

# SCIENCE

FRIDAY, SEPTEMBER 13, 1912

THE NATURE OF HEAT<sup>1</sup>

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I PROPOSE to consider on the present occasion some of our fundamental ideas with regard to the nature of heat, and in particular to suggest that we might with advantage import into our modern theory some of the ideas of the old caloric or material theory which has for so long a time been forgotten and discredited. In so doing I may appear to many of you to be taking a retrograde step, because the caloric theory is generally represented as being fundamentally opposed to the kinetic theory and to the law of the conservation of energy. I would, therefore, remark at the outset that this is not necessarily the case, provided that the theory is rightly interpreted and applied in accordance with experiment. Mistakes have been made on both theories, but the method commonly adopted of selecting all the mistakes made in the application of the caloric theory and contrasting them with the correct deductions from the kinetic theory has created an erroneous impression that there is something fundamentally wrong about the caloric theory, and that it is in the nature of things incapable of correctly representing the facts. I shall endeavor to show that this fictitious antagonism between the two theories is without real foundation. They should rather be regarded as different ways of describing the same phenomena. Neither is complete without the other. The kinetic theory is generally preferable for elementary exposition, and has come to

<sup>1</sup> Address of the president to the Mathematical and Physical Science Section of the British Association for the Advancement of Science. Dundee, 1912. The introductory remarks have been omitted.

be almost exclusively adopted for this purpose; but in many cases the caloric theory would have the advantage of emphasizing at the outset the importance of fundamental facts which are too often obscured in the prevailing method of treatment.

The explanation of the development of heat by friction was one of the earliest difficulties encountered by the caloric theory. One explanation, maintained by Cavendish and others, was simply that caloric was generated *de novo* by friction in much the same way as electricity. Another explanation, more commonly adopted, was that the fragments of solid, abraded in such operations as boring cannon, had a smaller capacity for heat than the original material. Caloric already existing in the substance was regarded as being squeezed or ground out of it without any fresh caloric being actually generated. The probability of the second explanation was negated by the celebrated experiments of Rumford and Davy; who concluded that friction did not diminish the capacities of bodies for heat, and that it could not be a material substance because the supply obtainable by friction appeared to be inexhaustible. Rumford also showed that no increase of weight in a body when heated could be detected by the most delicate apparatus available in his time. Caloric evidently did not possess to any marked extent the properties of an ordinary ponderable fluid; but, if it had any real existence and was not merely a convenient mathematical fiction, it must be something of the same nature as the electric fluids, which had already played so useful a part in the description of phenomena, although their actual existence as physical entities had not then been demonstrated. Heat, as Rumford and Davy maintained, might be merely a mode of motion or a vibration of the ultimate particles of matter, but the

idea in this form was too vague to serve as a basis of measurement or calculation. The simple conception of caloric, as a measurable quantity of something, sufficed for many purposes, and led in the hands of Laplace and others to correct results for the ratio of the specific heats, the adiabatic equation of gases, and other fundamental points of theory, though many problems in the relations of heat and work remained obscure.

The greatest contribution of the caloric theory to thermodynamics was the production of Carnot's immortal "Reflections on the Motive Power of Heat." It is one of the most remarkable illustrations of the undeserved discredit into which the caloric theory has fallen, that this work, the very foundation of modern thermodynamics, should still be misrepresented, and its logic assailed, on the ground that much of the reasoning is expressed in the language of the caloric theory. In justice to Carnot, even at the risk of wearying you with an oft-told tale, I can not refrain from taking this opportunity of reviewing the essential points of his reasoning, because it affords incidentally the best introduction to the conception of caloric, and explains how a quantity of caloric is to be measured.

At the time when Carnot wrote, the industrial importance of the steam engine was already established, and the economy gained by expansive working was generally appreciated. The air-engine, and a primitive form of the internal-combustion engine, had recently been invented. On account of the high value of the latent heat of steam, it was confidently expected that more work might be obtained from a given quantity of heat or fuel by employing some other working substance, such as alcohol or ether, in place of steam. Carnot set himself to investigate the conditions under which motive-power was obtainable

from heat, how the efficiency was limited, and whether other agents were preferable to steam. These were questions of immediate practical importance to the engineer, but the answer which Carnot found embraces the whole range of science in its ever widening scope.

In discussing the production of work from heat it is necessary, as Carnot points out, to consider a complete series or cycle of operations in which the working substance, and all parts of the engine are restored on completion of the cycle to their initial state. Nothing but heat, or its equivalent fuel, may be supplied to the engine. Otherwise part of the motive power obtained might be due, not to heat alone, but to some change in the working substance, or in the disposition of the mechanism. Carnot here assumes the fundamental axiom of the cycle, which he states as follows: "*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.*" This does not limit the practical application of the theory, because all machines repeat a regular series of operations, which may be reduced in theory to an equivalent cycle in which everything is restored to its initial state.

