XIV. *The Caloric Theory of Heat and Carnot's Principle.** By
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"Difficile est proprie communia dicere."

1. *Introductory.*—It is the time-honoured privilege of a
President on these occasions, in place of providing new and
original material for discussion, to indulge in the retrospect or
review of some branch of physical science in which he may be
particularly interested. I propose to take advantage of this
presidential privilege by submitting for your approval some
reflections on the foundations of the science of heat. So much
has been written, and still continues to be written, on this
engrossing subject from the purely theoretical standpoint, that
I should not venture to abuse your patience by choosing so
hackneyed a theme if I did not feel that, by spending the best
part of my life in the practical teaching and experimental
investigation of the science, I had earned the right to an ex-
pression of opinion. I feel sure that, however, you may dis-
agree with my way of putting things, you will at least believe
that it is the outcome of practical experience, and represents
the point of view of a serious experimentalist. The subject
chosen is so large and the time at my disposal so limited that
I must be content with the merest outline of a suggestion, and
must leave you to fill in the details yourselves. It is impossible
to cover the whole ground, or to refer to a tithe of the ideas or
theories which have been from time to time proposed for
developing the fundamental principles of the science. If I
should appear to have omitted many considerations of impor-
tance I trust you will give me the benefit of the doubt, and
believe that the omission is due merely to exigencies of
space or time over which even a physicist has but a limited
control.

The caloric theory of heat is now so long forgotten that we
rarely hear it mentioned, except as an example of primeval
ignorance; but it was not really quite so illogical as it is

* Presidential Address, February 10, 1911.

generally represented to be.   The science of heat might have been developed along the lines of the caloric theory nearly, if not quite, as well as on the lines of the dynamic theory.   Some most important and fundamental ideas, which are obscured in the early stages of the present method of exposition, would, in fact, have been brought into greater prominence and more widely appreciated, and a clearer view of the whole subject might thus have been obtained.

The original conception of caloric as a subtle imponderable fluid, capable of flowing from one body to another, of expanding bodies, and of producing rise of temperature or change of state, was, in the main, merely a picturesque analogy, invented, like the electric or magnetic fluids, with the object of giving the mind a tangible something to reason about, a measurable entity remaining constant in various transformations or exchanges.   The fluid terminology remains a convenient method of expression even if the thing measured has not all the properties of a material fluid.

The first serious difficulties which the theory encountered were in explaining the apparent generation of heat by friction or compression.   It might have been boldly assumed, as Cavendish and others maintained, that heat was generated by friction in the same kind of way as electricity ; but a more generally acceptable explanation at the time appeared to be that some of the latent heat was ground or squeezed out of the bodies concerned and became sensible.   The abraded or compressed matter, according to this view, was not capable of containing so much heat as the original stuff, or its " capacity for heat " was diminished.   As there were no means of measuring the total heat content of a body, the " thermal capacity " was generally regarded as being proportional to the quantity of heat required to raise the temperature one degree, in which sense the phrase is still employed.   The possibility of this explanation of the production of heat by friction was negatived at an early date by the experiments of Rumford and Davy. Rumford (" Phil. Trans.," 1798) in one of his experiments using a boring machine with a blunt tool, succeeded in raising 26·5 pounds of cold water to the boiling point by means of friction in 2½ hours with the production of only 4,145 grains of metallic powder.   He then showed that the metallic powder required the same quantity of heat to raise its temperature 1 deg. as an equal weight of the original metal, or that its " capacity for heat " in this sense was unaltered.   He argued

that so small a quantity of powder could not possibly account for all the heat generated, and that the supply of heat appeared to be inexhaustible. Heat could not, therefore, be a material substance, but must be something of the nature of motion, as Newton and Bacon had surmised. The argument was not quite conclusive, because he was unable to show that the powder really contained the same total amount of heat as the solid metal. But the experiments must have satisfied every reasonable philosopher of the extreme improbability of the explanation then generally accepted. Davy's experiment (described in an essay "On Heat, Light and Combinations of Light," 1799), in which he melted two blocks of ice by rubbing them together, was more conclusive, since as he remarks " it is a well-known fact that the capacity of water for heat is greater than that of ice, and ice must have an absolute quantity of heat imparted to it before it can be converted into water. Friction consequently does not diminish the capacities of bodies for heat." In stigmatising the " last eleven words " as " a lame and impotent conclusion," Lord Kelvin (Ency. Brit., " Heat," 1882) inadvertently does Davy an injustice, because Davy evidently uses the phrase "capacity for heat " in both senses, as was common at the time. In a later passage of the same essay he defines capacity for heat as the total thermal content of the body, and employs the unfamiliar phrase " capability of temperature " to denote the heat required to raise the temperature. 1 deg.

Although it was clear from these and similar experiments that caloric was actually generated by friction and could not be regarded as a material fluid in the ordinary sense, insomuch as it did not in all cases obey the law of the conservation of matter, then recently established, the idea of heat as " a mode of motion " was at that time too vague to afford a satisfactory substitute for the fluid theory. Davy speaks of heat as " repulsive motion," and distinguishes it from light, which is " projective motion," and is capable of forming compounds with ordinary matter. Thus oxygen gas is not a simple substance, but a compound, termed by Davy " phosoxygen," of light and oxygen. A theory of this kind could not be usefully applied until it was shown how the motion corresponding to heat should be measured (whether by its momentum or *vis viva*, or otherwise), how much motion was required to generate a given quantity of heat, and whether the ratio of equivalence between heat and motion suitably measured was in all cases

invariable. These questions were, in fact, so difficult to settle that we can hardly wonder that it was 50 years before a satisfactory answer was obtained.

2. *Thermal Properties of Gases.*

Light was first thrown on the subject by investigations bearing on the thermal properties of gases. The laws of expansion of gases and the elementary properties of vapours were already familiar about this time from the researches of Dalton, Gay Lussac and others; but the data regarding the specific heats of gases were very meagre and conflicting. Dalton had found a rise of 50°F. produced by compressing air suddenly to half its volume. This was less than a third of the true rise of temperature, but in any case the result could not be interpreted in terms of quantity of heat generated without a knowledge of the specific heat.

The first reliable results for the specific heats were obtained shortly afterwards by Delaroche and Bérard ("Ann. Chim.," 1813). Their constant pressure method was a great advance on all previous work, and gave the mean specific heats referred to water between 15°C. and 100°C. They found that equal volumes of the permanent gases H_2, N_2, O_2 and CO at atmospheric pressure had nearly the same thermal capacities as air, the specific heat of which they found to be 0·267 calorie per gram at a pressure of 740 mm. of mercury. The compound condensable gases, CO_2, N_2O and C_2H_4, were correctly found to have larger thermal capacities per unit volume than air. They were unable to state whether the specific heats increased or diminished with temperature, but from an experiment with air at 1,000 mm. pressure, which gave the value 0·245 calorie per gramme, they concluded that the specific heats diminished with diminution of volume. The experiments of Regnault 40 years later showed that this observation was incorrect, but it appeared at the time to lend support to the view that the rise of temperature observed on suddenly compressing a gas was due to the diminution of its specific heat, a hypothesis otherwise unsupported by experimental evidence.

It was evident that the elasticity, or resistance of a gas to compression, would be greater in a rapid or adiabatic compression, on account of the rise of temperature, than in a slow compression at constant temperature. Laplace was the first

to see in this fact the probable explanation of the long-standing discrepancy between the observed velocity of sound and that calculated by Newton on the basis of Boyle's law of isothermal compression.   According to Boyle's law, a reduction of 1 per cent. in volume at constant temperature raised the pressure of air by 1 per cent.   The observed value of the velocity of sound required that in a rapid compression of 1 per cent. the pressure should be increased 1·41 per cent.   This result is more accurately expressed by the statement that the ratio of the adiabatic to the isothermal elasticity of air is 1·41.   At a later date ("Ann. Chim.," 1816) Laplace stated that he had succeeded in proving that the ratio of the adiabatic to the isothermal elasticity of a substance was the same as the ratio of the specific heat at constant pressure to the specific heat at constant volume.   This important result follows directly from the definitions of the two elasticities and the two specific heats, and is independent of any view as to the nature of heat or temperature.   But it appeared at the time to afford the strongest support to the caloric theory, because it showed that the specific heat was actually greater when the volume was allowed to increase than when the volume was kept constant, and because no explanation was forthcoming on the kinetic theory. The specific heats measured by Delaroche and Bérard were those at constant atmospheric pressure.   All attempts to measure the specific heats at constant volume had signally failed on account of experimental difficulties, but their values could be calculated from the known value of the ratio thus deduced by Laplace.

A few years later Clément and Désormes ("Journ. de Phys.," 1819) succeeded in verifying the value of the ratio deduced from the velocity of sound by directly measuring the changes of pressure produced by adiabatic and isothermal compression. They found the value 1·354, which was lower than the true value 1·41, because the compression in their experiments was not strictly adiabatic.   Gay Lussac and Welter ("Ann. Chim.," 1822) repeated the experiment with slight improvements, employing expansion instead of compression, and found a rather better approximation, namely, 1·375.   They found the ratio practically constant for a range of pressure from 144 to 1,460 mm., and for a range of temperature from —20°C. to +40°C.   Assuming on this evidence the constancy of the ratio of the specific heats of air, Laplace ("Œuvres," V., p. 143) showed that the specific heat per unit volume at a pressure p

should vary as $p^{1/\gamma}$, and the specific heat per unit mass as $p^{1/\gamma-1}$, according to the caloric theory, where γ is the ratio of the specific heats. This result happened to agree precisely with the values found by Delaroche and Bérard for air at 740 and 1,000 mm., and appeared to be an additional confirmation of the caloric theory. The same propositions were demonstrated by Poisson ("Ann. Chim.," 1823, XXIII., p. 337), who also gave the familiar relation, pv^γ=constant, between the pressure and volume of a gas in adiabatic expansion or compression. The last equation is evidently correct, but the reasoning with regard to the variation of the specific heat with pressure is somewhat obscure, and the result given does not appear to follow necessarily from the caloric theory.

