Art. XLVIII. On the Dynamical Theory of Heat, with numerical results deduced from Mr Joule's equivalent of a Thermal Unit, and M. Regnault's Observations on Steam.

[*Transactions of the Royal Society of Edinburgh*, March, 1851, *and Phil. Mag.* iv. 1852.]

Introductory Notice.

1. Sir Humphry Davy, by his experiment of melting two pieces of ice by rubbing them together, established the following proposition:—"The phenomena of repulsion are not dependent on a peculiar elastic fluid for their existence, or caloric does not exist." And he concludes that heat consists of a motion excited among the particles of bodies. "To distinguish this motion from others, and to signify the cause of our sensation of heat," and of the expansion or expansive pressure produced in matter by heat, "the name *repulsive* motion has been adopted *."

2. The dynamical theory of heat, thus established by Sir Humphry Davy, is extended to radiant heat by the discovery of phenomena, especially those of the polarization of radiant heat, which render it excessively probable that heat propagated through "vacant space," or through diathermanic substances, consists of waves of transverse vibrations in an all-pervading medium.

* From Davy's first work, entitled *An Essay on Heat, Light, and the Combinations of Light*, published in 1799, in "Contributions to Physical and Medical Knowledge, principally from the West of England, collected by Thomas Beddoes, M.D.," and republished in Dr Davy's edition of his brother's collected works, Vol. ii. Lond. 1836.

3. The recent discoveries made by Mayer and Joule*, of the generation of heat through the friction of fluids in motion, and by the magneto-electric excitation of galvanic currents, would either of them be sufficient to demonstrate the immateriality of heat; and would so afford, if required, a perfect confirmation of Sir Humphry Davy's views.

4. Considering it as thus established, that heat is not a substance, but a dynamical form of mechanical effect, we perceive that there must be an equivalence between mechanical work and heat, as between cause and effect. The first published statement of this principle appears to be in Mayer's *Bemerkungen über die Kräfte der unbelebten Natur*†, which contains some correct views regarding the mutual convertibility of heat and mechanical effect, along with a false analogy between the approach of a weight to the earth and a diminution of the volume of a continuous substance, on which an attempt is founded to find numerically the mechanical equivalent of a given quantity of heat. In a paper published about fourteen months later, "On the Calorific Effects of Magneto-Electricity and the Mechanical Value of Heat‡," Mr Joule of Manchester expresses very distinctly the consequences regarding the mutual convertibility of heat and mechanical effect which follow from the fact, that heat is not a substance but a state of motion; and investigates on unquestionable principles the "absolute numerical relations," according to which heat is connected with mechanical power; verifying experimentally, that whenever heat is generated from purely mechanical action, and no other effect produced, whether it be by means of the friction of fluids or by the magneto-electric excitation of galvanic currents, the same quantity is generated by the same amount of work spent; and determining the actual amount of work, in foot-pounds,

* In May, 1842, Mayer announced in the *Annalen* of Wöhler and Liebig, that he had raised the temperature of water from 12° to 13° Cent. by agitating it. In August, 1843, Joule announced to the British Association "That heat is evolved by the passage of water through narrow tubes;" and that he had "obtained one degree of heat per lb. of water from a mechanical force capable of raising 770 lbs. to the height of one foot;" and that heat is generated when work is spent in turning a magneto-electric machine, or an electro-magnetic engine. (See his paper "On the Calorific Effects of Magneto-Electricity, and on the Mechanical Value of Heat."—*Phil. Mag.*, Vol. XXIII., 1843.)

† *Annalen* of Wöhler and Liebig, May, 1842.

‡ British Association, August, 1843; and *Phil. Mag.*, Sept., 1843.

required to generate a unit of heat, which he calls "the mechanical equivalent of heat." Since the publication of that paper, Mr Joule has made numerous series of experiments for determining with as much accuracy as possible the mechanical equivalent of heat so defined, and has given accounts of them in various communications to the British Association, to the *Philosophical Magazine*, to the Royal Society, and to the French Institute.

5. Important contributions to the dynamical theory of heat have recently been made by Rankine and Clausius; who, by mathematical reasoning analogous to Carnot's on the motive power of heat, but founded on an axiom contrary to his fundamental axiom, have arrived at some remarkable conclusions. The researches of these authors have been published in the *Transactions* of this Society, and in Poggendorff's *Annalen*, during the past year; and they are more particularly referred to below in connexion with corresponding parts of the investigations at present laid before the Royal Society.

[Various statements regarding animal heat, and the heat of combustion and chemical combination, are made in the writings of Liebig (as, for instance, the statement quoted in the foot-note added to § 18 below), which virtually imply the convertibility of heat into mechanical effect, and which are inconsistent with any other than the dynamical theory of heat.]

6. The object of the present paper is threefold:—

(1) To show what modifications of the conclusions arrived at by Carnot, and by others who have followed his peculiar mode of reasoning regarding the motive power of heat, must be made when the hypothesis of the dynamical theory, contrary as it is to Carnot's fundamental hypothesis, is adopted.

(2) To point out the significance in the dynamical theory, of the numerical results deduced from Regnault's observations on steam, and communicated about two years ago to the Society, with an account of Carnot's theory, by the author of the present paper; and to show that by taking these numbers (subject to correction when accurate experimental data regarding the density of saturated steam shall have been afforded), in connexion with Joule's mechanical equivalent of a thermal unit, a complete theory

of the motive power of heat, within the temperature limits of the experimental data, is obtained.

(3) To point out some remarkable relations connecting the physical properties of all substances, established by reasoning analogous to that of Carnot, but founded in part on the contrary principle of the dynamical theory.

PART I.

Fundamental Principles in the Theory of the Motive Power of Heat.

7. According to an obvious principle, first introduced, however, into the theory of the motive power of heat by Carnot, mechanical effect produced in any process cannot be said to have been derived from a purely thermal source, unless at the end of the process all the materials used are in precisely the same physical and mechanical circumstances as they were at the beginning. In some conceivable "thermo-dynamic engines," as for instance Faraday's floating magnet, or Barlow's "wheel and axle," made to rotate and perform work uniformly by means of a current continuously excited by heat communicated to two metals in contact, or the thermo-electric rotatory apparatus devised by Marsh, which has been actually constructed; this condition is fulfilled at every instant. On the other hand, in all thermo-dynamic engines, founded on electrical agency, in which discontinuous galvanic currents, or pieces of soft iron in a variable state of magnetization, are used, and in all engines founded on the alternate expansions and contractions of media, there are really alterations in the condition of materials; but, in accordance with the principle stated above, these alterations must be strictly periodical. In any such engine, the series of motions performed during a period, at the end of which the materials are restored to precisely the same condition as that in which they existed at the beginning, constitutes what will be called a complete cycle of its operations. Whenever in what follows, *the work done* or *the mechanical effect produced* by a thermo-dynamic engine is mentioned without qualification, it must be understood that the mechanical effect produced, either in a non-varying engine, or in a complete cycle, or any number of complete cycles of a periodical engine, is meant.