The most essential feature of the working of all heat-engines, considered apart from details of mechanism, is the production of motive power by alternate expansion or contraction, or heating and cooling of the working substance. This necessitates the existence of a difference of temperature, produced by combustion or otherwise, between two bodies, such as the boiler and condenser of a steam engine, which may be regarded as the source and

sink of heat respectively. Wherever a difference of temperature exists, it may be made a source of motive power, and conversely without difference of temperature, no motive power can be obtained from heat by a cyclical or continuous process. From this consideration Carnot deduces the simple and sufficient rule for obtaining the maximum effect: "*In order to realize 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 sensibly different temperatures would be equivalent to wasting a difference of temperature which might have been utilized for the production of motive power. Equality of temperature is here assumed as the limiting condition of thermal equilibrium, such that an infinitesimal difference of temperature will suffice to determine the flow of heat in either direction. An engine satisfying Carnot's rule will be reversible so far as the thermal operations are concerned. Carnot makes use of this property of reversibility in deducing his formal proof that an engine of this type possesses the maximum efficiency. If in the usual or direct method of working such an engine takes a quantity of heat  $Q$  from the source, rejects heat to the condenser, and gives a balance of useful work  $W$  per cycle, when the engine is reversed and supplied with motive power  $W$  per cycle it will in the limit take the same quantity of heat from the condenser as it previously rejected, and return to the source the same quantity of heat  $Q$  as it took from it when working direct. All such engines must have the same efficiency (measured by the ratio  $W/Q$  of the work done to the heat taken from the source) whatever the working substance, provided that they work between the same temperature limits. For, if this

were not the case, it would be theoretically possible, by employing the most efficient to drive the least efficient reversible engine backwards, to restore to the source all the heat taken from it, and to obtain a balance of useful work without the consumption of fuel; a result sufficiently improbable to serve as the basis of a formal proof. Carnot thus deduces his famous principle, which he states as follows: "*The motive power obtainable from heat is independent of the agents set at work to realize it. Its quantity is fixed solely by the temperatures between which in the limit the transfer of heat takes place.*"

Objection is commonly taken to Carnot's proof, on the ground that the combination which he imagines might produce a balance of useful work without infringing the principle of conservation of energy, or constituting what we now understand as perpetual motion of the ordinary kind in mechanics. It has become the fashion to introduce the conservation of energy in the course of the proof, and to make a final appeal to some additional axiom. Any proof of this kind must always be to some extent a matter of taste; but since Carnot's principle can not be deduced from the conservation of energy alone, it seems a pity to complicate the proof by appealing to it. For the particular object in view, the absurdity of a heat engine working without fuel appears to afford the most appropriate improbability which could be invoked. The final appeal must be to experiment in any case. At the present time the experimental verification of Carnot's principle in its widest application so far outweighs the validity of any deductive proof, that we might well rest content with the logic that satisfied Carnot instead of confusing the issue by disputing his reasoning.

Carnot himself proceeded to test his prin-

ciple in every possible way by comparison with experiment as far as the scanty data available in his time would permit. He also made several important deductions from it, which were contrary to received opinion at the time, but have since been accurately verified. He appears to have worked out these results analytically in the first instance, as indicated by his footnotes, and to have translated his equations into words in the text for the benefit of his non-mathematical readers. In consequence of this, some of the most important conclusions appear to have been overlooked or attributed to others. Owing to want of exact knowledge of the properties of substances over extended ranges of temperature, he was unable to apply his principle directly in the general form for any temperature limits. We still labor to a less extent under the same disability at the present day. He showed, however, that a great simplification was effected in its application by considering a cycle of infinitesimal range at any temperature  $t$ . In this simple case the principle is equivalent to the assertion that the work obtainable from a unit of heat per degree fall (or per degree range of the cycle) at a temperature  $t$ , is some function  $F't$  of the temperature (generally known as Carnot's function), which must be the same for all substances at the same temperature. From the rough data then available for the properties of steam, alcohol and air, he was able to calculate the numerical values of this function in kilogrammeters of work per kilocalorie of heat at various temperatures between  $0^\circ$  and  $100^\circ$  C., and to show that it was probably the same for different substances at the same temperature within the limits of experimental error. For the vapor of alcohol at its boiling point,  $78^\circ.7$  C., he found the value  $F't = 1.230$  kilogrammeter per kilocalorie per degree fall. For

steam at the same temperature he found nearly the same value, namely,  $F't=1.212$ . Thus no advantage in point of efficiency could be gained by employing the vapor of alcohol in place of steam. He was also able to show that the work obtainable from a kilocalorie per degree fall probably diminished with rise of temperature, but his data were not sufficiently exact to indicate the law of the variation.

The equation which Carnot employed in deducing the numerical values of his function from the experimental data for steam and alcohol is simply the direct expression of his principle as applied to a saturated vapor. It is now generally known as Clapeyron's equation, because Carnot did not happen to give the equation itself in algebraic form, although the principle and details of the calculation were most minutely and accurately described. In calculating the value of his function for air, Carnot made use of the known value of the difference of the specific heats at constant pressure and volume. He showed that this difference must be the same for equal volumes of all gases measured under the same temperature and pressure, whereas it had always previously been assumed that the ratio (not the difference) of the specific heats was the same for different gases. He also gave a general expression for the heat absorbed by a gas in expanding at constant temperature, and showed that it must bear a constant ratio to the work of expansion. These results were verified experimentally some years later, in part by Dulong, and more completely by Joule, but Carnot's theoretical prediction has generally been overlooked, although it was of the greatest interest and importance. The reason of this neglect is probably to be found in the fact that Carnot's expressions contained the unknown function  $F't$  of the temperature, the form of which could not be de-

duced without making some assumptions with regard to the nature of heat and the scale on which temperature should be measured.