3. Carnot's Reflexions on the Motive Power of Heat.

The greatest step in advance was made about this time by Carnot in his famous essay, entitled " Reflexions on the Motive Power of Heat," Paris, 1824. Proposals had frequently been made to employ other agents, such as air, alcohol or ether, in place of steam in a heat engine, with a view to securing higher efficiency or a greater quantity of motive power for a given consumption of fuel. Carnot proposed to find the answer to the questions, how the efficiency was limited, and whether other agents were preferable to steam. In considering this problem he first points out that motive power (which he measures in kilogrammetres, and employs as equivalent to the modern term " work ") cannot be said to be produced from heat alone, unless nothing but heat, or its equivalent fuel, is supplied. All parts of the engine, including the working substance or agent, must be at the end of the process in precisely the same state as at the beginning. He here assumes a fundamental axiom, which had always been taken for granted, but not so precisely and explicitly stated by previous writers.

Carnot's Axiom for a Cyclical Process.

" When a body has undergone any changes and after a certain number of transformations is brought back identically to its original state, considered relatively to density, temperature and mode of aggregation, it must contain the same quantity

of heat as it contained originally."* The ideal engine for theoretical purposes must, therefore, be supposed to work in a complete cycle of operations in which everything is restored to its initial state, except that a certain quantity of heat has been supplied to and utilised by the engine. This does not seriously limit the application of the theory, because, although practical engines do not always use the same identical mass of working substance for each stroke, they necessarily repeat a regular cycle of operations continuously, and it is generally possible to devise an equivalent theoretical cycle in which the working substance is restored after each stroke to its initial state. Carnot proceeds to show that motive power cannot be obtained from heat by alternate expansion and contraction of the working substance, without postulating the existence of two bodies at different temperatures to serve as boiler and condenser, or source and sink of heat respectively ; and conversely that, wherever a difference of temperature exists, it is possible to utilise it for the production of motive power. He thus deduces the fundamental rule for obtaining the best results.

* Carnot goes on to say : " In other words, the quantities of heat absorbed or disengaged in its diverse transformations are exactly compensated. This fact has never been doubted ; it has been first assumed without reflection, and then verified by calorimetric experiments. To deny it would be to upset the whole theory of heat, for which it serves as a basis. For the rest, one may say in passing, the principal foundations on which the theory of heat rests, require the most attentive examination. Many experimental facts appear almost inexplicable in the present state of this theory." Clausius " Pogg. Ann.," 1850 ; " Phil. Mag.," IV., vol. II., p. 2, 1851) misquotes this passage most ingeniously. He fails to notice that the essential point assumed by Carnot in any cyclical process is that the quantity of heat remaining in the body is the same when it has been brought back identically to the same state. He makes Carnot " expressly state that no heat is lost in the process, that the quantity (transmitted from the fireplace to the condenser) remains unchanged." Clausius makes *this* " the fact which has never been doubted," &c. In reality, Carnot, in describing his cycle, does not make the assumption which Clausius here attributes to him, because it is not a necessary part of the reasoning. Carnot does not, even in the paraphrase of his axiom, say that the quantities of heat absorbed or disengaged in its diverse transformations are *equal,* but merely that they are *exactly compensated,* so far as the body itself is concerned. Whether they are equal or not depends on the way in which a quantity of heat is measured. The essential point of the reasoning in Carnot's description of his cycle is that the result is independent of any assumptions with regard to the way in which temperature or heat are measured, provided that the quantity of heat remaining in the body is the same when it has been brought back to its original state after any transformations. The special word " compensated," which Carnot employs in place of " equal " in paraphrasing his axiom, would appear to imply that he did not consider the quantities of heat absorbed and disengaged necessarily equal, and that this was one of the points which " required the most attentive examination."

Carnot's Criterion of Thermal Reversibility.

" In order to realise the maximum effect, it is necessary that, in the process employed, there should not be any direct interchange of heat between bodies at sensibly different temperatures." Direct transference of heat between bodies at different temperatures would be equivalent to wasting a difference of temperature which might have been utilised for the production of motive power. This rule excludes all the well-recognised thermal sources of waste of power, which practical engineers had already been most successful in reducing. The ideal engine was also assumed to be free from mechanical losses such as friction. Under these conditions there is equilibrium, both mechanical and thermal, at every stage of the process, so that each operation is reversible, and may be supposed to be performed in either direction at will.

4. *Carnot's Ideal Cycle.*

Carnot first gives a rough illustration of an imperfect cycle, using steam in much the same way as in an ordinary steam engine, but supposing most of the usual losses absent. After expansion to condenser pressure, the steam is supposed to be completely condensed, and then returned as cold water to the hot boiler. He points out that the last stage does not confoim to his rule for maximum effect, because, although the water is restored to its initial state, there is direct passage of heat from a hot body to a cold body in the last process. Having thus established the general notions of a perfect cycle, and of reversibility as the criterion of perfection, he proceeds to give a more exact illustration, employing a gas as the working substance. In this demonstration he assumes only the well-established experimental facts (1) that a gas may be heated or cooled by rapid compression or expansion, and (2) that, if compressed or expanded slowly in contact with conducting bodies, it may be made to evolve or absorb heat at constant temperature. Carnot's cycle itself is so familiar that it is scarcely necessary to describe it in detail. It is much to be regretted, however, that it is not always given as nearly as possible in Carnot's own words. His description is so nearly perfect that it could hardly be improved. Details which may appear superfluous at a first perusal are seen, on more careful study, to be exactly in the right place. Unnecessary assumptions have been introduced by others in describing the cycle, and have led to mistakes

which Carnot carefully avoided.   For instance, Clapeyron, in describing the cycle, directs one to compress the gas at the lower temperature in contact with the cold body B until the heat disengaged is equal to that which has been absorbed at the higher temperature.   This operation would be very difficult to perform, and involves the unnecessary assumption that the gas at this point contains the same quantity of heat as it contained at the beginning of the first stage, so that when the body B is removed, the gas will be restored to its original temperature by adiabatic compression to its original volume.   It was chiefly for this reason that Clausius, who was acquainted with Carnot's work chiefly through the medium of Clapeyron's summary, so completely misinterpreted it, and substituted another proof. The same mistake undoubtedly induced Lord Kelvin to state (" Phil. Mag.," IV., 1852) that " Carnot's original demonstration utterly fails," and was the cause of the " corrections " attributed to James Thomson and Clerk Maxwell respectively. In reality, Carnot's original description is independent of any assumption as to the nature of heat, and requires no correction.

After completing the description of the cycle, and showing its exact reversibility, Carnot proceeds to say : " The impossibility of producing by the agency of heat alone a quantity of motive power greater than that which we have obtained in our first series of operations, is now easy to prove.   It is demonstrated by reasoning exactly similar to that which we have already given.   The reasoning will have in this case a greater degree of exactitude ; the air of which we made use to develop the motive power is brought back at the end of each cycle of operations precisely to its initial state, whereas this was not quite exactly the case for the vapour of water, as we have already remarked."   Carnot considered the proof too obvious (as indeed it is) to be worth repeating.   Unfortunately his original demonstration, referring to an imperfect cycle given merely *comme un aperçu*, as an introduction to the method, is not so exactly worded that exception cannot be taken to it.   I will, therefore, repeat the proof in a slightly more definite and exact form, as Carnot probably intended it to run.   " If it were possible to produce from a given quantity of heat supplied a greater quantity of motive power than that obtained from a reversible engine, it would suffice to divert a portion of this power to return to the source by means of a reversible engine the quantity of heat taken from it.   We should thus obtain at each repetition of the cycle a balance of motive power without

taking any heat from the source—that is to say, without any
consumption of fuel." The extreme improbability of such a
result is a sufficient *reductio ad absurdum* to satisfy any reason-
able intelligence. Whether the condenser is heated or cooled
in the process is immaterial for practical purposes. The con-
denser might be the ocean or the whole earth. We should thus
obtain the practical equivalent of a perpetual motion, inter-
preted by Carnot as the continuous creation of motive power.
If the conservation of energy is assumed, it is true that the
condenser would be cooled. But it hardly seems necessary to
invoke the law of the conservation of energy, and to make a
final appeal to axioms, such as those of Kelvin* or Clausius,
which are far less self-evident. The conservation of energy as
applied to heat is itself an experimental law, and the final
appeal must be to experiment in any case.

5. *Carnot's Principle.*

Carnot stated his principle as follows :—
" The motive power of heat is independent of the agents set
at work to realise it ; its quantity is fixed solely by the tem-
peratures of the bodies between which in the limit the transfer
of heat is effected."
He adds to this statement : " It is necessary to understand
here that each of the methods of developing motive power
attains the perfection of which it is susceptible. This condi-
tion will be fulfilled if, as we have remarked above, there is not
produced in the body any change of temperature which is not
due to a change of volume, or, what is the same thing otherwise
expressed, if there is never contact between bodies at sensibly
different temperatures." He also explains that the principle
applies equally to different substances and to different states of
the same substance, provided that the temperature limits are
the same for the agents compared in any case.
Carnot's principle may be stated in a great variety of different
ways, which are more or less equivalent, but it seems best to
adhere as closely as possible to Carnot's own words, the mean-

* Carnot's proof does not assume either that heat is measured as energy
or that energy is conserved. If both these points are assumed, his axiom
that it is impossible to make a heat engine work without taking heat from
the source, or without consumption of fuel, is equivalent to Kelvin's axiom
that motive power cannot be obtained by cooling the condenser. One
may be deduced from the other; but Carnot's axiom is the most direct
result of experience with heat engines, involves the fewest assumptions, and
appears to be the most appropriate for the required formal proof.

ing of which is sufficiently clear and exact for all practical purposes.   Whatever form of words is adopted, it will always be
necessary to define the terms employed, and to explain how the
principle is to be applied.   On this understanding many
different modes of expression are equally valid and satisfactory but many paraphrases of Carnot's principle have been
given from time to time which appear to be distinctly objectionable as obscuring the real points at issue: Clausius, for
instance (" Pogg. Ann.," 1850, Vol. LXXIX., p. 369) quotes
Carnot's principle as follows : " The performance of work is
equivalent to a transference of heat from a hot body to a cold
body without the quantity of heat being thereby diminished."
This method of statement omits both the essential points, (1)
that the efficiency is independent of the working substance,
and (2) that it is a function solely of the temperature limits.
It also introduces an unnecessary assumption with regard to
the manner in which a quantity of heat is measured, which is
not an essential part of Carnot's reasoning.   The principle
itself is independent of the manner in which either heat or
temperature is measured.   Provided that the methods of
measuring heat and temperature are consistent, and are the
same for all substances compared, the only effect of altering
the temperature scale or the definition of the heat unit, is to
alter the form of the function representing the efficiency.

