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THE MEASUREMENT OF HEAT AND THE SCOPE OF CARNOT'S PRINCIPLE.

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Synopsis.—This paper outlines a symmetric form of exposition of the principles of thermodynamics made possible through recognizing on a parity from the outset the two kinds of conservation naturally called after Black and Carnot, each of which is physically valid under proper conditions, and which lead to the energy and entropy scales of measurement of heat; thus exhibiting both of these, together with the thermodynamic scale of temperature, as calorimetric concepts. In the two parts of the paper are given respectively an experimental and a deductive treatment.

In part I. the experimental meaning of conservation is considered in terms of certain conditions of consistency; first in connection with single-temperature transfers of heat, where those conditions underlie the uniqueness of meaning of an arbitrary scale of heat for various temperatures; second in connection with passages of heat between bodies at different temperatures, which reveal the dual nature of a quantity of heat, here illustrated by some analogies.

In part II. are investigated the deductive consequences of Carnot's hypothesis of the universal ratio of efficiency. With only the single-temperature conservation of heat assumed to be known experimentally (probably the mildest basis on which this principle is intelligible), it is shown that there follows practically the entire theory of reversible thermodynamics, in particular the existence of thermal energy and entropy and the equivalence of thermal energy and work.

SINCE the time when the basic principles of thermodynamics were given a standard form, chiefly by Clausius, Kelvin and Rankine, it has become customary not only to speak of "first" and "second" laws but to adopt a corresponding order of thought in the development of their more immediate consequences. It is recognized however that the two principles are at least to a certain extent independent, so that an inverse order of development is conceivable; as illustrated for instance by the fact that Kelvin was able, without using the principle of equivalence, to point out the implication in Carnot's theory of a universal or absolute scale of temperature.[1] Moreover, while the principle of equiva-

[1] Kelvin, Camb. Phil. Soc. Proc., June 5, 1848.

lence enters chiefly on an experimental basis, the second law is made to rest to a large extent on an a-priori hypothesis, in the form of Carnot's principle or its equivalent, to be judged by experimental test of its deductive consequences. An unsatisfactory result is that while the notion of thermal energy, already familiar from experimental calorimetry, becomes still more concrete through equivalence to mechanical work, the notion of entropy, introduced by theorem and definition, appears comparatively abstract and difficult of physical interpretation.

Still, this order of ideas is undoubtedly natural in presence of the general understanding that Carnot's original theory, though contributing the invaluable concepts of the reversible cycle and the universal ratio of efficiency, is in contradiction with experiment through assuming the conservation of caloric in the cases contemplated, the substitution in these cases of the principle of equivalence of heat and work having opened the way for the development of thermodynamics in its now classical form. To make the first law intelligible it is of course assumed that the measurement of heat by itself is already on an experimental basis. This is taken to have been accomplished through the processes of calorimetry, as initiated by the pioneer work of Black, which may be said to rest on the hypothesis or fact, according to the point of view, of the conservation of caloric in certain cases of conduction and the like where it is now known to be an essential feature that no mechanical work is done.

It has not escaped notice however that in some ways Carnot's "caloric" shows distinct resemblance to entropy rather than to thermal energy.[1] Detailed examination shows that most of the propositions of Carnot's essay, and of the formulas in Clapeyron's mathematical commentary and Kelvin's "account," [2] though so often called erroneous and even meaningless by commentators, have a meaning and are correct if "caloric" is taken to mean entropy. It is certain therefore that the amount of inconsistency with experimental results supposed to be present in Carnot's theory has usually been exaggerated and its exact nature not clearly set forth. From the point of view to be explained in this paper the only error of importance appears to be that, not realizing the type of conservation required by his theories to be physically distinct from that of Black, he borrowed numerical data obtained on the energy scale and applied them in cases where they should have been given on the entropy scale. For example, at constant volume the capacity of an ideal gas for change of thermal energy is constant but its capacity for change of entropy varies inversely as the absolute temperature.

[1] Callendar, presidential address, Phys. Soc. Proc., 23, 153–189, 1911.

[2] Clapeyron, J. de L'Éc. Pol., 14, cah. 23, 152, 1834. Kelvin, Trans. Ed. R. Soc., XVI., 1849.

One may say then that the hypothesis of conservation of caloric was used effectively by Black and Fourier in cases where one would now say that thermal energy is conserved and entropy increases, while Carnot assumed it for the case of his reversible engine where thermal energy changes but entropy is constant. The parallel though incomplete is unmistakable. It suggests that the whole basis of thermodynamic theory might be recast in a more symmetric form, securing at the same time a more completely experimental setting, by considering from the outset on a parity the two measurable properties of a quantity of heat and the corresponding scales of measurement based on two types of conservation, each valid in the respective class of cases whereby the experimental establishment of the scale is achieved. Such a formulation is attempted in part I. of this paper where the term "quantity of heat" is for convenience used, in a sense more generic than usual, as denoting a relatively primitive concept not really simple, but which rather may be said to bifurcate into the two distinct and more specific concepts, each of which corresponds in the appropriate cases to the respective types of conservation identified by the names of Black and Carnot.