It was my privilege to discover a few years ago that Carnot himself had actually given the correct solution of this fundamental problem in one of his most important footnotes, where it had lain buried and unnoticed for more than eighty years. He showed by a most direct application of the caloric theory, that if temperature was measured on the scale of a perfect gas (which is now universally adopted) the value of his function  $F't$  on the caloric theory would be the same at all temperatures, and might be represented simply by a numerical constant  $A$  (our "mechanical equivalent") depending on the units adopted for work and heat. In other words, the work  $W$  done by a quantity of caloric  $Q$  in a Carnot cycle of range  $T$  to  $T_0$  on the gas scale would be represented by the simple equation:

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

It is at once obvious that this solution, obtained by Carnot from the caloric theory, so far from being inconsistent with the mechanical theory of heat, is a direct statement of the law of conservation of energy as applied to the Carnot cycle. If the lower limit  $T_0$  of the cycle is taken at the absolute zero of the gas thermometer, we observe that the maximum quantity of work obtainable from a quantity of caloric  $Q$  at a temperature  $T$  is simply  $AQT$ , which represents the absolute value of the energy carried by the caloric taken from the source at the temperature  $T$ . The energy of the caloric rejected at the temperature  $T_0$  is  $AQT_0$ . The external work done is equal to the difference between the quantities of heat energy supplied and rejected in the cycle.

The analogy which Carnot himself em-

ployed in the interpretation of this equation was the oft-quoted analogy of the waterfall. Caloric might be regarded as possessing motive power or energy in virtue of elevation of temperature just as water may be said to possess motive power in virtue of its head or pressure. The limit of motive power obtainable by a reversible motor in either case would be directly proportional to the head or fall measured on a suitable scale. Caloric itself was not motive power, but must be regarded simply as the vehicle or carrier of energy, the production of motive power from caloric depending essentially (as Carnot puts it) not on the actual consumption of caloric, but on the fall of temperature available. The measure of a quantity of caloric is the work done per degree fall, which corresponds with the measure of a quantity of water by weight, *i. e.*, in kilogrammeters per meter fall.

That Carnot did not pursue the analogy further, and deduce the whole mechanical theory of heat from the caloric theory, is hardly to be wondered at if we remember that no applications of the energy principle had then been made in any department of physics. He appears, indeed, at a later date to have caught a glimpse of the general principle when he states that "motive power [his equivalent for work or energy] changes its form but is never annihilated." It is clear from the posthumous notes of his projected experimental work that he realized how much remained to be done on the experimental side, especially in relation to the generation of caloric by friction, and the waste of motive power by conduction of heat, which appeared to him (in 1824) "almost inexplicable in the present state of the theory of heat."

One of the points which troubled him most in the application of the theoretical

result that the work obtainable from a quantity of caloric was simply proportional to the fall of temperature available, was that it required that the specific heat of a perfect gas should be independent of the pressure. This was inconsistent with the general opinion prevalent at the time, and with one solitary experiment by Delaroche and Bérard, which appeared to show that the specific heat of a gas diminished with increase of pressure, and which had been explained by Laplace as a natural consequence of the caloric theory. Carnot showed that this result did not necessarily follow from the caloric theory, but the point was not finally decided in his favor until the experiments of Regnault, first published in 1852, established the correct values of the specific heat of gases, and proved that they were practically independent of the pressure.

Another point which troubled Carnot was that, according to his calculations, the motive power obtainable from a kilocalorie of heat per degree fall appeared to diminish with rise of temperature, instead of remaining constant. This might have been due to experimental errors, since the data were most uncertain. But, if he had lived to carry out his projected experiments on the quantity of motive power required to produce one unit of heat, and had obtained the result, 424 kilogrammeters per kilocalorie, subsequently found by Joule, he could hardly have failed to notice that this was the same (within the limits of experimental error) as the maximum work  $AQT$  obtainable from the kilocalorie according to his equation. (This is seen to be the case when the values calculated by Carnot per degree fall at different temperatures were multiplied by the absolute temperature in each case. *E. g.*, 1.212 kilogrammeter per degree fall with steam at 79° C. or 352° Abs.  $1.212 \times 352 = 426$  kilogram-

meters.) The origin of the apparent discrepancy between theory and experiment lay in the tacit assumption that the quantity of caloric in a kilocalorie was the same at different temperatures. There were no experiments at that time available to demonstrate that the caloric measure of heat as work per degree fall, implied in Carnot's principle, or more explicitly stated in his equation, was not the same as the calorimetric measure obtained by mixing substances at different temperatures. Even when the energy principle was established its exponents failed to perceive exactly where the discrepancy between the two theories lay. In reality both were correct, if fairly interpreted in accordance with experiment, but they depended on different methods of measuring a quantity of heat, which, so far from being inconsistent, were mutually complementary.