6. *Carnot's Applications of his Principle.*

Carnot endeavoured to apply his principle to the greatest
possible variety of cases, and to subject it to the most complete
experimental verification, so far as the data available at that
time would permit.   He succeeded in establishing for the first
time several important results, which have in some cases been
overlooked or attributed to others.   He appears to have
worked out most of these results analytically in the first instance as indicated by his footnotes, and to have subsequently
translated the formulæ into words in the text for the benefit
of his non-mathematical readers.   He expressed his principle
analytically in the following simple form.   If W is the quantity
of work or motive power obtained in a reversible cycle from a
quantity of heat, Q,* communicated to the working substance
at a temperature, t, C, the condenser, being assumed for convenience at 0°C., we may write

$$W/Q = F(t), \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

* It is not here assumed that heat is necessarily measured as energy.

where F(t) is some function of the temperature limits, depending on the way in which temperature and heat are measured but independent of the properties of the working substance. Owing to the limited state of knowledge with regard to the physical properties of bodies at that time, he was unable to apply the principle generally in this form. He points out that a great simplification is introduced in the application of the principle by considering a cycle of infinitesimal range, dt, but finite heat absorption Q, at a temperature t. He thus obtains by differentiation the corresponding expression,

$$d\mathrm{W}/dt = \mathrm{QF}'(t), \quad . \quad . \quad , \quad . \quad . \quad . \quad . \quad (2)$$

where F'(t) is the derived function of F(t), and is generally known as Carnot's function. This function evidently denotes the quantity of work obtainable per degree fall in a Carnot cycle per unit of heat supplied at the temperature t; and is the same for all substances at the same temperature.

Carnot, in the first instance, by applying the principle in this form to the discussion of the thermal properties of gases, endeavoured to complete the solution of the problem from the theoretical side by showing how the value of his function F(t) or F'(t) might be expected to vary with temperature, consistently with the ascertained laws of gases, and with various simple assumptions made with regard to properties which had not been experimentally determined.

7. *Properties of Gases deduced by Carnot from his Principle.*

Carnot's discussion will be followed as closely as possible with a few slight changes in the notation to render it more familiar. The work done in isothermal expansion at a temperature, T (Carnot writes $t+267$) by a gas obeying the law $pv = \mathrm{RT}$, in expanding from v_o to v is $\mathrm{RT} \log_e (v/v_o)$. The work done in a cycle of range $d\mathrm{T}$ per 1 deg. fall is evidently $d\mathrm{W}/d\mathrm{T}$ $= \mathrm{R} \log_e(v/v_o)$. By Carnot's principle this is equal to QF'(t), where Q is the corresponding quantity of heat absorbed. We thus obtain the expression for the heat absorbed by a gas in isothermal expansion,

$$\mathrm{Q} = \mathrm{R} \log_e (v/v_o)/\mathrm{F}'(t), \quad . \quad . \quad . \quad . \quad (3)$$

which must be the same for all gases at the same temperature for the same ratio of expansion v/v_o, provided that they obey the law $pv = \mathrm{RT}$, and that corresponding quantities of the different gases are taken (equal volumes at the same standard

temperature and pressure) so that the constant R is the same for all. In other words, the heat absorbed by a gas in iso-thermal expansion is proportional to the whole work done, and bears to it the ratio $1/TF'(t)$. This result is independent of the way in which temperature and heat are measured, provided that the gases obey the same law of isothermal expansion and give the same scale of temperature.

Since, when a gas absorbs a quantity of heat equal to the difference of the specific heats at constant pressure and volume, the work done in isothermal expansion is pv/T or R, Carnot deduces from the above general result that the difference of the specific heats (for equal volumes measured under the same conditions) must be the same—namely, $R/TF'(t)$—for different gases at the same temperature, and must also be independent of the pressure. He draws up a table showing the values of the specific heats at constant volume deduced from the results of Delaroche and Bérard at constant pressure. On this he re-marks that the *ratio* of the specific heats must be different for different gases, whereas it had generally been assumed to be the same. The elevation of temperature produced by a sudden compression must therefore be different for different gases, and he gives a table showing the results.

Since, according to the experiments of Gay Lussac and Welter the ratio of the specific heats of air is independent of the pres-sure and temperature, and according to his own theory the difference of the specific heats must also be independent of the pressure at the same temperature, it follows that the specific heats themselves must be independent of the pressure. Carnot points out that this is inconsistent with the result of Delaroche and Bérard previously cited for the specific heat of air at 1,000 mm. pressure—namely, 0·245—which is less than the value 0·267 found at 740 mm. The discrepancy must be due to errors of experiment. The variation of the specific heats with pressure was doubtful, because it rested on a single diffi-cult experiment, and the range of pressure was too restricted for a satisfactory conclusion to be drawn.

8. *Carnot's Application of the Caloric Theory.*

The results so far obtained by Carnot in his investigations with regard to the specific heats of gases, were independent of the caloric theory and remain equally true on the kinetic theory, although they have frequently been credited to other

writers.*   Because in some cases he employed the language and reasoning of the caloric theory, it does not follow, as most writers have hastily assumed, that his whole argument breaks down.   In attempting to unravel the relations of the specific heats, Carnot was compelled to employ some theory or assumption as to the nature of heat.   He naturally adopted the caloric theory, because no other theory was available at that time, and the experimental data were too inadequate to permit of any other method of treatment.

The most fundamental postulate peculiar to the caloric theory is that the quantity of caloric required to be added to a body to transform it from any state, defined, we may suppose, by temperature t_0 and specific volume v_0, to any other given state, defined by temperature t and specific volume v, is the same, in what ever way the change is effected. Carnot applies this assumption to the problem in hand in the following manner.   Suppose that unit mass of gas is first heated at constant volume v_0 up to the temperature t, absorbing a quantity of caloric U_0, and is then expanded at constant temperature t, absorbing a quantity of caloric $R \log_e (v/v_0)/F'(t)$, as proved in the last section.   Next suppose that the gas is first expanded from v_0 to v at constant temperature t_0, absorbing a quantity

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* Dulong (" Ann. de Chim.," XLI., p. 156, 1829), adopting a method due to Chladni, compared the velocities of sound in different gases by observing the pitch of a note given by the same tube when filled with the gases in question. He thus obtained the ratios of the specific heats.   For O_2, H_2 and CO the ratios were the same as for air.   But for CO_2, N_2O and C_2H_4 the ratios were much smaller than for air.   On comparing his results with the specific heats for the same gases found by Delaroche and Bérard, Dulong observed that the changes of temperature for the same compression were in the inverse ratio of the specific heats at constant volume.   He thus deduced the important conclusion, agreeing with that obtained theoretically by Carnot five years earlier, that " equal volumes of all gases under the same conditions evolve on compression the same absolute quantity of heat."   Carnot's result is more general and significant, and it is clear that he deserves some credit for the prediction.

Joule in 1845 showed by experiment that the ratio (Carnot's $TF'(t)$) of the work done to the heat evolved in compressing a gas was nearly, if not quite, the same as the ratio J of work spent in heating water by friction to the heat evolved.   The mechanical equivalent J must, therefore, be equal to Carnot's $TF'(t)$, if heat is measured as energy.   Since Joule's experiments were all performed practically at one temperature, they do not afford direct evidence as to the variation of $F'(t)$ with temperature, unless we assume that a quantity of heat is measured as a quantity of energy which cannot vary with temperature.   Admitting this, $F'(t)$ must be equal to J/T, as Joule himself suggested in a letter to Kelvin in 1848.   Carnot is entitled to some credit for having predicted that the ratio must be constant at any one temperature, or must be a function of the temperature only.   Mayer in 1842 assumed the equivalence on the basis of the old principle " *causa æquat effectum*," which could hardly be regarded as scientific demonstration.

of caloric given by $R \log_e(v/v_o)/F'(t_o)$, and is then heated at constant volume v from t_o to t, absorbing a quantity of caloric U. The total quantity of caloric Q required in either case must be the same on the caloric theory. Whence we have,

$$U_o + R \log_e (v/v_o)/F'(t) = Q = U + R \log_e (v/v_o)/F'(t_o). \quad . \quad (4)$$

From this equation it is immediately obvious that, if the specific capacity for caloric at constant volume is independent of the volume, since $U = U_o$, $F'(t)$ must be equal to $F'(t_o)$; or Carnot's function must be independent of the temperature, if the latter is measured on the gas scale and if the heat is measured as caloric.* We also observe, as Carnot points out, that it is not necessary for the specific capacity for caloric to be a function of the volume in order to explain the rise of temperature produced by compressing a gas. But this assumption had so frequently been made by Laplace and others that it had come to be regarded as an essential part of the explanation of the phenomenon on the caloric theory. Carnot also investigates the general law of the variation of specific heat with pressure, admitting the result of Delaroche and Bérard as correct. But since we know now, from the observations of Regnault, first published in 1852, that the result of Delaroche and Bérard was wrong, and that the specific heat of air is practically independent of the pressure, it is clear that Carnot deserves some credit for having given the correct solution of the problem on this assumption.