Such a bifurcation during the process of refinement into scientific precision of a primitive and relatively vague concept is by no means a rare event in the history of science, though as in the theory of heat it is often obscured by the continuance in use, to denote one only of the emerging concepts, of a term previously more comprehensive and indefinite. During the formative period of dynamics search was made for an acceptable measure of the amount of motion in a moving body and the controversies led to the appearance of two important and distinct concepts, momentum and kinetic energy; some traces of vagueness of language remain in the Principia of Newton, though technically he chose to restrict the term "quantity of motion" to the first of these. The "degree of electrification" of a body might be taken to include reference to both charge and potential; the coldness of metal on a winter day is an uncertain blend of low temperature and good conductivity; the distinct concepts quantity of heat and temperature arose from the scrutiny of judgments of "hot" and "cold." In a similar way it seems just to use the term "quantity of heat" in a generic sense, to comprise reference in combination to both of the two independent measurable properties, thermal energy and entropy, although since the foundation of calorimetry the expression has come to be restricted to one of them as a matter of custom. Further examples could easily be cited, but for the present purpose the point of view suggested is especially well illustrated by the following example, which will be seen to furnish a rather vivid and far-reaching analogy to the thermodynamic relations.

The term "amount of gas" may be treated as somewhat indefinite, referring to volume or mass or both jointly according to the interpretation intended, as in the specification of percentages in a gaseous mixture. Suppose then an extensible balloon containing air, with attached tube and shut-off permitting control of contents, be allowed to rise through water in which it is immersed. If the shut-off be closed the mass of air is constant while the volume increases; if the contents be allowed to escape at a suitable rate the volume may be kept constant while the mass diminishes. Here mass, volume, depth, pressure in water, atmospheric pressure at surface, correspond respectively to thermal energy, entropy, temperature on some empirical scale, temperature on thermodynamic scale, and temperature of conventional zero above absolute zero.

In the typical case of Black's calorimetry the heat leaving a body A at a certain temperature and that entering another body B at a lower temperature are such that the thermal energies are the same, but the entropy entering B is larger than that leaving A. In the typical case of Carnot's theory, where the transfer of heat occurs by mediation of a reversible engine working in a simple Carnot cycle between the two temperatures, the entropies involved are equal but B receives less thermal energy than A gives up. Thus the justice of the term "conservation of caloric," in two different senses, seems to be exactly the same in the two cases.

The incompleteness of the parallel with respect to other features may also be instructive. In both cases there is known to be conservation of energy, because the variations of mechanical energy in its various forms compensate those of the thermal energy; while there is not yet recognized any physical magnitude whose variations compensate those of the known thermal entropy, so as to allow the formulation of a law of conservation of entropy in some wider sense. Still it is conceivable, as Callendar suggests, that there may be other and equivalent forms of entropy, and especially does there seem to be a chance for speculation on this point in connection with the thermodynamics of radiation. Perhaps also there may be other and independent aspects of heat, beside energy and entropy, whose conservation could be established in some experimentally intelligible sense; for instance in connection with the aggregate result of the molecular Döppler effects, since energy and temperature alone do not determine spectrum of radiation if the black body condition be not imposed. Such novel aspects or magnitudes could probably not be sifted out by the study of bodies, like fluids in gross, whose state depends on only two independent thermodynamic coördinates.

As underlying the interpretation of thermal measurements the notion

of conservation or equivalence appears in various forms. These may be analyzed in terms of three fundamental types, corresponding to the following three elementary cases of experimental comparisons: (1) comparison of quantities of heat entering or leaving different bodies at the same temperature, (2) comparison of quantities of heat at different temperatures, (3) comparison of heat with other physical entities, especially completely available energy in some form.

The treatment given in Part I. shows that on the basis of the first two only, including the suggested dual aspect of the second, it is possible to exhibit entropy as well as thermal energy as a calorimetric magnitude, thus reaching a more symmetric experimental setting than the familiar forms of the theory. The equivalence of thermal energy and work is then introduced as an additional experimental result, while the existence of an analogous non-thermal equivalent for thermal entropy appears merely as a question.

As an alternative development a symmetrically deductive treatment is given in Part II. Here the only experimental comparisons assumed are of the type (1) above, while Carnot's hypothetical principle of the universal efficiency function is stated as a postulate. The existence of thermal energy and entropy, identifiable with the experimental concepts, is deduced, so that for reversible processes there follow both first and second laws as commonly understood. Thus, on what appears to be a minimum basis of experiment sufficient to make the measurement of heat an intelligible notion at all, Carnot's principle alone proves to be an adequate hypothetical basis for the entire general theory of the thermodynamics of reversible processes, having in particular the principle of equivalence of heat and work as a corollary. Distinct indications of the possibility of such a conclusion will be found in the apparently little known memoir by Reech,[1] in which the development is such that it can be specialized further by assuming either conservation of energy or conservation of caloric, considered as mutually incompatible. Results partially similar to those now obtained will also be found in the recent papers by Larmor and Raveau,[2] dealing with Carnot's principle apart from the principle of equivalence. Some reference will be made later to corresponding features in these papers, but the detailed comparison will be left to the reader.

PART I. EXPERIMENTAL SETTING.

Passing over the complex detail of experimental methods and the involved questions presented to the experimenter's judgment in the

[1] Reech, Liouv. J., ser. 1, 18, 357–568, 1853.