The same misconception, in a more subtle and insidious form, is still prevalent in such common phrases as the following: "We now know that heat is a form of energy and not a material fluid." The experimental fact underlying this statement is that our ordinary methods of measuring quantities of heat in reality measure quantities of thermal energy. When two substances at different temperatures are mixed, the quantity remaining constant, provided that due allowance is made for external work done and for external loss of heat, is the total quantity of energy. Heat is a form of energy merely because the thing we measure and call heat is really a quantity of energy. Apart from considerations of practical convenience, we might equally well have agreed to measure a quantity of heat in accordance with Carnot's principle, by the external work done in a cycle per degree fall. Heat would then not be a form of energy, but would possess all the properties postulated for

caloric. The caloric measure of heat follows directly from Carnot's principle, just as the energy measure follows from the law of conservation of energy. But the term *heat* has become so closely associated with the energy measure that it is necessary to employ a different term, *caloric*, to denote the simple measure of a quantity of heat as opposed to a quantity of heat energy. The measurement of heat as caloric is precisely analogous to the measure of electricity as a quantity of electric fluid. In the case of electricity, the quantity measure is more familiar than the energy measure, because it is generally simpler to measure electricity by its chemical and magnetic effects as a quantity of fluid than as a quantity of energy. The units for which we pay by electric meter, however, are units of energy, because the energy supplied is the chief factor in determining the cost of production, although the actual quantity of fluid supplied has a good deal to do with the cost of distribution. Both methods of measurement are just as important in the theory of heat, and it seems a great pity that the natural measure of heat quantity is obscured in the elementary stages of exposition by regarding heat simply as so much energy. The inadequacy of such treatment makes itself severely felt in the later stages.

Since Carnot's principle was adopted without material modification into the mechanical theory of heat, it was inevitable that Carnot's caloric, and his solution for the work done in a finite cycle, should sooner or later be rediscovered. Caloric reappeared first as the "thermo-dynamic function" of Rankine, and as the "equivalence value of a transformation" in the equations of Clausius; but it was regarded rather as the quotient of heat energy by temperature than as possessing any special physical significance. At a later date,

when its importance was more fully recognized, Clausius gave it the name of *entropy*, and established the important property that its total quantity remained constant in reversible heat exchanges, but always increased in an irreversible process. Any process involving a decrease in the total quantity of entropy was impossible. Equivalent propositions with regard to the possibility or impossibility of transformations had previously been stated by Lord Kelvin in terms of the dissipation of available energy. But, since Carnot's solution had been overlooked, no one at the time seems to have realized that entropy was simply Carnot's caloric under another name, that heat could be measured otherwise than as energy, and that the increase of entropy in any irreversible process was the most appropriate measure of the quantity of heat generated. Energy so far as we know must always be associated with something of a material nature acting as carrier, and there is no reason to believe that heat energy is an exception to this rule. The tendency of the kinetic theory has always been to regard entropy as a purely abstract mathematical function, relating to the distribution of the energy, but having no physical existence. Thus it is not a quantity of anything in the kinetic theory of gases, but merely the logarithm of the probability of an arrangement. In a similar way, some twenty years ago the view was commonly held that electric phenomena were due merely to strains in the ether, and that the electric fluids had no existence except as a convenient means of mathematical expression. Recent discoveries have enabled us to form a more concrete conception of a charge of electricity, which has proved invaluable as a guide to research. Perhaps it is not too much to hope that it may be possible to attach a similar conception

with advantage to caloric as the measure of a quantity of heat.

It has generally been admitted in recent years that some independent measure of heat quantity as opposed to heat energy is required, but opinions have differed widely with regard to the adoption of entropy as the quantity factor of heat. Many of these objections have been felt rather than explicitly stated, and are therefore the more difficult to answer satisfactorily. Others arise from the difficulty of attaching any concrete conception of a quantity of something to such a vague and shadowy mathematical function as entropy. The answer to the question "What is caloric?" must necessarily be of a somewhat speculative nature. But it is so necessary for the experimentalist to reason by analogy from the seen to the unseen, that almost any answer, however crude, is better than none at all. The difficulties experienced in regarding entropy as a measure of heat quantity are more of an academic nature, but may be usefully considered as a preliminary in attempting to answer the more fundamental question.

The first difficulty felt by the student in regarding caloric as the measure of heat quantity is that when two portions of the same substance, such as water, at different temperatures are mixed, the quantity of caloric in the mixture is greater than the sum of the quantities in the separate portions. The same difficulty was encountered by Carnot from the opposite point of view. The two portions at different temperatures represented a possible source of motive power. The question which he asked himself may be put as follows: "If the total quantity of caloric remained the same when the two portions at different temperatures were simply mixed, what had become of the motive power wasted?" The answer is that caloric is generated, and that the



quantity generated is such that its energy is the precise equivalent of the motive power which might have been obtained if the transfer of heat had been effected by means of a perfect engine working without generation of caloric. The caloric generated in wasting a difference of temperature is the necessary and appropriate measure of the quantity of heat obtained by the degradation of available motive power into the less available or transformable variety of heat energy.

The processes by which caloric is generated in mixing substances at different temperatures, or in other cases where available motive power is allowed to run to waste, are generally of so turbulent a character that the steps of the process can not be followed, although the final result can be predicted under given conditions from the energy principle. Such processes could not be expected *a priori* to throw much light on the nature of caloric. The familiar process of conduction of heat through a body, the parts of which are at different temperatures, while equally leading to the generation of a quantity of caloric equivalent to the motive power wasted, affords better promise of elucidating the nature of caloric, owing to the comparative simplicity and regularity of the phenomena, which permit closer experimental study. The earliest measurements of the relative conducting powers of the metals for heat and electricity showed that the ratio of the thermal to the electric conductivity was nearly the same for all the pure metals, and suggested that, in this case, the carriers of heat and electricity were the same. Later and more accurate experiments showed that the ratio of the conductivities was not constant, but varied nearly as the absolute temperature. At first sight this might appear to suggest a radical difference between the two conductivities, but

it results merely from the fact that heat is measured as energy in the definition of thermal conductivity, whereas electricity is measured as a quantity of fluid. If thermal conductivity were defined in terms of caloric or thermal fluid, the ratio of the two conductivities would be constant with respect to temperature almost, if not quite, within the limits of error of experiment. On the hypothesis that the carriers are the same for electricity and heat, and that the kinetic energy of each carrier is the same as that of a gas molecule at the same temperature, it becomes possible, on the analogy of the kinetic theory of gases, to calculate the actual value of the ratio of the conductivities. The value thus found agrees closely in magnitude with that given by experiment, and may be regarded as confirming the view that the carriers are the same, although the hypotheses and analogies invoked are somewhat speculative.