Putting $F'(t) = \text{constant} = A$, Carnot obtains for the work

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* The corresponding expression for $F'(t)$ on the mechanical theory may be obtained by an exactly similar process. If a quantity of heat is measured as energy, the difference of the quantities of heat absorbed and rejected in the cycle represented by equation (4)—namely, $U_o - U + R \log_e (v/v_o)[1/F'(t) - 1/F'(t_o)]$—must be equal to the external work done in the cycle—namely, $R \log_e (v/v_o)(T - T_o)$—divided by the mechanical equivalent J. If the specific heat at constant volume is independent of the pressure $U = U_o$, and $F'(t)$ must be equal to J/T. Substituting this value of $F'(t)$ in Carnot's expression (3) for the heat absorbed by a gas in isothermal expansion, we see that it is equivalent to the work done provided the gas obeys Boyle's law, and that its specific heat at constant volume is independent of the pressure. Clausius at a later date reversed this procedure. He began by assuming the equivalence of the heat absorbed to the work done by a gas in isothermal expansion, and deduced that the specific heat was independent of the pressure. But Carnot's method appears more logical and direct. The assumption of the equivalence of heat and work in a non-cyclical process, thus made by Mayer and Clausius, was, in effect, a violation of Carnot's fundamental axiom, and could not be justified theoretically. Carnot's assumption is also preferable from the experimental standpoint, because it proposes a more direct and simple test—namely, that the specific heat should be the same at different pressures.

done per unit of caloric supplied at a temperature $t°$C. in a finite cycle of range t to $0°$C., the simple expression $F(t) = At$. Expressing the same result in terms of temperature T on the gas scale, we obtain for the work, W, due to a quantity, Q, of caloric supplied at a temperature, T, in a Carnot cycle of range T to T_o, the expression

$$W = AQ\ (T - T_o). \quad \ldots \ldots \quad (5)$$

This expression is less general than equation (1), because it assumes that a quantity of heat is measured as caloric, and that temperature is measured on the scale of a gas obeying Boyle's law and possessing the property that its specific heat at constant volume is independent of the pressure.   Admitting these assumptions the solution is obviously correct.   The quantity of caloric, Q, supplied at the temperature, T, is necessarily the same as the quantity rejected at the temperature T_o, because the quantity of caloric in the working substance must remain constant, when no heat is supplied, in reversible expansion or compression such as is postulated by Carnot in his cycle.   We observe that, if heat is measured as caloric, it is quite correct to state that " the production of work from heat is due, not to an actual consumption of caloric, but to the transport of caloric from a higher to a lower temperature."   Carnot's analogy of the water-wheel is thus exactly justified.   Caloric, like water, is not itself motive power, but is capable of performing work under suitable conditions in virtue of its tendency to flow down a temperature gradient.   The quantity of motive power produced is directly proportional to the quantity of caloric and to the fall of temperature.

9. The Motive Power of a Quantity of Caloric.

The solution thus found by Carnot, and expressed in equation (5), was not merely the correct final solution of the problem on the caloric theory, it is also immediately obvious that it is perfectly consistent with the kinetic theory of heat, and supplies the master key to the relations between heat and motive power.   Caloric may be said to possess motive power in virtue of its elevation of temperature, just as water possesses motive power in virtue of its available head or pressure.   In the case of caloric there is a definite limit set by the absolute zero of temperature to the quantity of motive power obtainable by a cyclical process from a quantity of caloric supplied at any temperature.   Putting $T_o = 0$, the absolute zero, the maximum

quantity obtainable from a perfect gas as working substance, and therefore from any other substance whatever, is evidently AQT, which may be regarded as the absolute work-value of a quantity of caloric, Q, supplied at a temperature, T, on the absolute scale. The quantity of motive power developed, if the fall available is $T—T_o$, is $AQ(T—T_o)$. The limit of efficiency for such a fall, or the ratio of the motive power obtained to the total motive power of the caloric supplied, is $(T—T_o)/T$. The motive power of the caloric rejected at T_o is AQT_o. The sum of the quantities of motive power utilised and rejected is equal to the total motive power of the quantity supplied at T.*

Carnot's solution is not merely consistent with the mechanical theory; it directly states the principle of the conservation of motive power, and gives all the results which follow from that theory so far as they relate to reversible processes. He could not fairly have been expected to realise this at the time and to express his results in terms of the mechanical theory, because that theory had not been put in a definite form. His results are not necessarily incorrect because they were expressed in terms of the caloric theory. The numerical values which he calculated in various ways for the motive power of caloric were correct so far as the experimental data available at that time permitted. They deserve in reality to be regarded as the first calculations of the mechanical equivalent of heat, although they were expressed in a manner which renders them at first sight unfamiliar to modern readers.

10. *Carnot's Numerical Verification of his Principle.*

The investigation of the specific heats of gases having failed, on account of discordant experimental data, to lead to a *conclusive* result with regard to the variation of $F'(t)$ with tem-

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* This result, which is equivalent to the fundamental postulate of the mechanical theory, may readily be extended to a reversible cycle of any form. The given cycle may be supposed to be divided by a family of adiabatic or equicaloric curves into a number of elementary Carnot cycles of different ranges. For each of these elementary cycles, the quantity of caloric absorbed is equal to that rejected, and the difference of the energies of the caloric supplied and rejected is equal to the external work done. Taking the sum of the elementary cycles, the total quantity of caloric absorbed must be equal to that rejected in any cycle, which is the fundamental postulate of the caloric theory; and the difference of the quantities of heat energy absorbed and rejected in the cycle must be equal to the external work done, which is the fundamental postulate of the mechanical theory. The two postulates, so far from being opposed to each other, are mutually equivalent, and both are implied in Carnot's solution.

perature, Carnot next devotes his attention to the numerical calculation of the values of $F'(t)$ at different temperatures from the properties of different gases and vapours, so far as the scanty material at his disposal permitted.   His first calculation from the properties of air at 0°C. appears at first sight to be unnecessarily long and involved, owing to his elaborate endeavour to avoid what he calls algebraic language ; but he probably deduced the answer directly in the first instance from his expresison for the heat absorbed in isothermal expansion, applied to the difference of the specific heats—namely, $R/TF'(t)$. Employing his data, the value of $F'(t)$, or the work done in a cycle per degree fall per unit of heat supplied, comes out 1·395 kilogrammetres per kilocalorie per degree fall at 0°C.   This method of calculation, based on the work done in a cycle, does not, like that of Mayer or Clausius, involve the assumption that the *whole work* done in isothermal expansion is equivalent to the heat supplied, which is true only for a perfect gas.   Carnot's method applies to any gas or vapour, however imperfect, and would give the same result exactly for all substances at the same temperature if the experimental data were correct.   The absolute equivalent of the kilocalorie is obtained, as explained in the last section, by multiplying this result by the absolute temperature corresponding to 0°C. on the scale of a perfect gas— namely, 273—which gives 380 kilogrammetres for the mechanical equivalent of the kilocalorie.   The discrepancy from the true value, 427 kilogrammetres per kilocalorie, is due merely to errors in the experimental data.

For steam at 100°C., taking Dalton's value of (dp/dt), the rate of increase of pressure with temperature—namely, 26 mm. of mercury, or 0·36 metre of water—and taking the specific volume of steam at 100°C. as 1,700 litres per kilogramme, Carnot finds the motive power dW/dt per degree fall in a cycle employing 1 kg. of steam, to be 1,700×0·36=611 kilogrammetres.   The quantity of heat supplied is the latent heat of vaporisation per kilogramme at 100°C., which he takes as 550 kilocalories.   The work in kilogrammetres per kilocalorie per degree fall, or the value of $F'(t)$ is

$$F'(t) = 611/550 = 1·112 \text{ at } 100°C.$$

Multiplying this result by the absolute temperature 373°, we obtain 415 kilogrammetres as the absolute equivalent of the kilocalorie, which is a better approximation, because the data for steam were more accurate than those for air.

The method of calculation employed for steam is equivalent to the formula

$$(v-w)\,(dp/dt) = LF'(t), \quad \ldots \ldots \quad (6)$$

where $(v-w)$ is the change of volume on vaporisation, and L the latent heat. This formula is generally known as Clapeyron's, but Carnot appears to be entitled to some credit for it, because it is simply the direct expression of his principle as applied to change of state, and because he was the first to employ it for numerical calculation, although he does not happen to give the formula itself in algebraic form in his footnotes.

Applying the same calculation to the vapour of alcohol at its boiling-point, 78·7°C., Carnot found the value $F'(t) = 1\cdot230$ kilogrammetre per kilocalorie per degree fall. This would not necessarily agree with the value found from steam at 100°C., because the temperature was different. Assuming, in accordance with Watt's law, that the total heat of steam reckoned from 0°C. was constant and equal to 650 kilocalories per kilogramme, the latent heat at 78·7°C. would be 571 kilocalories. Taking the appropriate value of (dp/dt) from Dalton's tables, Carnot thus finds $F'(t) = 1\cdot212$ from steam at 78·7°C., which agrees very fairly with the result deduced from alcohol at the same temperature. A similar calculation for steam at 0°C., taking the latent heat as 650 from Watt's law, gave the value $F'(t) = 1\cdot290$, which differs materially from the value $1\cdot395$ found for air at the same temperature; but the data for steam were here so uncertain, that no stress could be laid on the discrepancy. The value $F'(t) = 1\cdot290$ gives 352 kilogrammetres for the kilocalorie. The discrepancy in the values of the kilocalorie deduced in this way from steam at different temperatures is not to be wondered at, because Lord Kelvin (" Trans." R.S. Edn., XIV., 1849) in re-calculating by a modification of Carnot's method the mechanical equivalent J from Regnault's greatly improved data for steam, found values ranging from 1,357 ft.-pounds per pound degree C. at 0°C. to 1,578 ft.-pounds at 230°C. Joule had then by direct experiment found values ranging from 1,368 to 1,476 ft.-pounds at 10°C. to 16°C. Lord Kelvin was not satisfied that the value of J was the same at different temperatures. It required a bold speculator like Clausius to argue that there could be no variation with temperature.