8. The *source of heat* will always be supposed to be a hot body at a given constant temperature, put in contact with some part of the engine; and when any part of the engine is to be kept from rising in temperature (which can only be done by drawing off whatever heat is deposited in it), this will be supposed to be done by putting a cold body, which will be called the refrigerator, at a given constant temperature in contact with it.

9. The whole theory of the motive power of heat is founded on the two following propositions, due respectively to Joule, and to Carnot and Clausius.

PROP. I. (Joule).—When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated.

PROP. II. (Carnot and Clausius).—If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.

10. The former proposition is shown to be included in the general "principle of mechanical effect," and is so established beyond all doubt by the following demonstration.

11. By whatever direct effect the heat gained or lost by a body in any conceivable circumstances is tested, the measurement of its quantity may always be founded on a determination of the quantity of some standard substance, which it or any equal quantity of heat could raise from one standard temperature to another; the test of equality between two quantities of heat being their capability of raising equal quantities of any substance from any temperature to the same higher temperature. Now, according to the dynamical theory of heat, the temperature of a substance can only be raised by working upon it in some way so as to produce increased thermal motions within it, besides effecting any modifications in the mutual distances or arrangements of its particles which may accompany a change of temperature. The work necessary to produce this total mechanical effect is of course proportional to the quantity of the substance raised from one

standard temperature to another; and therefore when a body, or a group of bodies, or a machine, parts with or receives heat, there is in reality mechanical effect produced from it, or taken into it, to an extent precisely proportional to the quantity of heat which it emits or absorbs. But the work which any external forces do upon it, the work done by its own molecular forces, and the amount by which the half *vis viva* of the thermal motions of all its parts is diminished, must together be equal to the mechanical effect produced from it; and consequently, to the mechanical equivalent of the heat which it emits (which will be positive or negative, according as the sum of those terms is positive or negative). Now let there be either no molecular change or alteration of temperature in any part of the body, or, by a cycle of operations, let the temperature and physical condition be restored exactly to what they were at the beginning; the second and third of the three parts of the work which it has to produce vanish; and we conclude that the heat which it emits or absorbs will be the thermal equivalent of the work done upon it by external forces, or done by it against external forces; which is the proposition to be proved.

12. The demonstration of the second proposition is founded on the following axiom:—

*It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects**.

13. To demonstrate the second proposition, let *A* and *B* be two thermo-dynamic engines, of which *B* satisfies the conditions expressed in the enunciation; and let, if possible, *A* derive more work from a given quantity of heat than *B*, when their sources and refrigerators are at the same temperatures, respectively. Then on account of the condition of complete *reversibility* in all its operations which it fulfils, *B* may be worked backwards, and made to restore any quantity of heat to its source, by the expenditure of the amount of work which, by its forward action, it would derive from the same quantity of heat. If, therefore, *B* be

* If this axiom be denied for all temperatures, it would have to be admitted that a self-acting machine might be set to work and produce mechanical effect by cooling the sea or earth, with no limit but the total loss of heat from the earth and sea, or, in reality, from the whole material world.

worked backwards, and made to restore to the source of A (which we may suppose to be adjustable to the engine B) as much heat as has been drawn from it during a certain period of the working of A, a smaller amount of work will be spent thus than was gained by the working of A. Hence, if such a series of operations of A forwards and of B backwards be continued, either alternately or simultaneously, there will result a continued production of work without any continued abstraction of heat from the source; and, by Prop. I., it follows that there must be more heat abstracted from the refrigerator by the working of B backwards than is deposited in it by A. Now it is obvious that A might be made to spend part of its work in working B backwards, and the whole might be made self-acting. Also, there being no heat either taken from or given to the source on the whole, all the surrounding bodies and space except the refrigerator might, without interfering with any of the conditions which have been assumed, be made of the same temperature as the source, whatever that may be. We should thus have a self-acting machine, capable of drawing heat constantly from a body surrounded by others at a higher temperature, and converting it into mechanical effect. But this is contrary to the axiom, and therefore we conclude that the hypothesis that A derives more mechanical effect from the same quantity of heat drawn from the source than B, is false. Hence no engine whatever, with source and refrigerator at the same temperatures, can get more work from a given quantity of heat introduced than any engine which satisfies the condition of reversibility, which was to be proved.

14. This proposition was first enunciated by Carnot, being the expression of his criterion of a perfect thermo-dynamic engine*. He proved it by demonstrating that a negation of it would require the admission that there might be a self-acting machine constructed which would produce mechanical effect indefinitely, without any source either in heat or the consumption of materials, or any other physical agency; but this demonstration involves, fundamentally, the assumption that, in "a complete cycle of operations," the medium parts with exactly the same quantity of heat as it receives. A very strong expression of doubt regarding the truth of this assumption, as a universal principle, is given by

* Account of Carnot's *Theory*, § 13.

Carnot himself*; and that it is false, where mechanical work is, on the whole, either gained or spent in the operations, may (as I have tried to show above) be considered to be perfectly certain. It must then be admitted that Carnot's original demonstration utterly fails, but we cannot infer that the proposition concluded is false. The truth of the conclusion appeared to me, indeed, so probable, that I took it in connexion with Joule's principle, on account of which Carnot's demonstration of it fails, as the foundation of an investigation of the motive power of heat in air-engines or steam-engines through finite ranges of temperature, and obtained about a year ago results, of which the substance is given in the second part of the paper at present communicated to the Royal Society. It was not until the commencement of the present year that I found the demonstration given above, by which the truth of the proposition is established upon an axiom (§ 12) which I think will be generally admitted. It is with no wish to claim priority that I make these statements, as the merit of first establishing the proposition upon correct principles is entirely due to Clausius, who published his demonstration of it in the month of May last year, in the second part of his paper on the motive power of heat†. I may be allowed to add, that I have given the demonstration exactly as it occurred to me before I knew that Clausius had either enunciated or demonstrated the proposition. The following is the axiom on which Clausius' demonstration is founded:—

It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.

It is easily shown, that, although this and the axiom I have used are different in form, either is a consequence of the other. The reasoning in each demonstration is strictly analogous to that which Carnot orginally gave.

15. A complete theory of the motive power of heat would consist of the application of the two propositions demonstrated above, to every possible method of producing mechanical effect from thermal agency‡. As yet this has not been done for the

* Account of Carnot's *Theory*, § 6.

† Poggendorff's *Annalen*, referred to above.