[2] Larmor, Roy. Soc. Proc., 94, 326–339, 1918. Raveau, C. R., 167, 20–23, July 1, 1918.

attempt to sift from among secondary or accidental aspects the main
elements of the phenomena to which attention is to be directed, it will
be sufficient here merely to notice certain salient features of the results,
that either have been obtained or with appropriate experiments would be
obtained if thermodynamics in its familiar form is valid. As to ther-
mometry, it will be supposed that means have already been secured for
identifying particular physical temperatures, and that the various tem-
peratures are known to form a simple or linear ordinal series, in connec-
tion with which the terms "higher" and "lower" have their usual
meaning. If data are to be transcribed with the aid of some numerical
specification of temperature it will be understood that the physical order
of rising temperature corresponds to the order of increasing values of
the index variable t, without implying any initial physical interpretation
for equality or comparison of intervals in different parts of the scale.
In most cases it will be clear that t could be understood merely as some
symbol of identification, not necessarily numerical.

Viewing then to begin with as merely tentative the notion that heat
can be measured at all, one may ask what there is in the experimental
processes developed and the results reached to show that heat possesses
properties truly measurable, and such that the results of measurement
can be described justly in terms of the standard language of equivalence
and conservation. In the main the answer is that in all the types of
comparison involved in thermal measurements there appears a certain
unanimity in satisfying what may be called conditions of transitivity,
or conditions of consistency as they become in the phrasing suggested
by the point of view represented in the notion of equivalence; conditions
as to sense or algebraic sign, and as to value or measure. Between these
two kinds also there is a certain formal analogy that needs no attention
here. It is because these conditions are satisfied that it is possible to
formulate the meaning of a "quantity of heat" as something having
value and sign. This formulation, found by experience to be both just
to the facts and convenient in describing them, is best thought of as
occurring in connection with observation of such variations in physical
properties, supposedly due to thermal processes, as affect features already
known to admit of algebraic representation, like length, volume, density,
mass of a particular phase. Both kinds of conditions of course appear
in a variety of forms, corresponding to the various kinds of bodies involved
and the various kinds of thermal exchange between them.

In language made unconventional in order to avoid specific terms
already adopted as technical, the conditions of sense may be described as
referring to a distinction between some change called "waxing" and its

opposite "waning," the terms bearing various meanings for various bodies
or kinds of change. Suppose then in each single experiment of a set a
certain pair of bodies in thermal exchange, all other bodies being found
unaffected in certain prescribed respects. With A and B in exchange let
A vary in a way called waxing by definition, then what B does may be
called waning; in exchange with C suppose B waxes, then what C does is
naturally called waning; no more definition being needed, there is
content of fact in saying that with A and C in exchange if A waxes C
wanes. In case n bodies were paired off in all possible ways there
would be one arbitrary definition, $n - 1$ definitional pairings, and
$(n - 1)(n - 2)/2$ pairings for test of fact. There are also in connection
with processes that can be reversed items of fact to the effect that
reversals of sense correspond in the two bodies of a pair. In view also
of the number of ways in which the same body may be affected by thermal
exchange according to the conditions imposed, it is clear how broad is
the justification in fact for speaking of heat as something entering or
leaving a body.

The matter of numerical value is closely similar. The magnitudes of
corresponding changes in the bodies of a pair are found to be related
in some way, and the observed relation for A and C can also be computed
from the relations for A and B and for B and C by algebraic elimination.
The character of the algebraic process depends on the choice of variables
used in transcribing the measurements, the usual case being the multipli-
cation of ratios. With any number of bodies in the set to be compared,
a particular one may be chosen to be paired off with each of the others,
either to decide on convenient definition of terms or by process of calibra-
tion to fix on a suitable choice of variables; then all other pairings give
tests of fact. The consistency thus revealed is the ground for speaking
of heat as something admitting quantitative estimate.

Whether every type of sequence, or in what sense any particular
sequence, of thermal comparisons would satisfy these conditions need
not be discussed here; some of the outstanding problems relate to the
question whether other and independent quantitative aspects of heat
remain to be discovered. The few special types to be mentioned here
are actually of the consistent or conservative type, and prove to be suffi-
cient as basis for the theory aimed at. In each case the meaning of the
conditions of consistency in sense or sign may be passed over as obvious
without comment; the conditions of consistency in value or magnitude
will be sufficiently illustrated by the forms that they take in certain
standard cases of the three types of comparison listed above.

Comparisons of the first type, of quantities of heat entering or leaving

bodies at the same temperature, lead to the conclusion that all such can be compared among themselves and represented consistently by simple ratios; or in other words that for such single-temperature comparisons a quantity of heat can be considered a simple thing, capable of representation by a single number in terms of any chosen unit belonging to that temperature, regardless of the kind of body concerned or the kind of change produced in it according to collateral conditions imposed. This leads to the introduction of what may be called an empirical or arbitrary scale of heat, including a single specific unit for each temperature, but not implying anything as to the possibility of comparing two quantities of heat when the temperatures are different. An approximate example of such a scale is found in the system of differential calories, according to which the specific heat of water is by definition unity at every temperature. A better example for the purpose is to be found in strictly isothermal processes, especially changes of state, though latent heats of expansion would also serve. Through a suitable variation of pressure the latent heat of transition between liquid and vapor of a single substance could furnish such a scale for a considerable range of temperature.