Carnot laments that data were lacking, especially the values

of (dp/dt), to enable him to calculate $F'(t)$ for solids and liquids, and particularly for the case of fusion of ice.   If he had been in possession of Lord Kelvin's value—namely, 130 atmospheres—of the pressure required to lower the freezing point of water 1°C., he would have found $F'(t)=1\cdot53$, or 418 kilogrammetres as the equivalent of the kilocalorie at 0°C.   With the data at his disposal, one can hardly wonder that he was baffled at every turn in his attempts to verify his theory.

Reviewing the numerical data for $F'(t)$, which varied from $1\cdot112$ kilogrammetres per kilocalorie per degree fall at 100°C. to $1\cdot290$ and $1\cdot395$ at 0°C., Carnot was led to the conclusion that $F'(t)$ probably diminished with rise of temperature on the gas scale, but that the numerical data were not sufficiently exact to determine the law of variation with temperature.   Unfortunately the apparent diminution of $F'(t)$ with rise of temperature was most readily explained by supposing that the specific heat of a gas was not independent of the volume, but increased with increase of volume, as Delaroche and Bérard had found. We see immediately from Carnot's equation (4) that if v is greater than v_o, and U greater than U_o, then $F'(t)$ must be less than $F'(t_o)$.   In other words, $F'(t)$ must diminish with rise of temperature.   It happened that the mistake made by Delaroche and Bérard was very nearly of the right order of magnitude to account for the observed rate of diminution of $F'(t)$ with rise of temperature.   Carnot was thus dissuaded from pursuing further the simple and obvious solution—namely, that $F'(t)$ was constant—which he had founded on the assumption that the specific heats were independent of the pressure.

If Carnot had not been misled by this fundamental error in the work of Delaroche and Bérard, and if his numerical data had been a little more accurate, he could not have failed to notice that the quantity of caloric in a kilocalorie varied inversely as the absolute temperature, or that its equivalent motive power was the same at all temperatures.   In other words, that the kilocalorie was a unit of motive power, and not a unit of caloric.   According to his data, neither the work obtainable per degree fall, nor the total work obtainable from a kilocalorie, was the same at different temperatures.   Both appeared to vary to about the same extent, but in opposite directions.   The point which naturally did not occur to Carnot, and which the experimental data were too uncertain to suggest, was the extremely fundamental point (which was also missed by subsequent writers in dealing with the caloric theory)

that a quantity of caloric as measured by his equation, did not remain constant under the conditions of an ordinary calorimetric experiment, when heat was allowed to flow directly from a hot body to a cold body.

11. *Measurement of Caloric.*

According to Carnot's solution, $W = AQ(T-T_o)$, the natural measure of a quantity of caloric is the work done per degree fall in a Carnot cycle.

The constant A in this relation may be reduced to unity by a suitable choice of units. The absolute unit of caloric is that quantity which is capable of doing unit work per degree fall in a Carnot cycle. If the absolute unit of work is taken as the joule or watt-second, the absolute unit of caloric may appropriately be styled the CARNOT.

The CARNOT is that quantity of caloric which is capable of producing one joule of work in a Carnot cycle per 1°C. fall on the scale of a perfect gas.

The number of carnots of caloric required to vaporise one gramme of water at 100°C. under standard conditions is readily calculated from Carnot's data. Since the work done per gramme vaporised per degree fall is 0·611 kilogrammetres, or nearly 6 joules, the caloric of vaporisation is nearly 6 carnots. The work done per degree fall per kilocalorie of heat supplied at 100°C. is 1·112 kilogrammetres, or nearly 11 joules. The number of carnots of caloric in a kilocalorie at 100°C. is nearly 11. Taking 130 atmospheres C.G.S. as the pressure required to lower the melting point of ice 1°C., and 0·092 cubic cm. as the diminution of volume per gramme on melting, the work obtainable from 1 gramme of ice at 0°C. in a Carnot cycle per degree fall is $130 \times 0·092/10 = 1·2$ joules. The caloric of fusion is, therefore, 1·2 carnots. The mechanical equivalent of Q carnots supplied at T Abs. is QT joules. These values are calculated from the work which might be done in a reversible cycle, and are quite independent of calorimetric data. The caloric absorbed by 1 gramme molecule of a perfect gas (R = 8·3 joules per 1 deg.) in expanding at constant temperature from v_o to v, is given by Carnot's equation (3) as $Q = 8·3 \log_e (v/v_o)$ carnots, and is independent of the temperature. The difference of the specific capacities for caloric at constant pressure and volume at a temperature, T, is 8·3/T carnots per degree or the absolute work value of the difference is 8·3 joules per degree.

12. *Equivalence of the Caloric and Kinetic Theories.*

The exact correspondence between the solution obtained by Carnot on the caloric theory with that subsequently obtained by Clausius, Rankine and Kelvin on the kinetic theory, is most easily appreciated if we compare the steps by which each solution was obtained. For this purpose we may follow the exposition of the kinetic theory as given by Clausius, as it is the most direct, and corresponds most nearly with the method of Carnot. Clausius starts with assuming Carnot's relation in the form $dW/dt = QF'(t)$, which is equally true on either theory, whether heat is measured as energy or as caloric. The divergence begins with the assumption that heat is measured either as a quantity of caloric (denoted by Q)*, or as a quantity of energy (denoted by q). Adopting the gas scale of temperature, these assumptions determine the form of the function $F'(t)$.

Carnot shows, as already explained, that if the specific heat of a gas at constant volume is independent of the pressure, $F'(t)$ must be constant, $=A$, on the caloric theory, if temperature is measured on the gas scale. This gives $dW/dt = AQ$, or $W = AQ(t - t_o)$ in a finite cycle. The measure of caloric is work per degree fall, and the work equivalent of caloric is found by multiplying the caloric by the absolute temperature and by a constant A. It follows that the work done by a perfect gas in isothermal expansion is the equivalent, AQT, of the caloric supplied, and that the difference of the specific capacities for caloric R/AT, is the same for all gases if equal volumes are taken.

Clausius proceeds in the opposite direction. He begins by assuming with Mayer as highly probable on general grounds that the work done by a gas in isothermal expansion is the equivalent Jq of the heat absorbed, which gives immediately, from Carnot's equation, $F'(t) = J/T$ when heat is measured as a quantity of energy. This had been previously suggested by Holtzmann (1845), but Clausius, having the advantage of Joule's experiments, was able to show that the numerical values of J/T were all reasonably consistent with Carnot's values of $F'(t)$ for the calorimetric unit. Applying this assumption to gases, it follows that the specific heat at constant volume must be independent of the pressure, and that the difference of the specific heats must be equal to R/J. Clausius

* To indicate that a quantity of heat is measured differently in the two sets of formulæ, capitals will be used for quantities depending on the caloric measure of heat, and small letters for the corresponding symbols in energy measure.

ignores the evidence of Delaroche and Bérard on the variation
of the specific heat with pressure, which gave Carnot so much
trouble, but adopts that of Gay Lussac and Welter on the con-
stancy of the ratio, which he (erroneously) states " cannot be
reconciled with the theory of Carnot as heretofore treated."
Assuming the constancy of the specific heats, he deduces
Poisson's equation for the adiabatics. He finally obtains for
the heat absorbed by a gas in isothermal expansion from v_o to
v the expression $q = RT \log_e (v/v_o)/J$, which is the same as the
assumption with which he started, and is equivalent to Carnot's
expression (3). The results thus obtained were not new, ex-
cept in the manner of expression. They were given to show
that the kinetic theory was consistent with the then ascer-
tained properties of gases.

   We have already seen that Carnot's principle takes the form
given in equation (6) when applied to vapours. Substituting
$F'(t) = A$, this becomes $(v-w)(dp/dt) = AL$, where L is the latent
caloric. On the kinetic theory we must substitute $F'(t) = J/T$,
and the equation becomes $(v-w)(dp/dt) = Jl/T$, where l is the
latent heat energy, and is equal to the latent caloric L multi-
plied by T, if the units are chosen so that the constants A and J
are the same. Assuming J constant, Clausius employs this
equation (in the reverse way to Lord Kelvin) to calculate the
deviations of steam from the ideal state, which he regards as
being the explanation of the variation of J with temperature
deduced by Lord Kelvin from Regnault's experiments. This
calculation was well meant, but indecisive, because, as we now
know, Regnault's formula for the latent heat was erroneous.

   Joule, by his experiments on gases, had arrived at the con-
clusion that in the performance of a heat engine the heat
energy converted into work was not given back to the conden-
ser. This is true of heat measured as energy, and appeared at
first not only to be a conclusive disproof of the caloric theory,
but also to be quite irreconcilable with the proof of Carnot's
principle as given by Clapeyron. Clausius showed that this
result was not necessarily inconsistent with Carnot's principle
itself ; but that, on the kinetic theory, in any cyclical process,
the heat returned to the condenser must be less than that
taken from the source by a quantity equivalent to the external
work done. Applying this principle to an infinitesimal cycle
with steam as the working substance, he deduced a new and
unexpected result, discovered about the same time by Rankine.
If saturated steam is compressed, heat must be abstracted

from it to reduce it to the state of saturation at the higher pressure and temperature ; in other words, the specific heat of steam maintained in the state of saturation is negative. This result is so good an illustration of the difference between the kinetic and caloric theories that it deserves fuller explanation.