‡ "There are at present known two, and only two, distinct ways in which

electrical method, as far as regards the criterion of a perfect engine implied in the second proposition, and probably cannot be done without certain limitations; but the application of the first proposition has been very thoroughly investigated, and verified experimentally by Mr Joule in his researches "On the Calorific Effects of Magneto-Electricity;" and on it is founded one of his ways of determining experimentally the mechanical equivalent of heat. Thus, from his discovery of the laws of generation of heat in the galvanic circuit*, it follows that when mechanical work by means of a magneto-electric machine is the source of the galvanism, the heat generated in any given portion of the fixed part of the circuit is proportional to the whole work spent; and from his experimental demonstration that heat is developed in any moving part of the circuit at exactly the same rate as if it were at rest, and traversed by a current of the same strength, he is enabled to conclude—

(1) That heat may be created by working a magneto-electric machine.

(2) That if the current excited be not allowed to produce any other than thermal effects, the total quantity of heat produced is in all circumstances exactly proportional to the quantity of work spent.

16. Again, the admirable discovery of Peltier, that cold is produced by an electrical current passing from bismuth to antimony, is referred to by Joule†, as showing how it may be proved

mechanical effect can be obtained from heat. One of these is by the alterations of volume which bodies experience through the action of heat; the other is through the medium of electric agency."—"Account of Carnot's Theory," § 4. (*Transactions*, Vol. XVI. part 5.)

* That, in a given fixed part of the circuit, the heat evolved in a given time is proportional to the square of the strength of the current, and for different fixed parts, with the same strength of current, the quantities of heat evolved in equal times are as the resistances. A paper by Mr Joule, containing demonstrations of these laws, and of others on the relations of the chemical and thermal agencies concerned, was communicated to the Royal Society on the 17th of December, 1840, but was not published in the *Transactions*. (See abstract containing a statement of the laws quoted above, in the *Philosophical Magazine*, Vol. XVIII. p. 308.) It was published in the *Philosophical Magazine* in October, 1841 (Vol. XIX. p. 260).

† [Note of March 20, 1852, added in *Phil. Mag.* reprint. In the introduction to his paper on the "Calorific Effects of Magneto-Electricity," &c., *Phil. Mag.*, 1843.

I take this opportunity of mentioning that I have only recently become acthat, when an electrical current is continuously produced from a purely thermal source, the quantities of heat evolved electrically in the different homogeneous parts of the circuit are only compensations for a loss from the junctions of the different metals, or that, when the effect of the current is entirely thermal, there must be just as much heat emitted from the parts not affected by the source as is taken from the source.

17. Lastly*, when a current produced by thermal agency is made to work an engine and produce mechanical effect, there will be less heat emitted from the parts of the circuit not affected by the source than is taken in from the source, by an amount precisely equivalent to the mechanical effect produced; since Joule demonstrates experimentally, that a current from any kind of

quainted with Helmholtz's admirable treatise on the principle of mechanical effect (*Ueber die Erhaltung der Kraft*, von Dr H. Helmholtz. Berlin. G. Reimer, 1847), having seen it for the first time on the 20th of January of this year; and that I should have had occasion to refer to it on this, and on numerous other points of the dynamical theory of heat, the mechanical theory of electrolysis, the theory of electro-magnetic induction, and the mechanical theory of thermo-electric currents, in various papers communicated to the Royal Society of Edinburgh, and to this Magazine, had I been acquainted with it in time.—W. T., March 20, 1852.]

* This reasoning was suggested to me by the following passage contained in a letter which I received from Mr Joule on the 8th of July, 1847. "In Peltier's experiment on cold produced at the bismuth and antimony solder, we have an instance of the conversion of heat into the mechanical force of the current," which must have been meant as an answer to a remark I had made, that no evidence could be adduced to show that heat is ever put out of existence. I now fully admit the force of that answer; but it would require a proof that there is more heat put out of existence at the heated soldering [or in this and other parts of the circuit] than is created at the cold soldering [and the remainder of the circuit, when a machine is driven by the current] to make the "evidence" be *experimental*. That this is the case I think is certain, because the statements of § 16 in the text are demonstrated consequences of the first fundamental proposition; but it is still to be remarked, that neither in this nor in any other case of the production of mechanical effect from purely thermal agency, has the ceasing to exist of an equivalent quantity of heat been demonstrated otherwise than theoretically. It would be a very great step in the experimental illustration (or *verification*, for those who consider such to be necessary) of the dynamical theory of heat, to actually show in any one case a loss of heat; and it might be done by operating through a very considerable range of temperatures with a good air-engine or steam-engine, not allowed to waste its work in friction. As will be seen in Part. II. of this paper, no experiment of any kind could show a considerable loss of heat without employing bodies differing considerably in temperature; for instance, a loss of as much as ·098, or about one-tenth of the whole heat used, if the temperature of all the bodies used be between 0° and 30° Cent.

source driving an engine, produces in the engine just as much less heat than it would produce in a fixed wire exercising the same resistance as is equivalent to the mechanical effect produced by the engine.

18. The quality of thermal effects, resulting from equal causes through very different means, is beautifully illustrated by the following statement, drawn from Mr Joule's paper on magneto-electricity*.

Let there be three equal and similar galvanic batteries furnished with equal and similar electrodes; let A_1 and B_1 be the terminations of the electrodes (or wires connected with the two poles) of the first battery, A_2 and B_2 the terminations of the corresponding electrodes of the second, and A_3 and B_3 of the third battery. Let A_1 and B_1 be connected with the extremities of a long fixed wire; let A_2 and B_2 be connected with the "poles" of an electrolytic apparatus for the decomposition of water; and let A_3 and B_3 be connected with the *poles* (or *ports* as they might be called) of an electro-magnetic engine. Then if the length of the wire between A_1 and B_1, and the speed of the engine between A_3 and B_3, be so adjusted that the strength of the current (which for simplicity we may suppose to be continuous and perfectly uniform in each case) may be the same in the three circuits, there will be more heat given out in any time in the wire between A_1 and B_1 than in the electrolytic apparatus between A_2 and B_2, or the working engine between A_3 and B_3. But if the hydrogen were allowed to burn in the oxygen, within the electrolytic vessel, and the engine to waste all its work without producing any other than thermal effects (as it would do, for instance, if all its work were spent in continuously agitating a limited fluid mass), the total heat emitted would be precisely the same in each of these two pieces of apparatus as in the wire between A_1 and B_1. It is worthy of remark that these propositions are *rigorously* true, being demonstrable consequences of the fundamental principle of the dynamical theory of heat, which have been discovered by Joule,

* In this paper reference is made to his previous paper "On the Heat of Electrolysis" (published in Vol. VII. part 2, of the second series of the Literary and Philosophical Society of Manchester) for experimental demonstration of those parts of the theory in which chemical action is concerned.

and illustrated and verified most copiously in his experimental researches*.