When the electrons or corpuscles of negative electricity were discovered it was a natural step to identify them with the carriers of energy, and to imagine that a metal contained a large number of such corpuscles, moving in all directions, and colliding with each other, and with the metallic atoms, like the molecules of a gas on the kinetic theory. If the mass of each carrier were  $\frac{1}{1700}$  of that of an atom of hydrogen, the velocity at 0° C. would be about sixty miles a second, and would be of the right order of magnitude to account for the observed values of the conductivities of good conductors, on the assumption that the number of negative corpuscles was the same as the number of positive metallic atoms, and that the mean free path of each corpuscle was of the same order as the distance between the atoms. The same hypothesis served to give a qualitative account of thermo-electric phenomena, such

as the Peltier and Thomson effects, and of radiation and absorption of heat, though in a less satisfactory manner. When extended to give a consistent account of *all* the related phenomena, it would appear that the number of free corpuscles required is too large to be reconciled, for instance, with the observed values of the specific heat, on the assumption that each corpuscle possesses energy of translation equal to that of a gas molecule at the same temperature.

Sir J. J. Thomson has accordingly proposed and discussed another possible theory of metallic conduction, in which the neutral electric doublets present in the metal are supposed to be continually interchanging corpuscles at a very high rate. Under ordinary condition these interchanges take place indifferently in all directions, but under the action of an electric field the axes of the doublets are supposed to become more or less oriented, as in the Grotthus-chain hypothesis of electrolytic conduction, producing a general drift or current proportional to the field. This hypothesis, though fundamentally different from the preceding or more generally accepted view, appears to lead to practically the same relations, and is in some ways preferable, as suggesting possible explanations of difficulties encountered by the first theory in postulating so large a number of free negative corpuscles. On the other hand, the second theory requires that each neutral doublet should be continually ejecting corpuscles at the rate of about  $10^{15}$  per second. There are probably elements of truth in both theories, but, without insisting too much on the exact details of the process, we may at least assert with some confidence that the corpuscles of caloric which constitute a current of heat in a metal are very closely related to the cor-

puses of electricity, and have an equal right to be regarded as constituting a material fluid possessing an objective physical existence.

If I may be allowed to speculate a little on my own account (as we are all here together in holiday mood, and you will not take anything I may say too seriously), I should prefer to regard the molecules of caloric, not as being identical with the corpuscles of negative electricity, but as being neutral doublets formed by the union of a positive and negative corpuscle, in much the same way as a molecule of hydrogen is formed by the union of two atoms. Nothing smaller than a hydrogen atom has yet, so far as I know, been discovered with a positive charge. This may be merely a consequence of the limitations of our experimental methods, which compel us to employ metals to so large an extent as electrodes. In the symmetry of nature it is almost inconceivable that the positive corpuscles should not exist, if only as the other end of the Faraday-tube or vortex-filament representing a chemical bond. Professor Bragg has identified the X or  $\gamma$  rays with neutral corpuscles traveling at a high velocity, and has maintained this hypothesis with brilliant success against the older view that these rays are not separate entities, but merely thin, spreading pulses in the ether produced by the collisions of corpuscles with matter. I must leave him to summarize the evidence, but if neutral corpuscles exist, or can be generated in any way, it should certainly be much easier to detach a neutral corpuscle from a material atom or molecule than to detach a corpuscle with a negative charge from the positive atom with which it is associated. We should therefore expect neutral corpuscles to be of such exceedingly common and universal occurrence

that their very existence might be overlooked, unless they happened to be traveling at such exceptionally high velocities as are associated with the  $\gamma$  rays. According to the pulse theory, it is assumed that all  $\gamma$  rays travel with the velocity of light, and that the enormous variations observed in their penetrative power depend simply on the thickness of the pulse transmitted. On the corpuscular theory, the penetrative power, like that of the  $\alpha$  and  $\beta$  rays, is a question of size, velocity, and electric charge. Particles carrying electric charges, like the  $\alpha$  and  $\beta$  rays, lose energy in producing ions by their electric field, perhaps without actual collision. Neutral or  $\gamma$  rays do not produce ions directly, but dislodge either  $\gamma$  rays or  $\beta$  rays from atoms by direct collisions, which are comparatively rare. The  $\beta$  rays alone, as C. T. R. Wilson's photographs show, are responsible for the ionization. Personally, I have long been a convert to Professor Bragg's views on the nature of X rays, but even if we regard the existence of neutral corpuscles as not yet definitely proved, it is, I think, permissible to assume their existence for purposes of argument, in order to see whether the conception may not be useful in the interpretation of physical phenomena.