Consider then a variety of substances such that the respective pressures can be adjusted so that the temperatures of transition agree. In the absence of such adjustment for any two particular substances A and B, suppose thermal exchange between them for a certain time leads to the transformation of the respective masses m_A, m_B, the transition being reversed in both bodies with reversal of sense of the temperature difference. With temperature difference approaching zero the ratio m_A/m_B of corresponding masses approaches a limiting value μ_{AB} to be understood as the ratio of masses transformed in the ideal limiting case of reversible or single-temperature conduction.

The main experimental facts of significance here are then: that the ratio μ_{AB}, depending on the temperature of transition and the nature of the substances, is independent of the absolute mass transformed, and that for the same temperature the various ratios for the various bodies of the set satisfy conditions of transitivity in the form $\mu_{AB}\mu_{BC} = \mu_{AC}$. This multiplication of ratios is of course not merely a mathematical identity, though conveniently given a mnemonic form as such, the meaning being that if m_A be the same in the experiments (AB) and (AC) and m_B the same in experiments (AB) and (BC) then as an experimental fact m_C will be the same in (AC) and (BC). The fact that the ratio of masses is characteristic suggests that a quantity of heat can be numerically indexed as proportional to the mass transformed of some particular substance.

The conditions of consistency in the compounding of the ratios furnish one instance of the universal consistency in the comparison of various temporary units of heat belonging to the same temperature, though in general the mathematical form varies. In such facts is found the experimental basis for the effective accuracy of the language of conservation, according to which for example one can speak of a quantity of heat going from A to C either directly or through B. In the sense illustrated it will now be supposed that the meaning of a quantity h of heat at a temperature t has been established. Certain familiar terms, like the differential specific heat dh/dt, become intelligible in connection with any definite choice of the scales of heat and temperature.

For the second type or multiple-temperature comparisons consider a set of bodies or reservoirs maintained at their respective various temperatures, any certain three of which, such as will be referred to, being labelled in descending order as t_1, t_2, t_3. The two distinct forms of conservation already alluded to will then appear in connection with thermal exchange between these bodies of the two kinds naturally named after Black and Carnot.

The first form, fundamental in classical calorimetry, occurs when the bodies communicate by pure irreversible conduction or radiation, or by the mediation of some mechanism such that the various quantities of heat are related in the same way. The second occurs when the bodies communicate by mediation of a reversible engine working in Carnot cycles between the two temperatures. In the first case suppose h_1 units of "t_1-heat" leave the first body and h_2 units of "t_2-heat" enter the second body; let $h_1/h_2 = b_{12}$. Similarly in the second case, the two quantities of heat being h_1' and h_2', passing when the engine is on the isothermals, put $h_1'/h_2' = c_{12}$.

Now calorimetry as ordinarily understood, or the measurement of heat by itself in Black's sense, rests largely on the experimental facts: that b_{12} depends on the two temperatures only save for its obvious variation according to the choice of the scale of heat; and that in terms of any one scale of heat the ratios for various pairs of bodies satisfy the condition $b_{12}b_{23} = b_{13}$. But according to standard thermodynamic theory it is indirectly understood to be a fact, and by suitable apparatus could doubtless be shown to be experimentally verifiable with considerable directness, that the ratios c_{12} and the like satisfy similar conditions. The fact that the b's are independent of the physical nature of the reservoirs and the character of the changes produced in them is paralleled by the fact of a similar independence on the part of the c's of the properties of the reservoirs and the nature of the mediating engine.

Thus in each case there is complete ground for concluding that there is a sense in which the heat is conserved in passing out of one reservoir and into the other. But it is also to be understood as found experimentally that $b_{12} < c_{12}$; accordingly the two types of conservation must be physically distinct.

Thus a quantity of heat h, entering or leaving a body at temperature t, exhibits two distinct measurable properties, thermal energy and entropy, whose measures q and s are related to the empirical measure of heat by equations of the form

$$q = hB(t), \qquad s = hC(t),$$

where the reducing factors $B(t)$, $C(t)$, appropriate to any particular scale of heat, are determined, except for an arbitrary constant factor in each depending on the choice of the units for q and s, by the conditions

$$B(t_2)/B(t_1) = b_{12}, \qquad C(t_2)/C(t_1) = c_{12},$$

which are the transcription of the equality of q_1 and q_2 in the Black process and of s_1 and s_2 in the Carnot process.

A change of the scale of heat can be represented by putting $h = h'\rho(t)$ where $\rho(t)$ is the ratio of the new to the old unit of t-heat; the corresponding new reducing factors are then $\rho(t)B(t)$ and $\rho(t)C(t)$, supposing the units of q and s not altered. In particular ρ could be taken as the reciprocal of either B or C, thus reducing the arbitrary scale of heat to the energy or entropy scale.