19. Both the fundamental propositions may be applied in a perfectly rigorous manner to the second of the known methods of producing mechanical effect from thermal agency. This application of the first of the two fundamental propositions has already been published by Rankine and Clausius; and that of the second, as Clausius showed in his published paper, is simply Carnot's unmodified investigation of the relation between the mechanical effect produced and the thermal circumstances from which it originates, in the case of an expansive engine working within an infinitely small range of temperatures. The simplest investigation of the consequences of the first proposition in this application, which has occurred to me, is the following, being merely the modification of an analytical expression of Carnot's axiom regarding the permanence of heat, which was given in my former paper†, required to make it express, not Carnot's axiom, but Joule's.

20. Let us suppose a mass‡ of any substance, occupying a volume v, under a pressure p uniform in all directions, and at a temperature t, to expand in volume to $v + dv$, and to rise in tem-

[* Note of March 20, 1852, added in *Phil. Mag.* reprint. I have recently met with the following passage in Liebig's *Animal Chemistry* (3rd edit. London, 1846, p. 43), in which the dynamical theory of the heat both of combustion and of the galvanic battery is indicated, if not fully expressed:—"When we kindle a fire under a steam-engine, and employ the power obtained to produce heat by friction, it is impossible that the heat thus obtained can ever be greater than that which was required to heat the boiler; and if we use the galvanic current to produce heat, the amount of heat obtained is never in any circumstances greater than we might have by the combustion of the zinc which has been dissolved in the acid."

A paper "On the Heat of Chemical Combination," by Dr Thomas Woods, published last October in the *Philosophical Magazine*, contains an independent and direct experimental demonstration of the proposition stated in the text regarding the comparative thermal effects in a fixed metallic wire, and an electrolytic vessel for the decomposition of water, produced by a galvanic current.—W. T., March 20, 1852.]

† "Account of Carnot's Theory," foot-note on § 26.

‡ This may have parts consisting of different substances, or of the same substance in different states, provided the temperature of all be the same. See below Part III., § 53—56.

perature to $t+dt$. The quantity of work which it will produce will be

$$pdv;$$

and the quantity of heat which must be added to it to make its temperature rise during the expansion to $t+dt$ may be denoted by

$$Mdv + Ndt.$$

The mechanical equivalent of this is

$$J(Mdv + Ndt),$$

if J denote the mechanical equivalent of a unit of heat. Hence the mechanical measure of the total external effect produced in the circumstances is

$$(p - JM)\,dv - JNdt.$$

The total external effect, after any finite amount of expansion, accompanied by any continuous change of temperature, has taken place, will consequently be, in mechanical terms,

$$\int\{(p - JM)\,dv - JNdt\};$$

where we must suppose t to vary with v, so as to be the actual temperature of the medium at each instant, and the integration with reference to v must be performed between limits corresponding to the initial and final volumes. Now if, at any subsequent time, the volume and temperature of the medium become what they were at the beginning, however arbitrarily they may have been made to vary in the period, the total external effect must, according to Prop. I., amount to nothing; and hence

$$(p - JM)\,dv - JNdt^*$$

must be the differential of a function of two independent variables, or we must have

$$\frac{d(p-JM)}{dt} = \frac{d(-JN)}{dv} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1),$$

this being merely the analytical expression of the condition, that the preceding integral may vanish in every case in which the

[* The integral function $\int\{(JM-p)\,dv + JNdt\}$ may obviously be called the *mechanical energy* of the fluid mass; as (when the constant of integration is properly assigned) it expresses the whole work the fluid has in it to produce. The consideration of this function is the subject of a short paper communicated to the Royal Society of Edinburgh, Dec. 15, 1851, as an appendix to the paper at present republished; (see below Part v. §§ 81—96).]

initial and final values of v and t are the same, respectively. Observing that J is an absolute constant, we may put the result into the form

$$\frac{dp}{dt} = J\left(\frac{dM}{dt} - \frac{dN}{dv}\right) \quad \text{.....................(2).}$$

This equation expresses, in a perfectly comprehensive manner, the application of the first fundamental proposition to the thermal and mechanical circumstances of any substance whatever, under uniform pressure in all directions, when subjected to any possible variations of temperature, volume and pressure.

21. The corresponding application of the second fundamental proposition is completely expressed by the equation

$$\frac{dp}{dt} = \mu M \quad \text{............................(3),}$$

where μ denotes what is called "Carnot's function," a quantity which has an absolute value, the same for all substances for any given temperature, but which may vary with the temperature in a manner that can only be determined by experiment. To prove this proposition, it may be remarked in the first place that Prop. II. could not be true for every case in which the temperature of the refrigerator differs infinitely little from that of the source, without being true universally. Now, if a substance be allowed first to expand from v to $v+dv$, its temperature being kept constantly t; if, secondly, it be allowed to expand further, without either emitting or absorbing heat till its temperature goes down through an infinitely small range, to $t-\tau$; if, thirdly, it be compressed at the constant temperature $t-\tau$, so much (actually by an amount differing from dv by only an infinitely small quantity of the second order), that when, fourthly, the volume is further diminished to v without the medium's being allowed to either emit or absorb heat, its temperature may be exactly t; it may be considered as constituting a thermo-dynamic engine which fulfils Carnot's condition of complete reversibility. Hence, by Prop. II., it must produce the same amount of work for the same quantity of heat absorbed in the first operation, as any other substance similarly operated upon through the same range of temperatures. But $\frac{dp}{dt}\tau \, . \, dv$ is obviously the whole work done in the complete cycle, and (by the definition of M in § 20) Mdv is the quantity of heat absorbed in the first operation. Hence the value of

$$\frac{\frac{dp}{dt}\tau . dv}{Mdv}, \text{ or } \frac{\frac{dp}{dt}}{M}\tau,$$

must be the same for all substances, with the same values of t and τ; or, since τ is not involved except as a factor, we must have

$$\frac{\frac{dp}{dt}}{M} = \mu \quad\text{..............................(4)},$$

where μ depends only on t; from which we conclude the proposition which was to be proved.

[Note of Nov. 9, 1881. Elimination of $\frac{dp}{dt}$ by (2) from (4) gives

$$\frac{J\left(\frac{dM}{dt} - \frac{dN}{dv}\right)}{M} = \mu \quad\text{....................(4')},$$

a very convenient and important formula.]