If, for instance, we assume that these neutral corpuscles or molecules of caloric exist in conductors and metallic bodies in a comparatively free state of solution, and are readily dissociated into positive and negative electrons owing to the high specific inductive capacity of the medium, the whole theory of metallic conduction follows directly on the analogy of conduction in electrolytic solutions. But, whereas in electrolytes the ions are material atoms moving through a viscous medium with comparatively low velocities, the ions in metallic conductors are electric corpuscles moving

with high velocities more after the manner postulated in the kinetic theory of gases. It is easy to see that this theory will give similar numerical results to the electronic theory when similar assumptions are made in the course of the work. But it has the advantage of greater latitude in explaining the vagaries of sign of the Hall effect, and many other peculiarities in the variation of resistance and thermo-electric power with temperature. For good conductors, like the pure metals, we may suppose, on the electrolytic analogy, that the dissociation is practically complete, so that the ratio of the conductivities will approach the value calculated on the assumption that all the carriers of heat are also carriers of electricity. But in bad conductors the dissociation will be far from complete, and it is possible to see why, for instance, the electric resistance of cast iron should be nearly ten times that of pure iron, although there is comparatively little difference in their thermal conductivities. The numerical magnitude of the thermo-electric effect, which is commonly quoted in explanation of the deviation of alloys from the electronic theory, is far too small to produce the required result; and there is little or no correspondence between the thermo-electric properties of the constituents of alloys and the variations of their electric conductivities.

One of the oldest difficulties of the material theory of heat is to explain the process of the production of heat by friction. The application of the general principle of the conservation of energy leads to the undoubted conclusion that the thermal energy generated is the equivalent of the mechanical work spent in friction, but throws little or no light on the steps of the process, and gives no information with regard to the actual nature of the energy

produced in the form of heat. It follows from the energy principle that the quantity of caloric generated in the process is such that its total energy at the final temperature is equal to the work spent. If a quantity of caloric represents so many neutral molecules of electricity, one can not help asking where they came from, and how they were produced. It is certain that in most cases of friction, wherever slip occurs, some molecules are torn apart, and the work spent is represented in the first instance by the separation of electric ions. Some of these ions are permanently separated as frictional electricity, and can be made to perform useful work; but the majority recombine before they can be effectively separated, leaving only their equivalent in thermal energy. The recombination of two ions is generally regarded simply as reconstituting the original molecule at a high temperature, but in the light of recent discoveries we may perhaps go a step further. It is generally admitted that X or  $\gamma$  rays are produced by the sudden stoppage of a charged corpuscle, and Lorentz, in his electron theory of radiation, has assumed that such is the case however low the velocity of the electron. A similar effect must occur in the sudden stoppage of a pair of ions rushing together under the influence of their mutual attraction. Rays produced in this way would be of an exceedingly soft or absorbable character, but they would not differ in kind from those produced by electrons except that their energy, not exceeding that of a pair of ions, would be too small to produce ionization, so that they could not be detected in the usual way. If the X rays are corpuscular in their nature, we can not logically deny the corpuscular character even to the slowest moving rays. We know that X rays continually produce other X rays of lower velocity. The final

stage is probably reached when the average energy of an X corpuscle or molecule of caloric is the same as that of a gas molecule at the same temperature, and the number of molecules of caloric generated is such that their total energy is equal to the work originally spent in friction.

In this connection it is interesting to note that Sir J. J. Thomson, in a recent paper on "Ionization by Moving Particles," has arrived, on other grounds, at the conclusion that the character of the radiation emitted during the recombination of the ions will be a series of pulses, each pulse containing the same amount of energy and being of the same type as very soft X rays. If the X rays are really corpuscular, these definite units or quanta of energy generated by the recombination of the ions bear a close resemblance to the hypothetical molecules of caloric.

It may be objected that in many cases of friction, such as internal or viscous friction in a fluid, no electrification or ionization is observable, and that the generation of caloric can not in this case be attributed to the recombination of ions. It must, however, be remarked that the generation of a molecule of caloric requires less energy than the separation of two ions; that, just as the separation of two ions corresponds with the breaking of a chemical bond, so the generation of one or more molecules of caloric may correspond with the rupture of a physical bond, such as the separation of a molecule of vapor from a liquid or solid. The assumption of a molecular constitution for caloric follows almost of necessity from the molecular theories of matter and electricity, and is not inconsistent with any well-established experimental facts. On the contrary, the many relations which are known to exist between the specific heats of similar substances, and also between the latent

heats, would appear to lead naturally to a molecular theory of caloric. For instance, it has often been noticed that the molecular latent heats of vaporization of similar compounds at their boiling points are proportional to the absolute temperature. It follows that the molecular latent caloric of vaporization is the *same* for all such compounds, or that they require the same number of molecules of caloric to effect the same change of state, irrespective of the absolute temperatures of their boiling points. From this point of view one may naturally regard the liquid and gaseous states as conjugate solutions of caloric in matter and matter in caloric respectively. The proportion of caloric to matter varies regularly with pressure and temperature, and there is a definite saturation limit of solubility at each temperature.

