Rudolf Clausius, "Concerning Several Conveniently Applicable Forms for the Main Equations of the Mechanical Heat Theory"

Excerpted from <u>Annalen der Physik und der Chemie</u>, Vol. 125 (1865), pp. 353-400.<sup>1</sup>

1. The whole mechanical heat theory rests on two main theses: the equivalence of heat and work, and the equivalence of the transformations.

For an analytical expression of the first thesis, we think of any kind of body that changes its state, and we consider the quantity of heat that has to be imparted to it to effect the change of state. Designating this quantity of heat by Q, and counting heat given off from the body as negative absorbed heat, the element dQ of heat absorbed during an infinitely small change of state follows the equation:

$$dQ = dU + AdW$$

Here *U* means the entity which I first introduced into heat theory in my paper of 1850 and which I there defined as the sum of the added free heat and the heat consumed for inner work. *W* means the external work done during a change of state, and *A* the heat equivalent for the unit of work; i.e., the caloric equivalent of work. Thus, *AW* is the external work measured in heat units or, according to my recently proposed more convenient nomenclature, the external work.

By designating this external work, for the sake of brevity, by a single letter,

$$AW = w$$
,

the equation above can be written:

(1) 
$$dQ = dU + dw$$
.

For the simplest analytical expression of the second law,<sup>2</sup> we assume the changes undergone by the body as forming a cyclic process through which the body finally returns to its initial state. Again, dQ means an element of heat absorbed, and T the temperature, counted from the absolute zero, of the body at the moment when it absorbs this heat element, or, in case the body had different temperatures in different parts, the temperature of that part which absorbs dQ. When the heat element is

divided by the corresponding absolute temperature and the differential thus obtained is integrated for the entire cycle, then this integral is represented by

$$\int \frac{dQ}{T} \le 0$$

where the equal sign is valid for those cases in which all changes in the cyclic process occur in a reversible manner, while for the cases of nonreversible changes the "greater" sign is valid.

2. The external work (w) done while the body goes from one given initial state to another state depends not only on the state at the start and at the end but also on the kind of transition.

The energy U of the body ... behaves in an entirely different manner. When the states at the start and at the end are given, the change of energy is completely defined; it is not necessary to know how the change from one state to the other has occurred, since neither the pathway of the change nor whether it is reversible or irreversible has any influence on the change of energy.

If, according to equation 2, the integral

 $\sqrt{T}$  always becomes zero when the body returns reversibly from any initial state through any intermediates into the initial state,

then T must be the complete differential of a quantity that depends only on the momentary state and not on the way by which the body came to it. By designating this quantity as S, we can write

$$dS = \frac{dQ}{T}$$

or, integrating this equation for any reversible process through which the body can reach its

present state, starting from the selected initial state and designating by  $S_0$  the value of S in the initial state,

$$(60) S = S_0 + \int \frac{dQ}{T}$$

In searching for a significant name for S, we could say, similar to what we said of U being the heat and work content of the body, that S should be the transformation content of the body. However, I believe it is better to take the names of such scientifically important units from the classical languages so that they can be used unchanged in all modern languages; therefore I propose to designate S by the Greek word  $\dot{\eta}$   $\tau \rho o \pi \dot{\eta} = the$  transformation, the *entropy* of the body.

. . .

Finally I may allow myself to touch on a matter whose complete treatment would not be in place here, because the statements necessary for that purpose would take up too much room, but of which I believe that even the following short indication will not be without interest, in that it will contribute to the recognition of the importance of the quantities which I have introduced into the formulation of the second law of the mechanical theory of heat. The second law, in the form which I have given it, states the fact that all transformations which occur in nature occur in a certain sense which I have taken as positive, of themselves, that is, without compensation, but that they can only occur in the opposite or negative sense in such a way that they are compensated by positive transformations which occur at the same time. The application of this law to the universe leads to a conclusion to which W. Thomson first called attention and about which I have already spoken in a recently published paper. This conclusion is that if among all the changes of state which occur in the universe the transformations in one sense exceed in magnitude those in the opposite sense, then the general condition of the universe will change more and more in the former sense, and the universe will thus persistently approach a final state.

The question now arises whether this final state can be characterised in a simple and also a definite way. This can be done by treating the transformations, as I have done, as mathematical quantities, whose equivalent values can be calculated and united in a sum by algebraic addition.

In my papers so far published I have carried out such calculations with respect to the heat present in bodies and to the arrangement of the constituents of the bodies. For each body there are found two quantities, the transformation value of its heat content and its disgregration, the sum of which is its entropy. This however does not complete the business. The discussion must also be extended to the radiant heat, or otherwise expressed, to the heat transmitted through the universe in the form of advancing vibrations of the ether, and also to such motions as cannot be comprehended under the name heat.

The treatment of these latter motions, at least as far as they are the motions of ponderable masses, can be briefly settled, since we come by a simple argument to the following conclusion: If a mass, which is so great that in comparison with it an atom may be considered as vanishingly small, moves as a whole, the transformation value of this motion is to be looked on as vanishingly small in the same way in comparison with its kinetic energy; from which it follows that if such a motion is transformed into heat by a passive resistance, then the equivalent value of the uncompensated transformation which then occurs is simply represented by the transformation value of the heat produced. The radiant heat, however, cannot be treated so briefly, since there is need still of a certain special treatment in order to find out how its transformation value is to be determined. Although, in the paper which was recently published and to which I have previously referred, I have already discussed radiant heat in its connection with the mechanical theory of heat, yet I have not as yet treated the question which has here come up, since it was then only my purpose to prove that there was no

contradiction between the laws of radiant heat and a fundamental law which I assumed in the mechanical theory of heat. I reserve for future consideration the more particular application of the mechanical theory of heat and especially of the law of equivalents of transformation to radiant heat.

In the meantime, I shall limit myself to mentioning one result: Imagine the same quantity that, relative to one body, I have called its entropy, consequently, with due

<sup>1</sup>[This extract combines excerpts and translations from William Francis Magie (*A Source Book in Physics*, McGraw-Hill, New York, 1935) and Eduard Farber (*Milestones of Modern Chemistry*, Basic

regard to all circumstances, applied to the entire universe, and also that other, simpler concept, energy, applied at the same time: then the fundamental laws of the universe that correspond to the two laws of mechanical heat theory can be pronounced in the following form:

- 1. The energy of the universe is constant.
- 2. The entropy of the universe strives toward a maximum.

Books, New York, 1966, pp 153-156. — CJG]

<sup>2</sup>[He means the second thesis above, the equivalence of transformations. —Farber]