}$$

with \int and \int_r denoting integrations over the irreversible and reversible parts of the cycle. The second integral could be evaluated with Eq. (20), so

$$N = - \int_1^2 dQ/T + S(2) - S(1),$$

and the entropy calculation was simply

$$S(2) - S(1) = \int_1^2 dQ/T + N. \quad (21)$$

This was the generalized entropy calculation Clausius needed. It could be applied to reversible processes, for which $N = 0$, or to irreversible processes, for which $N > 0$. The integral $\int dQ/T$ was vital in both cases. For any reversible process it was exactly equal to the entropy change; for any irreversible process, it was always less than the entropy change,

$$S(2) - S(1) > \int_1^2 dQ/T. \quad (22)$$

Equation (21) and the inequality (22) stated for Clausius, and state for us today, the Second Law of Thermodynamics.

Clausius may have the dubious distinction of being the most forgotten major nineteenth century scientist. Clausius' equations, some of them written exactly as he expressed them a century or so earlier, are on display in all modern thermodynamics texts, and in an astonishing variety of other texts where the methods of thermodynamics are applied. Yet Clausius himself, even his name, has all but disappeared. In a typical modern thermodynamics text, we find his name associated with a single, comparatively minor equation (the "Clausius-Clapeyron" equation). There have been no biographies; the known facts of his personal life fill only a few paragraphs.

What we do have from Clausius is his collected papers. They have little to say about Clausius as a human being, but they tell us about the other half of his story, his scientific work. We can read Clausius' papers and fully appreciate his place in the beautifully clear line of development of thermodynamics between 1824 and 1875—from Carnot to Clausius, and then to Clausius' greatest successor, Willard Gibbs. Clausius' role in this was pivotal. He knew exactly how to interpret and rebuild Carnot's message, and then to express his own conclusions so they could be used by another genius, Gibbs. The grandest theories make their own vital contributions and then inspire the creation of other great theories. Clausius' achievement was of this very rare kind.

¹Rudolf Clausius, "On a Modified Form of the Second Fundamental Theorem in the Mechanical Theory of Heat," reprinted as the "Fourth Memoir" in *The Mechanical Theory of Heat*, translated by T. Archer Hirst (van Voorst, 1867), pp. 111–135.

²Rudolf Clausius, "On the Moving Force of Heat and the Laws of Heat

Which May Be Deduced Therefrom," reprinted as the "First Memoir" in the *Mechanical Theory of Heat*, op. cit., p. 28.

³William Thomson, *Mathematical and Physical Papers* (Cambridge U. P., Cambridge, 1911), Vol. 1, p. 223.

⁴*Ibid.*, p. 437.

⁵Hermann von Helmholtz, "Über die Thermodynamik der Chemischen Processen," Akademie der Wissenschaften, Berlin Sitzungsberichte 1882, 29.

⁶Rudolf Clausius, "On several Convenient Forms of the Fundamental Equations of the Mechanical Theory of Heat," reprinted as the "Ninth Memoir" in *The Mechanical Theory of Heat*, op. cit., p. 328.

⁷Rudolf Clausius, "On a Modified Form...", op. cit., p. 117.

⁸*Ibid.*

⁹Clausius did not use this notation. For M and N he wrote, with some mathematical ambiguity dQ/dv and dQ/dt .

¹⁰Clifford Truesdell, *The Tragicomical History of Thermodynamics, 1822-1854* (Springer, New York, 1980), pp. 15-27.

¹¹Rudolf Clausius, "On the Moving Force of Heat...", op. cit., p. 28.

¹²See Keith Hutchinson, "Mayer's Hypothesis: A Study of the Early Years of Thermodynamics," *Centaurus* 20, 279-304 (1976).

¹³Rudolf Clausius, "On Several Convenient Forms...", op. cit., p. 329.

¹⁴*Ibid.*, pp. 327-376.

A summer program for high school physics teachers

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In the summer of 1985 we ran a workshop for high school physics teachers, sponsored by the National Science Foundation under its program of Honors Workshops for Pre-College Teachers of Science and Mathematics. The summer experience consisted of a five-week workshop and a four-week industrial experience. The teachers had a wide variety of backgrounds and needs, which were accommodated in the workshop. This paper describes how the workshop was run, what activities were successful, and where we encountered problems.

I. INTRODUCTION

Recently the United States, after several years of neglect, has rediscovered the precollege classroom. One of the results has been the availability of money from the National Science Foundation to provide honors workshops for pre-college teachers of science and mathematics. Their basic goal is to "motivate and increase the capabilities of pre-college mathematics and science teachers and thereby improve the instruction of students." In the summer of 1985 we ran a workshop for high school physics teachers, under this program. We provided the teachers an intensive five-week workshop which carried ten quarter credits of graduate credit in physics, reviewed selected topics in classical and contemporary physics, and provided extensive experience in demonstration and laboratory. The teachers also participated in a four-week experience working in industry.

There were many features of the workshop which differed from summer institutes we had run in the past. The NSF guidelines were for workshops to identify and honor teachers "of proven high quality and performance." We proposed not to measure quality by years of experience. Instead we planned to select some experienced teachers and some who started to teach physics only recently, either because of age or reassignment. We hoped to establish a buddy system between experienced and less experienced teachers.

We proposed to honor the selected teachers in two ways. First, we sought to treat them as professionals and to be very sensitive to what they said they needed to improve the learning experience for their students. To this end we proposed to establish rapport with them through classroom

visits. The purpose of these visits was twofold: to introduce our staff to the life of a high school teacher so we would be more sensitive to their specific needs, and to elicit from the teachers both their general expectations and what they specifically wanted to learn in the workshop. Topics and activities in the workshop were planned after these visits.

We also felt that the school districts should honor the selected teachers. We proposed to see how many school districts would provide one month's salary for the professional development of their teachers, along with \$500 of supply and equipment money to be used at the teacher's discretion to implement improvements.

This paper describes how the workshop was planned and run to meet the broad range of teacher backgrounds and needs, and how we made midcourse corrections to enhance the experience of the teachers.

II. PARTICIPANT SELECTION, TEACHER SUPPORT AND CREDIT

A brochure was mailed to all physics teachers and high schools in the state. There was no formal application form; we asked applicants to prepare an essay about how they would benefit from the experience and to have letters of recommendation sent from a student or parent and from a teacher colleague or principal. Seventy eight applications were received for the 40 positions. It was difficult to choose on the basis of the material available to us: each teacher expressed need eloquently, and the letters of recommendation said much more about those writing them than about the teachers. Half of the participants were experienced physics teachers; the other half were less experienced. We