If s', s'' are the saturation specific heats of water and steam respectively, l and $l+dl$ the latent heats of vaporisation at neighbouring temperatures T, and T$+d$T, the heat supplied in raising unit mass of water from T to T$+d$T and vaporising it at T$+d$T will be $s'd$T$+l+dl$. The heat abstracted in cooling the saturated steam to T, and condensing it at T, will be $s''d$T$+l$. The difference of the quantities of heat absorbed and abstracted—namely, $(s'-s'')d$T$+dl$—must, according to the kinetic theory, be equivalent to the work done in the cycle $(v-w)$ $(dp/dt)d$T. But this work by the previous equation (6) deduced from Carnot's principle, is itself equivalent to a quantity of heat $(l/$T$)d$T. Dividing the equation by dT, so as to obtain the difference in the quantities of heat absorbed and abstracted per degree range of the cycle, we obtain the well-known equation of Clausius,

$$s'-s''+dl/d\mathrm{T}=l/\mathrm{T}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Knowing the approximate vlaues of all the quantities except s'' at 100°C.—namely, $s'=1, dl/d\mathrm{T}=-0.70, l/\mathrm{T}=540/373=1.45$ calories per degree—we obtain with Clausius, $s''=s'+dl/d\mathrm{T}$ $-l/\mathrm{T}=-1.15$, or the specific heat of saturated steam 100°C. is negative and numerically greater than that of water. Clausius remarks that this is inconsistent with the caloric theory, which gives the formula $s''=s'+dl/d\mathrm{T}$, without the negative term $l/$T, and would make the specific heat *positive* and equal to $+0.30$, according to Regnault's data. In reality there is no inconsistency. It is merely a question of the difference between the caloric measure and the energy measure of heat.

On the caloric theory the corresponding equation is deduced as follows by Carnot's method. If S$'$, S$''$ are the specific capacities for caloric of water and steam in the state of saturation, and if L and L$+d$L are the values of the latent caloric of vaporisation at T and T$+d$T, the caloric absorbed in the cycle —namely, S$'d$T$+$L$+d$L—must be equal to the caloric abstracted—namely, S$''d$T$+$L—we thus obtain

$$\mathrm{S}''=\mathrm{S}'+d\mathrm{L}/d\mathrm{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which agrees *in form* with the equation ascribed by Clausius to the caloric theory, but the quantities involved are quan-

tities of caloric, and not quantities of energy. If we imagine s', s'' and l, expressed in joules, and S', S'' and L in carnots, the latter are reduced to joules by multiplying them by T. Muliti-plying through the last equation by T, and writing $S''T=s''$, $S'T=s'$ and $L=l/T$, we obtain

$$s''=s'+Td(l/T)/dT=s'+dl/dT-l/T, \quad . \quad . \quad . \quad (9)$$

which is *identical* with the equation deduced by Clausius from the kinetic theory.

We deduce from the above example, or from many others which might be given, that the fundamental postulate of the caloric theory, which Carnot employed in deducing his solution $W=AQ(T-T_o)$, and which Clausius was regarded as having conclusively disproved—namely, that the caloric absorbed is equal to that abstracted in any reversible cycle—so far from being opposed to the kinetic theory, is mathematically equivalent to Joule's proposition that the heat energy absorbed exceeds that abstracted by the equivalent of the work done.

It is surprising that Clausius in his first Paper did not give the complete solution for a Carnot cycle of finite range, which follows immediately from his assumption $F'(t)=J/T$ on the kinetic theory. Putting $H=Jq$ for the heat absorbed at T, measured in work units, and observing that dH, the difference between the quantities of heat absorbed and abstracted, is equal to dW the work done in the cycle, Carnot's equation $dW/dt=qF'(t)$ reduces to the form, $dH/dt=H/T$. From which it immediately follows that the ratio H/T of the heat H taken in at T to the temperature T in a finite cycle of range T to T_o, is the same as the ratio H_o/T_o of the heat rejected H_o to the temperature T_o at which it is rejected. Since $H-H_o=W$, the work done in the cycle, the solution may be written in the familiar form,

$$H/T=H_o/T_o=W/(T-T_o), \quad . \quad . \quad . \quad (10)$$

which is precisely equivalent to Carnot's solution, $Q=Q_o$ $=W/(T-T_o)$.

The solution in something approaching very nearly to this form appears first to have been given by Rankine, without proof, in a footnote to his Paper on the Mechanical Theory of Heat (" Phil. Mag.," Ser. IV., Vol. II., p. 65, 1851). He gives " the maximum value of the fraction of the whole heat converted into expansive power " as $(T-T_o)/(T-k)$, " where k is a constant, the same for all substances." which is apparently intended to take account of the difference between the absolute

zero of the gas thermometer, and the " absolute zero of heat."
Lord Kelvin (" Phil. Trans.," 1854) subsequently proceeded by
the inverse process.   Instead of adopting the scale of a perfect
gas, as assumed by Carnot, he defined absolute temperature,
by the above relations (10), in such a way as to agree with the
perfect gas scale ; and proceeded to investigate, with Joule's
assistance, the deviations of actual gases from the scale so
defined.

13. *Reappearance of Caloric in the Mechanical Theory.*

Since Carnot's equation, $dW/dt = QF'(t)$, was adopted with-
out material modification into the mechanical theory, so that
$QF'(t)$ remained simply a quantity of Carnot's caloric (though
Q was measured in energy units and $F'(t)$ received the appro-
priate value J/T required to reduce energy units to caloric), it
was inevitable that caloric should make its reappearance sooner
or later in the mechanical theory.   It first appears, disguised as
a triple integral, in Kelvin's solution (" Phil. Mag.," IV., p. 305,
1852) of the problem of finding the work obtainable from an
unequally heated body.   The solution (as corrected later) is
equivalent to the statement that the total quantity of caloric
remains constant when the equalisation of temperature is
effected by means of reversible engines.   Caloric reappears
next as the " thermodynamic function " of Rankine, and as the
" equivalence-value of a transformation " of Clausius (" Pogg.
Ann.," XCIII., p. 497, 1854).   Finally, in 1865, when its
importance was more fully recognised, Clausius (" Pogg. Ann.,"
CXXV., p. 390) gave it the name of " entropy," and defined it
as the integral of dQ/T.   This definition depends on the calori-
metric or energy measure of heat, and obscures the fact that
the caloric measure of heat follows directly from Carnot's prin-
ciple, and may be made independent of the calorimetric
measure.   No one at that time appears to have appreciated
Carnot's solution, or to have realised that entropy was merely
caloric under another name.   In justice to Carnot, it should be
called caloric, and should be defined directly by means of his
equation $W = AQ(T-T_o)$.   This method of procedure appears
to be justifiable both logically and historically, and leads to a
more practical and definite conception of entropy or caloric as
the true measure of a quantity of heat as opposed to a quantity
of thermal energy.   The mathematical definition of entropy,
as the integral of dQ/T under certain restrictions, is unintelli-

gible to the average student, for whom the conception of entropy possesses an artificial atmosphere of unreality. The conception of caloric defined by Carnot's equation would be more readily assimilated, and might be introduced at a much earlier stage. The direct investigation of the properties of caloric thus defined would probably lead to a more general and intimate appreciation of Carnot's principle itself and of many modern developments of thermodynamics which are practically beyond the comprehension of the majority of students under the present system.

14. Caloric in Irreversible Processes.

Carnot was the first to distinguish between reversible and irreversible processes in thermodynamics, and to lay down the simple and sufficient rules for the reversibility of a heat engine. (1) Such an engine must work without friction, which involves direct waste of mechanical power, and had long been recognised as the non-conservative element in mechanical systems. (2) There must be no direct passage of heat from a hotter to a colder body, which is the criterion of thermal reversibility. In order to complete the caloric theory of heat, it was necessary to find an answer to the questions : (1) What becomes of motive power spent in friction ? and (2) What happens to caloric when it passes directly from a body at a higher to a body at a lower temperature ?

Rumford and Davy had proved beyond cavil that caloric was generated by friction. Carnot (as we see from the notes published by his brother) had already, before his early death in 1832, arrived at the general theory of the equivalence of heat and motive power, and had projected a number of experiments in which the motive power consumed should be measured at the same time as the heat produced. From the purely theoretical side it would have been most natural to assume that the absolute motive power of the caloric generated was equal to the motive power consumed, as given by the equation $W = AQT$, for the maximum amount of motive power obtainable from a quantity Q of caloric at T, which with A for $F'(t)$ is the same as Carnot's expression for the heat evolved in compressing a perfect gas. We know now that this is the correct solution. But Carnot, being aware of the conflicting nature of the experimental evidence, felt that further experimental verification was necessary, which was first afforded by Joule.

Carnot showed that the direct passage of heat from a hotter to a colder body was equivalent to wasting a difference of temperature which might have been utilised for the production of motive power. It was natural to ask what became of the motive power wasted. In the analogous case of the waterfall, the answer is fairly obvious. If the water is allowed to fall freely, its motive power is expended in the production of *vis viva* equivalent to its fall, which is converted into heat by friction when its motion is arrested. Similarly, when a compressed gas is allowed to expand into a vacuum, the work which might have been obtained from it by reversible expansion in a cylinder provided with a piston, is spent in producing *vis viva* of the issuing current of gas, which is finally converted into heat by friction, so that the quantity of caloric in the gas is increased, instead of remaining constant as in reversible adiabatic expansion. Carnot considers a case of this kind in a footnote. Gay Lussac and Welter had observed that if a small opening were made in a large reservoir of compressed air, and the bulb of a thermometer were presented to the issuing current, there was no sensible lowering of temperature observed, such as would have been produced in a similar reversible expansion. Carnot attributes this result partly to the development of caloric by friction against the sides of the orifice, and partly to the increase of pressure close to the thermometer bulb due to the impact.

When a quantity of caloric, Q', supplied at a temperature, T', is allowed to fall directly by conduction to a temperature T'', without producing the equivalent motive power $AQ'(T'-T'')$, which might have been obtained from the fall $(T'-T'')$ by means of a reversible engine, it is not so immediately obvious, owing to our ignorance of the mechanism of conduction, what becomes of the motive power wasted. The case is analogous to the fall of a quantity of electricity in a conductor, through a difference of potential in the conductor, in which case the caloric generated is equivalent to the motive power wasted. On Weber's hypothesis the carriers of heat and electricity in metals are the same, and the methods by which caloric is generated in either case must be closely related. It would be reasonable to assume by analogy that a quantity of caloric, $Q'(T'-T'')/T''$, equivalent to the wasted motive power at the lower temperature, was generated in the fall by some process analogous to friction. Adding this to the original quantity Q', we find the quantity Q'' of caloric recovered at the lower temperature T'' equal to $Q'T'/T''$. In other

words, the quantity of caloric is increased by falling freely in such a way that its equivalent motive power $AQ''T''$ at the lower temperature is the same as that which it originally possessed—namely, $AQ'T'$—at the higher temperature. This is precisely what we now assume on the analogy of material systems in applying the principle of the conservation of energy to heat. Carnot appears to have foreseen this result, and to have devised experiments for verifying it, but so far as I know it has not been explicitly verified, merely because it has not occurred to anyone to define caloric explicitly in terms of work per 1 deg. fall in a cycle, and to compare this measure directly with the calorimetric units.