If by definition $T(t) = B(t)/C(t)$, then in view of the inequality $b_{12} < c_{12}$, which gives $B(t_1)/C(t_1) > B(t_2)/C(t_2)$ it follows that $T(t)$, the absolute or thermodynamic scale of temperature thus shown to exist, is a monotonic increasing function of the physical temperature, is independent of the choice of the scale of heat, and is determinate except for a constant factor depending on the units of q and s, whose values for the same quantity of heat are related by $q/s = T(t)$.

With the aid of this scale of temperature the two cases may then be epitomized as follows, the different equations in each set being equivalent but suggesting different interpretations:

B: $q_1 = q_2$; $s_1 T_1 = s_2 T_2$; $(s_2 - s_1)/s_1 = (T_1 - T_2)/T_2$;

$\qquad (s_2 - s_1)/s_2 = (T_1 - T_2)/T_1$; $s_2 - s_1 = q_1(1/T_2 - 1/T_1)$;

C: $s_1 = s_2$; $q_1/T_1 = q_2/T_2$; $(q_1 - q_2)/q_1 = (T_1 - T_2)/T_1$;

$\qquad (q_1 - q_2)/q_2 = (T_1 - T_2)/T_2$; $q_1 - q_2 = s_1(T_1 - T_2)$.

To each equation valid in one case there corresponds one valid in the other case obtained by interchanging q with s and T with $1/T$. For

example there are two instances of the Carnot simile of the waterfall: in C the thermal energy $s(T_1 - T_2)$ is lost when entropy s falls through the temperature difference $T_1 - T_2$, while in B entropy $q(1/T_2 - 1/T_1)$ is generated when thermal energy q rises through the difference of the reciprocals of the temperatures. In each case the statement of the condition of conservation in terms of the non-conserved quantity gives a kind of calorimetric aspect of the familiar Carnot ratio and its dual. The universality of these ratios, as depending on the temperatures only, is a consequence of the universality of the ratios b and c mentioned above, which is what makes it possible to abstract the notions of thermal energy and entropy out of the properties of particular bodies.

Up to this point only heat entering or leaving a body has been spoken of. But the conservation of entropy in the Carnot process leads by a familiar reasoning to the conclusion that all reversible transformations connecting two states of the working substance must agree in the amount of entropy absorbed, this amount being the integral of the calorimetric expression for ds in terms of reversible changes of the temperature and other observable properties of the body. The existence of a function of state properly called the entropy of the body is thus recognized, in a purely calorimetric setting. The question is at once suggested whether a corresponding identification of the internal energy of the body is possible by thermal tests alone.

This calls attention to a certain feature of incompleteness in the parallel as thus far drawn, in that the Carnot process implies the mediation of a working substance, while in the primitive form of the Black process only the two reservoirs are concerned, unless one considers the optical ether as mediator. It is, however, possible to imitate the net result of the irreversible conduction or radiation through the mediation of a gas, for instance, working in a cycle of the Carnot type except that such a part of the expansion on the upper isothermal is "free" that the net work of the cycle is zero. This illustrates that the primary condition for Black conservation during communication of the two reservoirs is of course not that there shall be no mediator but merely that the ultimate changes shall affect only those reservoirs; in contrast with the Carnot cycle, where some change in other bodies accompanies the non-vanishing work done. Accordingly, any case where it is possible to use a mediating body in such a way that this condition is satisfied, and such that the quantities of heat absorbed can be identified in terms of the changes in that body itself, can be thought of, not only as exhibiting conservation of thermal energy, but as leading also to a calorimetric identification of changes in what is to be called the internal energy of the body. The

simplest case is naturally that of a cycle passing through two states of the mediator, such as to connect those states in two different ways by a path consisting of an isothermal and an adiabatic, one path reversible, the other necessarily irreversible at least in part, and so adjusted that the net work of the cycle is zero. The experimental tests are then to be understood as verifying that the conditions of transitivity are satisfied, in fact with ratios identical with the b's above. In such a case the identification of the internal energy function is strictly analogous to that of the entropy by a Carnot cycle. That the identification of the two functions of state in this way can rightly be described as purely calorimetric is clear from the fact that, although the conditions involve full work in one case and no work in the other, still no quantitative comparison of heat and work is implied. Just how far the range of such cases extends it is not easy to say, but it may be guessed to be not far from coextensive with that in which a really experimental meaning attaches to the quantities of heat involved.

A more fundamental lack in the parallel appears when the further experimental facts are included which complete the classical first law, here more naturally called the last law. These show that in the case of the Carnot cycle the $q_1 - q_2$ is proportional to the work done, the factor of proportionality depending only on the units, or in other words that the conditions of transitivity are satisfied when mechanical energy is included with thermal energy; and more generally that work done is equivalent in any case to decrease in internal energy. The Carnot ratio then assumes the form of the ratio of efficiency; and, conversely, as Callendar has pointed out, the principle of efficiency combined with Carnot conservation leads to the principle of equivalence for reversible processes.

There is on the other hand, however, no physical quantity yet identified whose variations compensate those of the recognized thermal entropy. The discovery of such would be expected to make it possible to state certain conditions on irreversible processes in terms of an extended kind of Carnot conservation, instead of in terms of inequalities. It might also help to give physical meaning to the measure of probability, in terms of which entropy is expressed in statistical theories; perhaps utilizing some large scale coefficient related to the action constant of recent physical theory much as the gas constant is related to the agitation constant in the molecular theory. Many things suggest that if such a quantity exists, its setting may involve the relation of matter and radiation.