22. The very remarkable theorem that $\frac{\frac{dp}{dt}}{M}$ must be the same for all substances at the same temperature, was first given (although not in precisely the same terms) by Carnot, and demonstrated by him, according to the principles he adopted. We have now seen that its truth may be satisfactorily established without adopting the false part of his principles. Hence all Carnot's conclusions, and all conclusions derived by others from his theory, which depend merely on equation (3), require no modification when the dynamical theory is adopted. Thus, all the conclusions contained in Sections I., II., and III., of the Appendix to my "Account of Carnot's Theory" [Art. XLI. §§ 43—53 above], and in the paper immediately following it in the *Transactions* [and in the present reprint], entitled "Theoretical Considerations on the Effect of Pressure in Lowering the Freezing Point of Water," by my elder brother, still hold. Also, we see that Carnot's expression for the mechanical effect derivable from a given quantity of heat by means of a perfect engine in which the range of temperatures is infinitely small, expresses truly the greatest effect

which can possibly be obtained in the circumstances; although it is in reality only an infinitely small fraction of the whole mechanical equivalent of the heat supplied; the remainder being irrecoverably lost to man, and therefore "wasted," although not *annihilated.*

23. On the other hand, the expression for the mechanical effect obtainable from a given quantity of heat entering an engine from a "source" at a given temperature, when the range down to the temperature of the cold part of the engine or the "refrigerator" is finite, will differ most materially from that of Carnot; since, a finite quantity of mechanical effect being now obtained from a finite quantity of heat entering the engine, a finite fraction of this quantity must be converted from heat into mechanical effect. The investigation of this expression, with numerical determinations founded on the numbers deduced from Regnault's observations on steam, which are shown in Tables I. and II. of my former paper, constitutes the second part of the paper at present communicated.

PART II.

On the Motive Power of Heat through Finite Ranges of Temperature.

24. It is required to determine the quantity of work which a perfect engine, supplied from a source at any temperature, S, and parting with its waste heat to a refrigerator at any lower temperature, T, will produce from a given quantity, H, of heat drawn from the source.

25. We may suppose the engine to consist of an infinite number of perfect engines, each working within an infinitely small range of temperature, and arranged in a series of which the source of the first is the given source, the refrigerator of the last the given refrigerator, and the refrigerator of each intermediate engine is the source of that which follows it in the series. Each of these engines will, in any time, emit just as much less heat to its refrigerator than is supplied to it from its source, as is the equivalent of the mechanical work which it produces. Hence if t and $t + dt$ denote respectively the temperatures of the refrigerator and

source of one of the intermediate engines, and if q denote the quantity of heat which this engine discharges into its refrigerator in any time, and $q+dq$ the quantity which it draws from its source in the same time, the quantity of work which it produces in that time will be Jdq according to Prop. I., and it will also be $q\mu dt$ according to the expression of Prop. II., investigated in § 21; and therefore we must have

$$Jdq = q\mu dt.$$

Hence, supposing that the quantity of heat supplied from the first source, in the time considered is H, we find by integration

$$\log \frac{H}{q} = \frac{1}{J}\int_t^S \mu dt.$$

But the value of q, when $t = T$, is the final remainder discharged into the refrigerator at the temperature T; and therefore, if this be denoted by R, we have

$$\log \frac{H}{R} = \frac{1}{J}\int_T^S \mu dt \quad\text{..........(5)};$$

from which we deduce

$$R = H\epsilon^{-\frac{1}{J}\int_T^S \mu dt} \quad\text{..........(6)}.$$

Now the whole amount of work produced will be the mechanical equivalent of the quantity of heat lost; and, therefore, if this be denoted by W, we have

$$W = J(H - R) \quad\text{..........(7)},$$

and consequently, by (6),

$$W = JH\{1 - \epsilon^{-\frac{1}{J}\int_T^S \mu dt}\} \quad\text{..........(8)}.$$

26. To compare this with the expression $H\int_T^S \mu dt$, for the duty indicated by Carnot's theory*, we may expand the exponential in the preceding equation, by the usual series. We thus

$$\left.\begin{aligned} &\text{find} \quad W = \left(1 - \frac{\theta}{1.2} + \frac{\theta^2}{1.2.3} - \&c.\right).H\int_T^S \mu dt \\ &\text{where} \quad \theta = \frac{1}{J}\int_T^S \mu dt \end{aligned}\right\} \quad\text{......(9)},$$

* "Account," &c., Equation 7, § 31. [Art. XLI. above.]

This shows that the work really produced, which always falls short of the duty indicated by Carnot's theory, approaches more and more nearly to it as the range is diminished; and ultimately, when the range is infinitely small, is the same as if Carnot's theory required no modification, which agrees with the conclusion stated above in § 22.

27. Again, equation (8) shows that the real duty of a given quantity of heat supplied from the source increases with every increase of the range; but that instead of increasing indefinitely in proportion to $\int_T^S \mu dt$, as Carnot's theory makes it do, it never reaches the value JH, but approximates to this limit, as $\int_T^S \mu dt$ is increased without limit. Hence Carnot's remark* regarding the practical advantage that may be anticipated from the use of the air-engine, or from any method by which the range of temperatures may be increased, loses only a part of its importance, while a much more satisfactory view than his of the practical problem is afforded. Thus we see that, although the full equivalent of mechanical effect cannot be obtained even by means of a perfect engine, yet when the actual source of heat is at a high enough temperature above the surrounding objects, we may get more and more nearly the whole of the admitted heat converted into mechanical effect, by simply increasing the effective range of temperature in the engine.

28. The preceding investigation (§ 25) shows that the value of Carnot's function, μ, for all temperatures within the range of the engine, and the absolute value of Joule's equivalent, J, are enough of data to calculate the amount of mechanical effect of a perfect engine of any kind, whether a steam-engine, an air-engine, or even a thermo-electric engine; since, according to the axiom stated in § 12, and the demonstration of Prop. II., no inanimate material agency could produce more mechanical effect from a given quantity of heat, with a given available range of temperatures, than an engine satisfying the criterion stated in the enunciation of the proposition.

* "Account," &c. Appendix, Section IV. [Art. XLI. above.]

29. The mechanical equivalent of a thermal unit Fahrenheit, or the quantity of heat necessary to raise the temperature of a pound of water from 32° to 33° Fahr., has been determined by Joule in foot-pounds at Manchester, and the value which he gives as his best determination is 772·69. Mr Rankine takes, as the result of Joule's determination 772, which he estimates must be within $\frac{1}{300}$ of its own amount, of the truth. If we take $772\frac{2}{9}$ as the number, we find, by multiplying it by $\frac{9}{5}$, 1390 as the equivalent of the thermal unit Centigrade, which is taken as the value of J in the numerical applications contained in the present paper. [Note of Jan. 12, 1882. Joule's recent redetermination gives 771·8 Manchester foot-pounds as the work required to warm 1 lb. of water from 32° to 33° Fahr.]