One of the most difficult cases of the generation of caloric to follow in detail is that which occurs whenever there is exchange of heat by radiation between bodies at different temperatures. If radiation is an electro-magnetic wave-motion, we must suppose that there is some kind of electric oscillator or resonator in the constitution of a material molecule which is capable of responding to the electric oscillations. If the natural periods of the resonators correspond sufficiently closely with those of the incident radiation the amplitude of the vibration excited may be sufficient to cause the ejection of a corpuscle of caloric. It is generally admitted that the ejection of an electron may be brought about in this manner, but it would evidently require far less energy to produce the emission of a neutral corpuscle, which ought therefore to be a much more common effect. On this view, the conversion of energy of radiation into energy of caloric is a discontinuous process taking place by definite molecular incre-

ments, but the absorption or emission of radiation itself is a continuous process. Professor Planck, by a most ingenious argument based on the probability of the distribution of energy among a large number of similar electric oscillators (in which the entropy is taken as the logarithm of the probability, and the temperature as the rate of increase of energy per unit of entropy), has succeeded in deducing his well-known formula for the distribution of energy in full radiation at any temperature; and has recently, by a further extension of the same line of argument, arrived at the remarkable conclusion that, while the absorption of radiation is continuous, the emission of radiation is discontinuous, occurring in discrete elements or quanta. Where an argument depends on so many intricate hypotheses and analogies the possible interpretations of the mathematical formulæ are to some extent uncertain; but it would appear that Professor Planck's equations are not necessarily inconsistent with the view above expressed that both emission and absorption of radiation are continuous, and that his *elementa quanta*, the energy of which varies with their frequency, should rather be identified with the molecules of caloric, representing the conversion of the electro-magnetic energy of radiation into the form of heat, and possessing energy in proportion to their temperature.

Among the difficulties felt rather than explicitly stated, in regarding entropy or caloric as the measure of heat quantity, is its awkward habit of becoming infinite, according to the usual approximate formulæ, at extremes of pressure or temperature. If caloric is to be regarded as the measure of heat quantity, the quantity existing in a finite body must be finite, and must vanish at the absolute zero of temperature. In

reality there is no experimental foundation for any other conclusion. According to the usual gas formulæ it would be possible to extract an infinite quantity of caloric from a finite quantity of gas by compressing it at constant temperature. It is true that (even if we assumed the law of gases to hold up to infinite pressures, which is far from being the case) the quantity of caloric extracted would be of an infinitely low order of infinity as compared with the pressure required. But, as a matter of fact, experiment indicates that the quantity obtainable would be finite, although its exact value can not be calculated owing to our ignorance of the properties of gases at infinite pressures. In a similar way, if we assume that the specific heat as ordinarily measured remains constant, or approaches a finite limit at the absolute zero of temperature, we should arrive at the conclusion that an infinite quantity of caloric would be required to raise the temperature of a finite body from  $0^{\circ}$  to  $1^{\circ}$  absolute. The tendency of recent experimental work on specific heats at low temperatures, by Tilden, Nernst, Lindemann and others, is to show, on the contrary, that the specific heats of all substances tend to vanish as the absolute zero is approached and that it is the specific capacity for caloric which approaches a finite limit. The theory of the variation of the specific heats of solids at low temperatures is one of the most vital problems in the theory of heat at the present time, and is engaging the attention of many active workers. Professor Lindemann, one of the leading exponents of this work, has kindly consented to open a discussion on the subject in our section. We are very fortunate to have succeeded in securing so able an exponent, and shall await his exposition with the greatest interest. For the present I need only add

that the obvious conclusion of the caloric theory bids fair to be completely justified.

A most interesting question, which early presented itself to Rumford and other inquirers into the caloric theory of heat, was whether caloric possessed *weight*. While a positive answer to this question would be greatly in favor of a material theory, a negative answer, such as that found by Rumford, or quite recently by Professor Poynting and Phillips, and by Mr. L. Southern working independently, would not be conclusively against it. The latter observers found that the change in weight, if any, certainly did not exceed 1 in  $10^8$  per  $1^{\circ}$  C. If the mass of a molecule of caloric were the same as that generally attributed to an electron, the change of weight, in the cases tested, should have been of the order of 1 in  $10^7$  per  $1^{\circ}$  C., and should not have escaped detection. It is generally agreed, however, that the mass of the electron is entirely electro-magnetic. Any such statement virtually assumes a particular distribution of the electricity in a spherical electron of given size. But if electricity itself really consists of electrons, an argument of this type would appear to be so perfectly circular that it is questionable how much weight should be attached to it. If the equivalent mass of an electron in motion arises solely from the electro-magnetic field produced by its motion, a neutral corpuscle of caloric should not possess mass or energy of translation as a whole, though it might still possess energy of vibration or rotation of its separate charges. For the purpose of mental imagery we might picture the electron as the free or broken end of a vortex filament, and the neutral corpuscle as a vortex ring produced when the positive and negative ends are united; but a mental picture of this kind does not carry us any further than the

sphere coated with electricity, except in so far as either image may suggest points for experimental investigation. In our ignorance of the exact mechanism of gravity it is even conceivable that a particle of caloric might possess mass without possessing weight, though, with the possible exception of the electron, nothing of the kind has yet been demonstrated. In any case it would appear that the mass, if any, associated with a quantity of caloric must be so small that we could not hope to learn much about it by the direct use of the balance.