At the present time so many data exist for the verification of the increase of caloric in an irreversible process, that it is unnecessary to perform a special experiment. The inevitable result of such an experiment may be predicted by a simple calculation, such as the following. We have already seen that the caloric of vaporisation of steam at 100°C., measured in terms of Carnot's equation, is approximately 6 carnots per gramme, and the caloric of fusion of ice at 0°C. is 1·2 carnots per gramme. Arrange an experiment in which steam is condensed at 100°C. on one side of a conducting partition, while ice is melted at 0°C. on the other side, without allowing any heat to escape. Measure both the steam condensed and the ice melted in a given time. We know, as the result of innumerable calorimetric experiments of this kind, that for each gramme of steam condensed, 540/79·5 grammes of ice approximately would be melted. Six carnots at 100°C. when allowed to fall directly to 0°C. by conduction, produce $540 \times 1·2/79·5 = 8·17$ carnots at 0°C. The quantity of caloric at 0°C. is greater than that supplied at 100°C. in the proportion of 8·17 to 6, which is nearly the same as the ratio 373/273 of the absolute temperatures. The motive power of the caloric at 100°C.—namely, $6 \times 373 = 2{,}238$ joules—is the same as the motive power of the caloric found at 0°C—namely $817 \times 273 = 2{,}231$ joules—within the limits of error of the data. Similarly in other cases, whenever available motive power is wasted " in the useless re-establishment of the equilibrium of caloric," an equivalent quantity of caloric is generated, so that the total motive power, including any useful work done, remains constant. In a reversible cycle, when there is no waste and the efficiency is a maximum, the total quantity of caloric remains constant. The increase of caloric, if any, due to

friction or conduction, is a measure of the motive power wasted.

Caloric is not conserved in the old sense that its total quantity remains constant in any system of exchanges under all conditions. It remains constant only in the restricted sense, provided that all the exchanges are reversible or take place under conditions of equilibrium. But since in any irreversible exchanges the total quantity of caloric is always increased, the principle of the conservation of caloric can still be stated in the modified form that " the total quantity of caloric in a system *cannot be diminished* by any internal reactions or by the performance of work by or on the system, provided that no heat is allowed to escape." Applied in this form, with various modifications to suit special conditions, it has proved to be one of the most fruitful principles of modern thermodynamics ; but it might have been reached sooner, and more generally appreciated, if the caloric theory had not been so hastily abandoned.

14. *The Calorimetric Measure of Heat.*

The only defect of the caloric theory as developed by Carnot lay in the tacit assumption that the ordinary calorimetric units were units of caloric. This, no doubt, was one of the fundamental points in the theory of heat, which, in Carnot's opinion, " required the most attentive examination." He had himself supplied the key to the difficulty in his criterion of thermal reversibility. But no experimental data were available to decide the point. The pioneers of the mechanical theory made the same tacit assumption when they took it for granted that a given quantity of work done in compressing a gas at any temperature would produce the same number of units of heat in a calorimeter. Granting that heat was measured as energy in a calorimeter, and that energy was conserved, the required result followed ; but this was the very point which was to be proved. Even Joule's experiments were not sufficient in themselves to decide the point, because they were all performed at nearly the same temperature, so that it made no difference whether heat was measured as caloric or as energy. According to Carnot's equation (3), the ratio of the caloric evolved to the work done should be constant at any one temperature, and should vary comparatively slowly with the temperature. Lord Kelvin appears to have appreciated this point when he endeavoured to calculate, by means of Regnault's data for steam, the number

of foot-pounds of work required to generate 1 calorimetric unit of heat by compressing a gas at different temperatures. The number varied from 1,357 to 1,578 foot-pounds per pound-degree C., but this result was not conclusively against the mechanical theory, because, as Clausius showed, it admitted a different interpretation. The first experiments which were sufficiently definite and accurate to decide the point were those of Regnault ("Phil. Mag.," V., p. 473, 1853), which showed that the specific heat of air, measured calorimetrically, was nearly independent of pressure and temperature over a wide range. It follows from Carnot's expression $R/TF'(t)$ for the difference of the specific heats, that if heat is measured calorimetrically, $F'(t)$ must be equal to J/T as required by the mechanical theory, assuming the ratio of the specific heats to be constant. But if Carnot's solution (deduced on the assumption that the specific heat of air was independent of the pressure) had not been overlooked, it would have been obvious that caloric itself was not energy, and that Regnault's result was not inconsistent with the measure of heat as caloric, but only with the tacit assumption that the caloric measure was identical with the calorimetric measure. If this had been recognised at the time, it would have been quite unnecessary to recast and revolutionise the entire theory of heat. Evolution would have proceeded along safer lines with the retention of caloric, and the investigation of its properties, which are so important in all questions of equilibrium in physics.

15. Caloric the True Measure of Heat Quantity.

Since a quantity of heat is measured most directly as a quantity of thermal energy in an ordinary calorimetric experiment, we have become so saturated with the idea that heat is energy and must be measured in units of energy, that we are apt to forget that a quantity of heat is not completely specified by its energy equivalent. The absurdity would be at once apparent, to take an analogous case, if we were to measure a quantity of electricity always in kilowatt-hours. The equivalent energy determines the cost of production, and is for many purposes the appropriate and sufficient measure, but we should fare very badly in electrical theory without the separate units of quantity in ampere-hours and pressure in volts. In electricity, the conditions of practical measurement have led us naturally to units of quantity defined in terms of electric and magnetic

forces, and the unit difference of potential follows as that difference through which unit quantity must fall in doing unit work. In the science of heat Carnot's equation provides us with a precisely analogous measure of heat quantity or caloric as distinct from a quantity of energy. The unit of caloric is that which does unit work in falling reversibly through 1 deg. of temperature. The unit of caloric might be defined directly in terms of the expansion of a gas at constant temperature by the equation $Q = R \log_e (v/v_o)$, in which case the scale of temperature would follow. But since this method would be inconvenient for the practical measurement of caloric, we define the temperature scale first, as that of the perfect gas, and deduce the natural unit of heat quantity, which comes to the same thing. It is true that we can solve most questions in heat in terms of energy and temperature, without explicit reference to caloric or its equivalent. We could similarly solve most electrical problems without mentioning amperes. But since caloric possesses the important property, essential to the natural measure of heat quantity, of remaining constant in reversible exchanges (which the energy measure of heat does not) all our equations and methods of reasoning with regard to questions of equilibrium are greatly simplified and rendered more direct if we adopt caloric as the true measure of heat quantity, and regard it as possessing energy in virtue of its temperature. With all our preconceived notions of heat as a " form of energy," it is difficult now to retrace our steps and express everything in terms of caloric. But, if Carnot's solution had not been overlooked 60 years ago, it would have seemed equally absurd to regard a quantity of heat merely as a quantity of energy, and we should probably have been far ahead of our present position.

16. *The Material Nature of Caloric.*

The objection most commonly urged against the caloric theory from the earliest times has always been that it was absurd to suppose that anything which could be generated without limit could possibly be regarded even in thought as a material fluid. Some 20 years ago, the fluid theory of electricity was regarded as being equally illogical and physically unsound, although it was generally retained on account of the many useful analogies which it suggested. A natural reaction, consequent on fresh discoveries, has caused the pendulum to

swing far in the opposite direction.   Electricity is now more
material than ever, and is continually invading other branches
of physics with materialistic notions.   So long as a quantity
of heat is regarded as being necessarily a quantity of energy, the
fluid conception is of little or no use.   It is true that a quantity
of energy cannot be created or destroyed, but since it may be
transformed into an equivalent quantity of any other kind of
energy, it cannot be identified as remaining constant in any one
state.   This objection does not apply to caloric.   It is true
that caloric can be created without limit, just as we think and
speak of electricity as being generated ; but it has the most
important attribute that, when once generated, it can never, so
far as we know, be destroyed.   Moreover, caloric remains con-
stant under precisely those limiting conditions of equilibrium
which are most important for purposes of practical calculation.
It is true that it may be difficult to isolate a particular set of
material particles and label them caloric.   It is conceivable
that caloric may not be material at all, but merely, as Boltz-
mann puts it, " the logarithm of the probability of a com-
plexion."   But if this is really the case, it is all the more neces-
sary for our sanity and progress to think and speak of it as a
material fluid.   Although this conception of caloric may ap-
pear at first sight to run counter to some of our most cherished
popular illusions with regard to heat, there could be no serious
objection to adopting it as a convenient method of expression.
The more shadowy the conception to be visualised, the greater
the need of a definite material analogy.   From this point of
view the old picturesque phraseology of the material fluid,
implied in Carnot's waterfall, so far from being a valid objection,
is one of the chief advantages of the caloric theory.