30. With regard to the determination of the values of μ for different temperatures, it is to be remarked that equation (4) shows that this might be done by experiments upon any substance whatever of indestructible texture, and indicates exactly the experimental data required in each case. For instance, by first supposing the medium to be air; and again, by supposing it to consist partly of liquid water and partly of saturated vapour, we deduce, as is shown in Part III. of this paper, the two expressions (6), given in § 30 of my former paper ("Account of Carnot's Theory"), for the value of μ at any temperature. As yet no experiments have been made upon air which afford the required data for calculating the value of μ through any extensive range of temperature; but for temperatures between 50° and 60° Fahr., Joule's experiments* on the heat evolved by the expenditure of a given amount of work on the compression of air kept at a constant temperature, afford the most direct data for this object which have yet been obtained; since, if Q be the quantity of heat evolved by the compression of a fluid subject to "the gaseous laws" of expansion and compressibility, W the amount of mechanical work spent, and t the constant temperature of the fluid, we have by (11) of § 49 of my former paper,

$$\mu = \frac{W . E}{Q(1 + Et)} \quad\text{.........................(10)},$$

* "On the Changes of Temperature produced by the Rarefaction and Condensation of Air," *Phil. Mag.*, Vol. XXVI., May, 1845.

which is in reality a simple consequence of the other expression for μ in terms of data with reference to air. Remarks upon the determination of μ by such experiments, and by another class of experiments on air originated by Joule, are reserved for a separate communication, which I hope to be able to make to the Royal Society on another occasion. [*Dyn. Theory of Heat,* below, Part IV. §§ 61—80.]

31. The second of the expressions (6), in § 30 of my former paper, or the equivalent expression (32), given below in the present paper, shows that μ may be determined for any temperature from determinations for that temperature of—

(1) The rate of variation with the temperature, of the pressure of saturated steam.

(2) The latent heat of a given weight of saturated steam.

(3) The volume of a given weight of saturated steam.

(4) The volume of a given weight of water.

The last mentioned of these elements may, on account of the manner in which it enters the formula, be taken as constant, without producing any appreciable effect on the probable accuracy of the result.

32. Regnault's observations have supplied the first of the data with very great accuracy for all temperatures between $-32°$ Cent. and $230°$.

33. As regards the second of the data, it must be remarked that all experimenters, from Watt, who first made experiments on the subject, to Regnault, whose determinations are the most accurate and extensive that have yet been made, appear to have either explicitly or tacitly assumed the same principle as that of Carnot which is overturned by the dynamical theory of heat; inasmuch as they have defined the "total heat of steam" as the quantity of heat required, to convert a unit of weight of water at $0°$, into steam in the particular state considered. Thus Regnault, setting out with this definition for "the total heat of saturated steam," gives experimental determinations of it for the entire range of temperatures from $0°$ to $230°$; and he deduces the

"latent heat of saturated steam" at any temperature, from the "total heat," so determined, by subtracting from it the quantity of heat necessary to raise the liquid to that temperature. Now, according to the dynamical theory, the quantity of heat expressed by the preceding definition depends on the manner (which may be infinitely varied) in which the specified change of state is effected; differing in different cases by the thermal equivalents of the differences of the external mechanical effect produced in the expansion. For instance, the total quantity of heat required to evaporate a quantity of water at 0°, and then, keeping it always in the state of saturated vapour *, bring it to the temperature 100°, cannot be so much as three-fourths of the quantity required, first, to raise the temperature of the liquid to 100°, and then evaporate it at that temperature; and yet either quantity is expressed by what is generally received as a *definition* of the "total heat" of the saturated vapour. To find what it is that is really determined as "total heat" of saturated steam in Regnault's researches, it is only necessary to remark, that the measurement actually made is of the quantity of heat emitted by a certain weight of water in passing through a calorimetrical apparatus, which it enters as saturated steam, and leaves in the liquid state, the result being reduced to what would have been found if the final temperature of the water had been exactly 0°. For there being no external mechanical effect produced (other than that of sound, which it is to be presumed is quite inappreciable), the only external effect is the emission of heat. This must, therefore, according to the fundamental proposition of the dynamical theory, be independent of the intermediate agencies. It follows that, however the steam may rush through the calorimeter, and at whatever reduced pressure it may actually be condensed †, the

* See below (Part III. § 58), where the "negative" specific heat of saturated steam is investigated. If the mean value of this quantity between 0° and 100° were $-1\cdot5$ (and it cannot differ much from this) there would be 150 units of heat emitted by a pound of saturated vapour in having its temperature raised (by compression) from 0° to 100°. The latent heat of the vapour at 0° being 606·5, the final quantity of heat required to convert a pound of water at 0° into saturated steam at 100°, in the first of the ways mentioned in the text, would consequently be 456·5, which is only about $\frac{5}{7}$ of the quantity 637 found as "the total heat" of the saturated vapour at 100°, by Regnault.

† If the steam have to rush through a long fine tube, or through a small aperture within the calorimetrical apparatus, its pressure will be diminished before it is

heat emitted externally must be exactly the same as if the condensation took place under the full pressure of the entering saturated steam; and we conclude that *the total heat*, as actually determined from his experiments by Regnault, is the quantity of heat that would be required, first to raise the liquid to the specified temperature, and then to evaporate it at that temperature; and that the principle on which he determines the latent heat is correct. Hence, through the range of his experiments, that is from 0° to 230°, we may consider the second of the data required for the calculation of μ as being supplied in a complete and satisfactory manner.

34. There remains only the third of the data, or the volume of a given weight of saturated steam, for which accurate experiments through an extensive range are wanting; and no experimental researches bearing on the subject having been made since the time when my former paper was written, I see no reason for supposing that the values of μ which I then gave are not the most probable that can be obtained in the present state of science; and, on the understanding stated in § 33 of that paper, that accurate experimental determinations of the densities of saturated steam at different temperatures may indicate considerable errors in the densities which have been assumed according to the "gaseous laws," and may consequently render considerable alterations in my results necessary, I shall still continue to use Table I.

condensed; and there will, therefore, in two parts of the calorimeter be saturated steam at different temperatures (as, for instance, would be the case if steam from a high pressure boiler were distilled into the open air); yet, on account of the heat developed by the fluid friction, which would be precisely the equivalent of the mechanical effect of the expansion wasted in the rushing, the heat measured by the calorimeter would be precisely the same as if the condensation took place at a pressure not appreciably lower than that of the entering steam. The circumstances of such a case have been overlooked by Clausius (Poggendorff's *Annalen*, 1850, No. 4, p. 510), when he expresses with some doubt the opinion that the latent heat of saturated steam will be truly found from Regnault's "total heat," by deducting "the sensible heat;" and gives as a reason that, in the actual experiments, the condensation must have taken place "under the same pressure, or nearly under the same pressure," as the evaporation. The question is not, *Did the condensation take place at a lower pressure than that of the entering steam?* but, *Did* Regnault *make the steam work an engine in passing through the calorimeter, or was there so much noise of steam rushing through it as to convert an appreciable portion of the total heat into external mechanical effect?* And a negative answer to this is a sufficient reason for adopting *with certainty* the opinion that the principle of his determination of the latent heat is correct.

of that paper, which shows the values of μ for the temperatures $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$...$230\frac{1}{2}$, or, the mean values of μ for each of the 230 successive Centrigrade degrees of the air-thermometer above the freezing-point, as the basis of numerical applications of the theory. It may be added, that any experimental researches sufficiently trustworthy in point of accuracy, yet to be made, either on air or any other substance, which may lead to values of μ differing from those, must be admitted as proving a discrepancy between the true densities of saturated steam, and those which have been assumed*.