The fundamental property of caloric, that its total quantity can not be diminished by any known process and that it is not energy but merely the vehicle or carrier of energy, is most simply represented in thought by imagining it to consist of some indestructible form of matter. The further property, that it is always generated in any turbulent or irreversible process, appears at first sight to conflict with this idea, because it is difficult to see how anything indestructible can be so easily generated. When, however, we speak of caloric as being generated, what we really mean is that it becomes associated with a material body in such a way that we can observe and measure its quantity by the change of state produced. The caloric may have existed previously in a form in which its presence could not be detected. In the light of recent discoveries we might suppose the caloric generated to arise from the disintegration of the atoms of matter. No doubt some caloric is produced in this way, but those corpuscles that are so strongly held as to be incapable of detection by ordinary physical methods require intense shocks to dislodge them. A more probable source of caloric is the ether, which, so far as we know, may consist entirely of neutral corpuscles of caloric. The hypothesis of a

continuous ether has led to great difficulties in the electro-magnetic theory of light and in the kinetic theory of gases. A molecular, or cellular-vortex, structure appears to be required. According to the researches of Kelvin, Fitzgerald and Hicks, such an ether can be devised to satisfy the requirements of the electro-magnetic theory without requiring it to possess a density many times greater than that of platinum. So far as the properties of caloric are concerned, a neutral pair of electrons would appear to constitute the simplest type of molecule, though without more exact knowledge of the ultimate nature of an electric charge it would be impossible to predict all its properties. Whether an ether composed of such molecules would be competent to discharge satisfactorily all the onerous functions expected from it, may be difficult to decide, but the inquiry, in its turn, would probably throw light on the ultimate structure of the molecule.

Without venturing too far into the regions of metaphysical speculation, or reasoning in vicious circles about the nature of an electric charge, we may at least assert with some degree of plausibility that material bodies under ordinary conditions probably contain a number of discrete physical entities, similar in kind to X rays or neutral corpuscles, which are capable of acting as carriers of energy, and of preserving the statistical equilibrium between matter and radiation at any temperature in virtue of their interchanges with electrons. If we go a step further and identify these corpuscles with the molecules of caloric, we shall certainly come in conflict with some of the fundamental dogmas of the kinetic theory, which tries to express everything in terms of energy, but the change involved is mainly one of standpoint or expression. The experimental facts remain the same,

but we describe them differently. Caloric has a physical existence, instead of being merely the logarithm of the probability of a complexion. In common with many experimentalists, I can not help feeling that we have everything to gain by attaching a material conception to a quantity of caloric as the natural measure of a quantity of heat as opposed to a quantity of heat energy. In the time at my disposal I could not pretend to offer you more than a suggestion of a sketch, an apology for the possibility of an explanation, but I hope I may have succeeded in conveying the impression that a caloric theory of heat is not so entirely unreasonable in the light of recent experiment as we are sometimes led to imagine.

H. L. CALLENDAR

#### THE PROBLEM OF MECHANICAL FLIGHT

##### HISTORICAL RÉSUMÉ

THE scientific period in aviation began in 1809 when Sir George Cayley published in *Nicholson's Journal* the first complete mechanical theory of the aeroplane, in which he put clearly in evidence the fundamental principle of sustentation obtained by velocity. This memoir passed unnoticed until unearthed some sixty years later by Pénau. Following Cayley there was a long unfruitful interval in which fell the projected aeroplane of Henson in 1842-43, the attempts at gliding by Le Bris in 1856, and the biplane gliders of Wenham in 1866. At the end of the Franco-Prussian war interest in heavier-than-air flying machines was revived, and the Société française de Navigation aérienne was from 1872 on composed of a number of investigators engaged in the conquest of the air. The history of their endeavors is found in "L'Aéronaute." Among them was Alphonse Pénau, a young mechanic whose early death prevented him from pushing his researches to their logical end. Pénau was less isolated than Cayley and one of his memoirs was crowned by the Académie des Sciences. He constructed the first toy aeroplane, with the propeller in

the rear and driven by a rubber band. This apparatus flew for an appreciable time, *utilizing motive energy which it carried with it*, and this property differentiates very sharply the experiment of Pénau from those of his predecessors, in which was realized only a fall more or less retarded by the air.

The German Lilienthal followed Pénau, and from 1891 studied the equilibrium, maneuvering and landing of gliders, falling to his death on his two thousandth flight, August 9, 1896. In this country the French engineer Chanute and the American Langley had meanwhile been experimenting and developing the laws of aerodynamics, Langley's work going as far back as 1887 and continuing until his unsuccessful attempts at flight in 1903. In 1891 he published<sup>1</sup> the results of his researches, and definitely stated that it was possible to construct machines which would give such velocity to inclined surfaces that bodies indefinitely heavier than air could be sustained upon it and moved through it with great speed.

By the end of the nineteenth century efforts to build aeroplanes had become numerous. Sir Hiram Maxim in England and Ader in France both constructed machines and made attempts to fly them. Maxim built in 1890-95 a flying machine with 557 square meters of surface and 3,640 kilograms weight, which was damaged before leaving the ground and abandoned. The "Avion" of Ader was tested on the field of Satory in 1897 before the representatives of the French War Department, but its performance led the department to withdraw its support and experiments were discontinued. Langley as early as 1896 had designed and built a small steam-driven model aerodrome weighing about 13 kilograms, and on May 6 of that year he flew it some 1,200 meters over the waters of the Potomac. The quarter-size model of his large man-carrying aerodrome flew successfully about 1,000 feet near Widewater, Va., on August 8, 1903, but the large machine itself, carrying Mr. Manly, was injured in launching

<sup>1</sup>"Experiments in Aerodynamics," Smithsonian Contributions to Knowledge, Vol. 27, 1891.