17. Conclusion.

The modes of thought and expression inherent in the caloric
theory lead most naturally and inevitably to the conception
of the conservation of caloric as the fundamental law peculiar
to thermodynamics.   To the mathematician, who loves to deal
in abstract mysteries, the substitution of the crude idea of
caloric for the esoteric conception of entropy may doubtless
prove repellent ; but to the experimentalist, who prefers to
think in concrete realities, the change of view point cannot fail
to be suggestive.   So long as entropy was merely a mathematical
abstraction it was unnecessary to attach any definite meaning

to the absolute quantity of entropy in a body, and no one objected to its being infinite when reckoned from zero pressure, temperature, or volume. But if we regard caloric as the natural measure of heat quantity, and push the conception to its logical conclusion, the absolute quantity of caloric in a finite body must be finite, and must vanish at the absolute zero of temperature. The specific heats in energy measure, instead of remaining constant or tending to a finite limit, as generally assumed, must tend to vanish as the zero is approached. The ideal gas of constant specific heat is an obvious objection to this rule, but the real gas avoids the difficulty by condensing in good time. This direct corollary of the caloric theory, so far from being inconsistent with experiment, is daily receiving confirmation from recent researches. It would be impossible, in a sketch like the present, to follow the caloric theory into all its possible developments, but enough has been said to show that the conception of caloric, as employed by Carnot, was not so misleading or erroneous as is generally supposed.

ABSTRACT.

The caloric theory of heat as developed by Carnot in his famous " Reflexions on the Motive Power of Heat " (Paris, 1824) leads immediately to the correct solution of the relations between heat and motive power (energy or work) in all reversible processes, and appears to be in some respects preferable to the mechanical theory as a method of expression, because it emphasises more clearly the distinction first clearly stated by Carnot, between reversible and irreversible transformations, and because it directly provides the natural measure of a quantity of heat as distinct from a quantity of thermal energy.

Carnot first introduced the method of the cyclical process in discussing the action of a heat engine, and showed that, in the ideal case, if there were no direct transference of heat between bodies at different temperatures, the transformations of heat and motive power in such a cycle were reversible. Assuming that it was impossible to imagine a heat engine capable of producing motive power perpetually without taking any heat from the boiler, he concluded that the quantity of motive power, W, produced from a given quantity of heat, Q, by means of a reversible engine, working between given temperature limits in a cyclical process, was the maximum obtainable ; or that the efficiency must be independent of the agents employed, and must be a function of the temperature limits alone. He expressed this by the equation $W/Q = F(t)$, between finite limits $0°$ and $t°C.$, or by the equivalent equation $dW/dt = QF'(t)$ for a cycle of infinitesimal range, dt, at a temperature, t, where $F'(t)$ (generally known as Carnot's function) is the derived function of $F(t)$, and must be the same for all substances at the same temperature.

Applying the equation in this form to a gas obeying the law $pv = RT$, he showed that the heat absorbed in isothermal expansion from v_0 to v

was given by the expression $Q = R \log_e(v/v_0)/F'(t)$, and that the difference of the specific heats at constant pressure and volume, given by the expression $S_p - S^v = R/TF'(t)$, must be independent of the pressure, and the same for equal volumes of all gases. These results were new, but were confirmed experimentally by Dulong five years later. Carnot showed, further, that if the ratio S_p/S_c was constant (as found by Gay Lussac and Welter, and assumed by Laplace and Poisson), both S_p and S_c must be independent of the pressure.

The results so far obtained by Carnot, including the description of his reversible cycle and the deduction of his fundamental principle, were independent of any assumption as to the nature of heat. Applying the assumption of the caloric theory, that the quantity of caloric required to change the state of a substance from (v_0, t_0) to (v, t) was the same by any reversible process, Carnot deduced that, if S_v was independent of the pressure, the function $F'(t)$ must be constant, $=A$. This assumes that heat is measured as caloric, and that temperature is measured on the scale of a gas, obeying the law $pv = RT$, and having S_c independent of the pressure, which is equivalent to the modern definition of a perfect gas. Putting $F'(t) = A$, he obtains for the work W produced from a quantity of caloric, Q, supplied at a temperature, T, in a cycle of finite range T to T_0, an expression equivalent to the following :—

$$W = AQ(T - T_0).$$

Carnot was unable to reconcile this solution with the imperfect experimental data available in his day, and particularly with the observation of Delaroche and Bérard, supported by Laplace's theory, that the specific heat of air, S_p, diminished with increase of pressure, which we know now, from the experiments of Regnault, to have been incorrect. He therefore made no serious attempt to apply the solution, and subsequent writers have apparently failed to observe that it is the correct final solution of the problem on the caloric theory. With our present knowledge, it is easy to see that this solution of Carnot's is also consistent with the mechanical theory, and contains implicitly all the relations of heat and work so far as they relate to reversible processes. The quantity, Q, of caloric remains constant in reversible expansion such as is postulated by Carnot, when no heat is supplied. The work done is directly proportional to the temperature range $T - T_0$. The absolute motive power or equivalent work-value of a quantity of caloric, Q, supplied at a temperature, T, is the maximum work obtainable from a perfect gas (and therefore from any other substance whatever) when $T_0 = 0$, namely, AQT. The efficiency of the cycle with range T to T_0 is $W/AQT = (T - T_0)/T$. The external work done in the cycle is the difference of the work-values of the caloric supplied and rejected, a result which is readily extended to cycles of any form.

To complete Carnot's solution, it is necessary to enquire what happens to caloric in irreversible processes, such as friction, or the direct passage of heat from a hotter to a colder body. Carnot, as we see from his posthumous notes, had already, before his early death in 1832, arrived at the general conception of the conservation of motive power, and had planned experiments in which the motive power consumed in friction should be measured at the same time as the caloric generated. According to his theory, it would have been natural to assume that the motive

power of the caloric generated at any temperature, namely AQT, should be equal to the motive power consumed in friction. But he realised that further experimental evidence was necessary, which was first supplied by Joule.

A quantity of caloric is defined in Carnot's equation as measured by work done in a Carnot cycle per degree fall. The absolute unit of caloric, which may appropriately be called the CARNOT, is that quantity which is capable of doing one joule of work per degree fall. The mechanical equivalent of Q carnots at T Abs. is QT joules. From Carnot's data, the work done in a cycle per gramme of steam vaporised at 100°C. per degree fall is 0·611 kilogrammetres, or nearly 6 joules. The caloric of vaporisation is 6 carnots. Similarly, from Kelvin's data for the pressure required to lower the freezing point 1°C., the caloric of fusion of ice is 1·2 carnots. Since this definition is independent of calorimetric measurements, it may be employed in a calorimetric test, in which steam is condensed at 100°C. on one side of a conducting partition while ice is melted at 0°C. on the other, to determine by direct experiment what happens when caloric falls irreversibly by conduction from 100°C. to 0°C. We know that for each gramme of steam condensed, or for each 6 carnots supplied at 100°C., 540/79·5 grammes of ice approximately would be melted, or 8·17 carnots of caloric would appear at 0°C. The quantity of caloric is increased in the proportion 373/273. The motive power of the caloric remains constant if no useful work is done. The increase of the quantity of caloric is the same as if the available motive power AQ(T−T₀) had been developed and converted into heat by friction at the lower temperature. Whenever motive power is wasted in friction, or "in the useless re-establishment of the equilibrium of caloric," a quantity of caloric equivalent to the wasted motive power is generated. The total quantity of caloric in an isolated system remains constant only if all the transformations are reversible, in which case the motive power developed exactly suffices to restore the initial state. In all other cases there is an increase of caloric. The old principle of the universal conservation of caloric, which is true only for reversible processes, must therefore be modified as follows :—" *The total quantity of caloric in any system cannot be diminished except by taking heat from it.*"

This principle, with various modifications to suit special cases (such as conditions of constant temperature, pressure, or volume) is immediately recognised as one of the most fruitful in modern thermodynamics. But it appeals more forcibly to the imagination of the student, if established, as roughly sketched above, by a direct investigation of the properties of Carnot's caloric.

The caloric theory is seen to be perfectly consistent with Carnot's principle and with the mechanical theory for all reversible processes. Caloric is the natural measure of a quantity of heat in accordance with Carnot's equation, if we adopt the gas-scale of temperature. The only defect of the caloric theory lay in the tacit assumption, so easily rectified, that the ordinary calorimetric units were units of caloric. The quantity measured in an ordinary calorimetric experiment is the motive power or energy of the caloric, and not the caloric itself. If this had been realised in 1850, it would have been quite unnecessary to recast and revolutionise the entire theory of heat. Evolution might have proceeded along safer lines, with the retention of caloric, and the investi-

gation of its properties, which are of such fundamental importance in all questions of equilibrium in physics.

Since Carnot's equation, $d\mathrm{W}/dt = \mathrm{QF}'(t)$, was adopted without material modification into the mechanical theory, and $\mathrm{QF}'(t)$ remained simply a quantity of Carnot's caloric (though Q was measured in energy units and $\mathrm{F}'(t)$ received the appropriate value $\mathrm{J/T}$ required to reduce energy units to caloric) it was inevitable that Carnot's caloric should make its reappearance sooner or later in the mechanical theory. It first reappears, disguised as a triple integral, in Kelvin's solution (" Phil. Mag.," 4, p. 305, 1852) of the problem of finding the available work in an unequally heated body. The solution (as corrected later) is equivalent to the statement that the total quantity of caloric remains constant when the equalisation of temperature is effected reversibly. Caloric reappeared next as the " thermodynamic function " of Rankine, and the " equivalence-value of a transformation " (Clausius "Pogg. Ann.," 93, p. 497, 1854). Finally, in 1865, when its importance was more fully recognised, Clausius (" Pogg. Ann.," 125, p. 390) gave it the name of " entropy," and defined it as the integral of $d\mathrm{Q/T}$. Such a definition appeals to the mathematician only. In justice to Carnot, it should be called caloric, and defined directly by his equation $\mathrm{W} = \mathrm{AQ}(\mathrm{T} - \mathrm{T}_0)$, which any schoolboy could understand. Even the mathematician would gain by thinking of caloric as a fluid, like electricity, capable of being generated by friction or other irreversible processes. Conduction of caloric is closely associated with the electrons, and the science of heat would gain, like the science of electricity, by attaching a more material conception to the true measure of a quantity of heat, as distinguished from a quantity of thermal energy.

A vote of thanks to Prof. CALLENDAR for his Presidential Address moved by Dr. CHREE and seconded by Dr. RUSSELL, was carried unanimously.

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