A certain "instinct for conservation" has sometimes been looked upon

as part of the natural equipment of the physical investigator, and the order of thought here sketched shows how fully successful in this subject is its guidance of the interpretation of experiment. With the exception of the single problematic instance mentioned—whose place so far as present knowledge goes is held by the inequalities that take such a unique place in physical theory—the basic features of thermodynamic phenomena are found in the four distinct types of transitivity listed, each admitting statement in terms of the language of conservation, which lead to the abstraction of the four corresponding fundamental notions: heat, thermal energy, entropy, thermo-mechanical energy. The corresponding arrangement suggested for the theory includes then five laws, four equations and one inequality. The experimental basis used is a blend of reversible and irreversible processes, and in particular the various experiments of Joule on equivalence deal mainly with irreversible processes of rather extreme type.

Since, however, mathematical developments in thermodynamics are so largely concerned with reversible processes it is natural to ask whether some basis could not be found for a theory of such processes by themselves, adequate for the complete theory so far as they are concerned. It will be shown in part II. that conservation of the first type only and Carnot's principle of efficiency, as formulated in terms of the empirical scale of heat, are together sufficient for such a basis.

PART II. THE SCOPE OF CARNOT'S PRINCIPLE.

The actual course of development of thermodynamics has tended to obscure the real reach of both of Carnot's fundamental ideas. First, his conservation of caloric was rejected as erroneous instead of being recognized as distinct from that of Black and Joule; the irony of this appears when one notices that, for the processes he defines, a conservation essentially equivalent to his occurs as a theorem in the classical theory. Second, his principle of efficiency did not have its consequences developed independently, but rather it was merely superposed on the principle of equivalence, adding thus to the theory only the extra content it had to offer. From the very nature of his principle, however, in that it refers to a ratio of heat and work as related to two distinct temperatures, it would seem inevitable that it should lead to some kind of quantitative comparison of heat at different temperatures as well as of heat with work, independently of his postulate of conservation. In order to reveal the full scope of the principle therefore, and especially its independence of the ordinary principle of equivalence, it is natural to develop its consequences with only so much additional assumption

as is required to yield the general notion of a quantity of heat, abstracted from the properties of particular bodies.

Accordingly, for the alternative theory now to be presented, relating to reversible processes only, the basis of assumption is the Carnot postulate of efficiency, that for reversible cycles of his type the ratio of work done to heat absorbed on the upper isothermal is a universal function of the two temperatures; where quantities of heat are to be understood as known to be measurable in the sense of an empirical scale of heat as above described. Thus of the various types of conservation mentioned in part I. only the first or single-temperature type is now assumed, this being apparently the mildest basis on which Carnot's principle has intelligible meaning as one of possible common application to all kinds of bodies. As thus understood it will be shown to yield the entire thermodynamics of reversible processes. The existence of thermal energy and of entropy proves to be deducible without reference to the experimental basis of irreversible phenomena on which the theory of energy ordinarily rests. The conservation during reversible conduction, which is assumed, is the type where conservation of energy and of entropy are not distinct, so that only the generic notion "quantity of t-heat" is needed.

The case to be for convenience considered first is that of a fluid as working substance, its thermodynamic properties under the limited calorimetry defined being embodied in differential expressions

$$(1) \qquad\qquad dh = kdt + ldv, \qquad dw = pdv,$$

for heat absorbed and work done during a differential change under equilibrium pressure, where the coefficients k, l, p are for each particular body certain definite functions of v and t. Now merely as a mathematical proposition there exists for any system of this kind, with only two independent variables, an integrating divisor ω such that dh/ω is an exact differential ds; the ω is of course not uniquely determined, but any particular choice gives a function s determinate except for an additive constant. The s chosen is to serve simply as parameter of the adiabatic lines, whose differential equation is $dh = 0$, and later naturally appears as some function of the entropy, the canonical choice of s being the entropy itself.

The reasoning can be carried out in terms of the original variables (v, t), but for brevity it is convenient to transform to (s, t) as new independent variables. These are independent except when the latent heat of expansion l vanishes, in which case a true Carnot cycle is not possible since then an adiabatic is also an isothermal; this is a physically unreal

case which need not be pursued. It is also essentially general for the main purpose to suppose that the Jacobian $\partial(v,\, t)/\partial(s,\, t)$ is positive, so that the sense of equivalent cycles is the same in the $(v,\, t)$ and $(s,\, t)$ planes when the coördinates are taken in this order. Whatever the choice of the s, this transformation offers the convenience that a Carnot cycle is represented by a rectangle in the $(s,\, t)$ plane. In terms of these new variables the heat and work take the forms

$$(2) \qquad\qquad dh = \omega ds, \qquad dw = ads + bdt,$$

where ω, a, b are to be considered as functions of s and t; the explicit formulas connecting them with k, l, p are not needed. It will be clear also that the proof really applies to the general case of a two-variable system, since the same forms would result if the original expression for dw had a term in dt, and if the v and p were interpreted as any coördinate and corresponding generalized force.