35. Table II. of my former paper, which shows the values of $\int_0^t \mu dt$ for $t=1$, $t=2$, $t=3$, ... $t=231$, renders the calculation of the mechanical effect derivable from a given quantity of heat by means of a perfect engine, with any given range included between the limits 0 and 231, extremely easy; since the quantity to be divided by J† in the index of the exponential in the expression (8) will be found by subtracting the number in that table corresponding to the value of T, from that corresponding to the value of S.

36. The following tables show some numerical results which have been obtained in this way, with a few (contained in the lower part of the second table) calculated from values of $\int_0^t \mu dt$

* I cannot see that any hypothesis, such as that adopted by Clausius fundamentally in his investigations on this subject, and leading, as he shows to determinations of the densities of saturated steam at different temperatures, which indicate enormous deviations from the gaseous laws of variation with temperature and pressure, is more probable, or is probably nearer the truth, than that the density of saturated steam does follow these laws as it is usually assumed to do. In the present state of science it would perhaps be wrong to say that either hypothesis is more probable than the other [or that the rigorous truth of either hypothesis is probable at all].

† It ought to be remarked, that as the unit of force implied in the determinations of μ is the weight of a pound of matter at Paris, and the unit of force in terms of which J is expressed is the weight of a pound at Manchester, these numbers ought in strictness to be modified so as to express the values in terms of a common unit of force; but as the force of gravity at Paris differs by less than $\frac{1}{2000}$ of its own value from the force of gravity at Manchester, this correction will be much less than the probable errors from other sources, and may therefore be neglected.

estimated for temperatures above 230°, roughly, according to the rate of variation of that function within the experimental limits.

37. *Explanation of the Tables.*

Column I. in each table shows the assumed ranges.

Column II. shows ranges deduced by means of Table II. of the former paper, so that the value of $\int_T^S \mu dt$ for each may be the same as for the corresponding range shown in column I.

Column III. shows what would be the duty of a unit of heat if Carnot's theory required no modification (or the actual duty of a unit of heat with additions through the range, to compensate for the quantities converted into mechanical effect).

Column IV. shows the true duty of a unit of heat, and a comparison of the numbers in it with the corresponding numbers in column III. shows how much the true duty falls short of Carnot's theoretical duty in each case.

Column VI. is calculated by the formula

$$R = \epsilon^{-\frac{1}{1390}\int_T^S \mu dt},$$

where $\epsilon = 2{\cdot}71828$, and for $\int_T^S \mu dt$ the successive values shown in column III. are used.

Column IV. is calculated by the formula

$$W = 1390\,(1 - R)$$

from the values of $1 - R$ shown in column V.

38. *Table of the Motive Power of Heat.*

Range of temperatures.				III. Duty of a unit of heat through the whole range.	IV. Duty of a unit of heat supplied from the source.	V. Quantity of heat converted into mechanical effect.	VI. Quantity of heat wasted.
I.		II.					
S.	*T.*	*S.*	*T.*	$\int_T^S \mu dt.$	*W.*	$1-R.$	*R.*
°		°	°	ft.-lbs	ft.-lbs.		
1	0	31·08	30	4·960	4·948	·00356	·99644
10	0	40·86	30	48·987	48·1	·0346	·9654
20	0	51·7	30	96·656	93·4	·067	·933
30	0	62·6	30	143·06	136	·098	·902
40	0	73·6	30	188·22	176	·127	·873
50	0	84·5	30	232·18	214	·154	·846
60	0	95·4	30	274·97	249	·179	·821
70	0	106·3	30	316·64	283	·204	·796
80	0	117·2	30	357·27	315	·227	·773
90	0	128·0	30	396·93	345	·248	·752
100	0	138·8	30	435·69	374	·269	·731
110	0	149·1	30	473·62	401	·289	·711
120	0	160·3	30	510·77	427	·308	·692
130	0	171·0	30	547·21	452	·325	·675
140	0	181·7	30	582·98	476	·343	·657
150	0	192·3	30	618·14	499	·359	·641
160	0	203·0	30	652·74	521	·375	·625
170	0	213·6	30	686·80	542	·390	·610
180	0	224·2	30	720·39	562	·404	·596
190	0	190	0	753·50	582	·418	·582
200	0	200	0	786·17	600	·432	·568
210	0	210	0	818·45	619	·445	·555
220	0	220	0	850·34	636	·457	·542
230	0	230	0	881 87	653	·470	·530

39. *Supplementary Table of the Motive Powers of Heat.*

Range of temperatures.				III. Duty of a unit of heat through the whole range.	IV. Duty of a unit of heat supplied from the source.	V. Quantity of heat converted into mechanical effect.	VI. Quantity of heat wasted.
I.		II.					
S.	*T.*	*S.*	*T.*	$\int_T^S \mu dt.$	*W.*	$1-R.$	*R.*
°	°	°	°	ft.-lbs.	ft.-lbs.		
101·1	0	140	30	439·9	377	·271	·729
105·8	0	230	100	446·2	382	·275	·725
300	0	300	0	1099	757	·545	·455
400	0	400	0	1395	879	·632	·368
500	0	500	0	1690	979	·704	·296
600	0	600	0	1980	1059	·762	·238
∞	0	∞	0	∞	1390	1·000	·000

40. Taking the range 30° to 140° as an example suitable to the circumstances of some of the best steam-engines that have yet

been made (see Appendix to "Account of Carnot's Theory," Sec. v.), we find in column III. of the supplementary table, 377 ft.-lbs. as the corresponding duty of a unit of heat instead of 440, shown in column III., which is Carnot's theoretical duty. We conclude that the recorded performance of the Fowey-Consols engine in 1845, instead of being only $57\frac{1}{2}$ per cent. amounted really to 67 per cent., or $\frac{2}{3}$ of the duty of a perfect engine with the same range of temperature; and this duty being ·271 (rather more than $\frac{1}{4}$) of the whole equivalent of the heat used; we conclude further, that $\frac{1}{5\cdot 49}$, or 18 per cent. of the whole heat supplied, was actually converted into mechanical effect by that steam-engine.