If t_1 and t_2 be the higher and lower temperatures in the cycle Carnot's principle then imposes the condition

$$(3) \qquad\qquad w/h_1 = H(t_1,\, t_2),$$

where H is the same function for all bodies when the same scales of heat and temperature are used for all. A change of the scale of heat, represented by putting $h = h'\rho(t)$ and thus giving $k' = k/\rho$, $l' = l/\rho$, is allowed for by putting

$$H'(t_1,\, t_2) = \rho(t_1)H(t_1,\, t_2).$$

This is still universal in the sense intended, so that if the principle is valid for one scale of heat it is valid for all.

The case in hand, for the cycle represented by the rectangle $(s = s_2 \cdots s_1,\, t = t_2 \cdots t_1)$ has

$$(4) \qquad h_1 = \int_{s_2}^{s_1} \omega(s,\, t_1)ds, \qquad w = \int_{s_2}^{s_1}\int_{t_2}^{t_1} \varphi(s,\, t)dsdt,$$

in which

$$(5) \qquad\qquad \varphi(s,\, t) = \frac{\partial a}{\partial t} - \frac{\partial b}{\partial s} = \frac{\partial(v,\, p)}{\partial(s,\, t)},$$

where the area-integral for w is obtained by a known lemma from the initial perimeter integral. The fundamental condition is then that the relation

$$(6) \qquad \int_{s_2}^{s_1}\int_{t_2}^{t_1} \varphi(s,\, t)dsdt = H(t_1,\, t_2)\int_{s_2}^{s_1} \omega(s,\, t_1)ds$$

must be an identity in $(s_1,\, s_2,\, t_1,\, t_2)$.

Consideration of a range infinitesimal in t suggests the introduction of the function

$$(7) \qquad \psi(t) = \left[-\frac{\partial H(t, t')}{\partial t'} \right]_{t'=t},$$

which is the familiar Carnot function adapted to an arbitrary scale of heat as well as of temperature. For a cycle infinitesimal in s only

$$(8) \qquad \int_{t_2}^{t_1} \varphi(s, t)dt = \omega(s, t_1)H(t_1, t_2),$$

whence

$$(9) \qquad \varphi(s, t_2) = -\omega(s, t_1)\frac{\partial H(t_1, t_2)}{\partial t_2},$$

the limiting form of which for range infinitesimal in t also is

$$(10) \qquad \varphi(s, t_1) = \omega(s, t_1)\psi(t_1),$$

so that division shows the ratio $\varphi(s, t_1)/\varphi(s, t_2)$ to be a function of t_1, t_2 only, say for abbreviation $f(t_1, t_2)$, identically in s, t_1, t_2. Because of the symmetry of notation it is no longer necessary to keep the condition $t_1 > t_2$. If then t_0 be any particular value of t this result is equivalent to

$$\varphi(s, t) = \varphi(s, t_0)f(t, t_0),$$

so that φ is built of two factors, each a function of one of the variables only, which for later convenience may be written as derivatives:

$$(11) \qquad \varphi(s, t) = \sigma'(s)\tau'(t),$$

where the factors can be understood as positive so that σ and τ are monotonic increasing functions. Then (10) gives

$$(12) \qquad \omega(s, t) = \sigma'(s)\theta(t),$$

where by definition

$$(13) \qquad \theta(t) = \tau'(t)/\psi(t).$$

The differential forms in (2) and the relation (5) become

$$(14) \qquad dh = \sigma'(s)\theta(t)ds, \qquad dw = ads + bdt,$$

$$\frac{\partial a}{\partial t} - \frac{\partial b}{\partial s} = \sigma'(s)\tau'(t),$$

the last being equivalent to

$$\frac{\partial}{\partial t}(a - \sigma'\tau) = \frac{\partial b}{\partial s},$$

which indicates the existence of a function u such that

$$(15) \qquad a = \sigma'(s)\tau(t) - \frac{\partial u}{\partial s}, \qquad b = -\frac{\partial u}{\partial t},$$

which make

(16) $$dw = \sigma'(s)\tau(t)ds - du = \frac{\tau(t)}{\theta(t)} dh - du.$$

This suggests the introduction of a particular scale of measurement of heat by the definition

(17) $$dq = \frac{\tau(t)}{\theta(t)} dh,$$

so that

(18) $$du = dq - dw, \qquad d\sigma = dh/\theta = dq/\tau,$$

where $d\sigma$, du are exact differentials, while dq in general would not be. In terms of the original differential forms (1) the result is then that there exist functions θ and τ of t only such that dh/θ and $\tau dh/\theta - dw$ are exact differentials. The dq and $d\sigma$ are the measures of heat on two special scales whose existence is implied in the Carnot principle.[1]

As to uniqueness, the mode of introduction of τ and θ shows that any two determinations for the same body or for different bodies are related by

$$\tau^* = \alpha\tau + \beta, \qquad \theta^* = \alpha\theta,$$

so that for the same dh:

$$dq^* = dq + \beta dh/\alpha\theta.$$

But since only the product $\sigma'\tau'$ is determined it is essentially general to hold α as unity, then the freedom left in the definition of dq can be used to arrange that equality in dh shall bring about equality in dq, by having $\beta = 0$; thus τ and θ may be understood as the same for all bodies.

In terms of the general and the two special scales of heat the efficiency ratio and the conditions of vanishing of the cyclic integrals of $d\sigma$ and du are

$$\frac{w}{h_1} = \frac{\tau_1 - \tau_2}{\theta_1}, \qquad \frac{w}{q_1} = \frac{\tau_1 - \tau_2}{\tau_1}, \qquad \frac{w}{\sigma_1} = \tau_1 - \tau_2;$$

$$\frac{h_1}{\theta_1} + \frac{h_2}{\theta_2} = 0, \qquad \frac{q_1}{\tau_1} + \frac{q_2}{\tau_2} = 0, \qquad \sigma_1 + \sigma_2 = 0;$$

$$w = \frac{h_1}{\theta_1/\tau_1} + \frac{h_2}{\theta_2/\tau_2} = q_1 + q_2 = \frac{\sigma_1}{1/\tau_1} + \frac{\sigma_2}{1/\tau_2};$$

[1] This proof should be compared with the deduction given by Larmor, *loc. cit.*, especially p. 332. He begins with the more primitive form of the Carnot postulate, that in order to have work done heat must fall in temperature, and considers also irreversible processes. The factorization which introduces one of his temperature functions results from a functional equation transcribing the coupling of two Carnot cycles. His $g(\theta)$ and $\psi(\theta)$ correspond to the $\theta(t)$ and $\tau(t)$ above; Raveau similarly deduces the existence of two distinct scales or functions of temperature. As to the use of the term "universal," however, the distinction should be noted, that the θ in the present paper, although the same for all bodies, depends on the scale of heat, while τ is independent of that scale. It is naturally the latter only that is to be considered truly universal as a scale of temperature.

inspection of which shows for one thing that θ depends on the scale of heat while τ does not. Thus τ/θ, $1/\theta$, and τ correspond to $B(t)$, $C(t)$, and $T(t)$ of Part I., while q and σ are thermal energy and entropy.

The parity of setting of the two special scales of heat is noticeable here as in Part I. It is hard to see how either can be said flatly to give the true measure of heat, though Callendar's view as to the preëminent claim of the entropy scale seems fully as reasonable as the common exclusive use of the energy scale. The latter has of course the obvious advantage for measurement and computation that it gives a constant ratio of work to thermal equivalent and approximate constancy of ordinary specific heats, but for theoretical purposes at least the entropy scale offers some advantages. For example, if for k/θ and l/θ be put κ and λ, these being then temperature-capacity for entropy and latent entropy of expansion, the differential forms with temperature on the τ-scale are

$$d\sigma = \kappa d\tau + \lambda dv, \qquad dw = pdv,$$

and the conditions are that $d\sigma$ and $\tau d\sigma - dw$ be exact differentials. These conditions are equivalent to the adapted Clapeyron and Clausius equations

$$\lambda = \frac{\partial p}{\partial \tau}, \qquad \frac{\partial \kappa}{\partial v} = \frac{\partial^2 p}{\partial \tau^2},$$

which are so simply interpretable on the graph of the isochoric (p, τ) curve.

To extend the theory to a system with more than two coördinates it is convenient to use the τ-scale of temperature and the σ-scale of heat, as determined for two-variable systems. A system with n coördinates of configuration, say $v_1 \cdots v_n$, will then be characterized by the differential forms

$$d\sigma = \kappa d\tau + \Sigma \lambda_i dv_i, \qquad dw = \Sigma p_i dv_i.$$

The Carnot principle may then be understood to be applicable to every two-variable process which such a system can undergo, through the presence of possible or conceivable constraints. This is equivalent to the condition that if for $v_1 \cdots v_n$ be put any arbitrary functions of τ and a single other parameter v, then $d\sigma$ and $\tau d\sigma - dw$ must be exact differentials in these two variables. The conditions for this prove to be equivalent to those under which the same expressions are exact differentials in the $n + 1$ variables, regarded as independent. To show this it is enough to consider only the following types of cycle: (a) where only one of the variables v_i varies, (b) where only two are affected, these undergoing variations proportionate but in arbitrary ratio. With such cycles,

starting at an arbitrary state of the system, the Carnot principle yields, from (*a*) the Clapeyron and Clausius equations for each of the variables separately, and from (*b*) the additional conditions

$$\frac{\partial p_i}{\partial v_j} = \frac{\partial p_j}{\partial v_i} \, , \qquad \frac{\partial \lambda_i}{\partial v_j} = \frac{\partial \lambda_j}{\partial v_i} \, ,$$

which indicate the conservation in an isothermal cycle of work and of heat separately. The scales θ and τ and the equations in (17) and (18) thus apply to these more general systems.

If for such a system the heat scale be still left arbitrary, the result is that dh/θ and $\tau dh/\theta - dw$ are exact differentials of functions of state σ and u, so that $dh = \theta d\sigma$, $dw = \tau d\sigma - du$. Now while a system with two variables only can have but two independent functions of state, one with more types of variation can have a corresponding number. But not more than two independent functions can have differentials linearly expressible in terms of the same two fundamental differential forms; in fact, in the case here, any function of state whose differential is a linear combination of dh and dw must be a function of σ and u. In this sense the theory of energy and entropy, and therefore the Carnot principle, yields the entire theory that can be based solely on dh and dw.

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