41. The numbers in the lower part of the supplementary table show the great advantage that may be anticipated from the perfecting of the air-engine, or any other kind of thermo-dynamic engine in which the range of the temperature can be increased much beyond the limits actually attainable in steam-engines. Thus an air-engine, with its hot part at 600°, and its cold part at 0° Cent., working with perfect economy, would convert 76 per cent. of the whole heat used into mechanical effect; or working with such economy as has been estimated for the Fowey-Consols engine, that is, producing 67 per cent. of the theoretical duty corresponding to its range of temperature, would convert 51 per cent. of all the heat used into mechanical effect. [Note, of Dec. 30, 1881. A great advance towards realizing this principle is now achieved in the gas-engine, of which the true dynamical economy is believed to be already superior to that of the best modern compound steam-engine.]

42. It was suggested to me by Mr Joule, in a letter dated December 9, 1848, that the true value of μ might be "inversely as the temperatures from zero *;" and values for various temperatures calculated by means of the formula,

$$\mu = J\frac{E}{1+Et} \qquad (11),$$

* If we take $\mu = k\frac{E}{1+Et}$ where k may be any constant, we find

$$W = J\left(\frac{S-T}{\frac{1}{E}+S}\right)^{\frac{k}{J}};$$

which is the formula I gave when this paper was communicated. I have since remarked, that Mr Joule's hypothesis implies essentially that the coefficient k must were given for comparison with those which I had calculated from data regarding steam. This formula is also adopted by Clausius, who uses it fundamentally in his mathematical investigations. If μ were correctly expressed by it, we should have

$$\int_T^S \mu dt = J \log \frac{1 + ES}{1 + ET};$$

and therefore equations (1) and (2) would become

$$W = J \frac{S - T}{\frac{1}{E} + S} \text{ ....(12)},$$

$$R = \frac{\frac{1}{E} + T}{\frac{1}{E} + S} \text{ ....(13)}.$$

43. The reasons upon which Mr Joule's opinion is founded, that the preceding equation (11) may be the correct expression for Carnot's function, although the values calculated by means of it differ considerably from those shown in Table I. of my former paper, form the subject of a communication which I hope to have an opportunity of laying before the Royal Society previously to the close of the present session. [Part IV. §§ 61—80, below.]

Part III.

Applications of the Dynamical Theory to establish Relations between the Physical Properties of all Substances.

44. The two fundamental equations of the dynamical theory of heat, investigated above, express relations between quantities of heat required to produce changes of volume and temperature in any material medium whatever, subjected to a uniform pressure in all directions, which lead to various remarkable conclusions. Such

be as it is taken in the text, the mechanical equivalent of a thermal unit. Mr Rankine, in a letter dated March 27, 1851, informs me that he has deduced, from the principles laid down in his paper communicated last year to this Society, an approximate formula for the ratio of the maximum quantity of heat converted into mechanical effect to the whole quantity expended, in an expansive engine of any substance, which, on comparison, I find agrees exactly with the expression (12) given in the text as a consequence of the hypothesis suggested by Mr Joule regarding the value of μ at any temperature.—[April 4, 1851.]

of these as are independent of Joule's principle (expressed by equation (2) of § 20), being also independent of the truth or falseness of Carnot's contrary assumption regarding the permanence of heat, are common to his theory and to the dynamical theory; and some of the most important of them* have been given by Carnot himself, and other writers who adopted his principles and mode of reasoning without modification. Other remarkable conclusions on the same subject might have been drawn from the equation $\frac{dM}{dt} - \frac{dN}{dv} = 0$, expressing Carnot's assumption (of the truth of which experimental tests might have been thus suggested); but I am not aware that any conclusion deducible from it, not included in Carnot's expression for the motive power of heat through finite ranges of temperature, has yet been actually obtained and published.

45. The recent writings of Rankine and Clausius contain some of the consequences of the fundamental principle of the dynamical theory (expressed in the first fundamental proposition above) regarding physical properties of various substances; among which may be mentioned especially a very remarkable discovery regarding the specific heat of saturated steam (investigated also in this paper in § 58 below), made independently by the two authors, and a property of water at its freezing-point, deduced from the corresponding investigation regarding ice and water under pressure by Clausius; according to which he finds that, for each $\frac{1}{10}$° Cent. that the solidifying point of water is lowered by pressure, its latent heat, which under atmospheric pressure is 79, is diminished by ·081. The investigations of both these writers involve fundamentally various hypotheses which may be or may not be found by experiment to be approximately true; and which render it difficult to gather from their writings what part of their conclusions, especially with reference to air and gases, depend merely on the necessary principles of the dynamical theory.

46. In the remainder of this paper, the two fundamental propositions, expressed by the equations

$$\frac{dM}{dt} - \frac{dN}{dv} = \frac{1}{J}\frac{dp}{dt} \text{..............(2) of § 20,}$$

* See above, § 22.

and $$M = \frac{1}{\mu} \cdot \frac{dp}{dt} \quad \text{.................(3) of § 21,}$$

are applied to establish properties of the specific heats of any substance whatever; and then special conclusions are deduced for the case of a fluid following strictly the "gaseous laws" of density, and for the case of a medium consisting of parts in different states at the same temperature, as water and saturated steam, or ice and water.

47. In the first place it may be remarked, that by the definition of M and N in § 20, N must be what is commonly called the "specific heat at constant volume" of the substance, provided the quantity of the medium be the standard quantity adopted for specific heats, which, in all that follows, I shall take as the unit of weight. Hence the fundamental equation of the dynamical theory, (2) of § 20, expresses a relation between this specific heat and the quantities for the particular substance denoted by M and p. If we eliminate M from this equation, by means of equation (3) of § 21, derived from the expression of the second fundamental principle of the theory of the motive power of heat, we find

$$\frac{dN}{dv} = \frac{d\left(\frac{1}{\mu}\frac{dp}{dt}\right)}{dt} - \frac{1}{J}\frac{dp}{dt} \quad \text{..................(14),}$$

which expresses a relation between the variation in the specific heat at constant volume, of any substance, produced by an alteration of its volume at a constant temperature, and the variation of its pressure with its temperature when the volume is constant; involving a function, μ, of the temperature, which is the same for all substances.

48. Again, let K denote the specific heat of the substance under constant pressure. Then, if dv and dt be so related that the pressure of the medium, when its volume and temperature are $v + dv$ and $t + dt$ respectively, is the same as when they are v and t, that is, if

$$0 = \frac{dp}{dv}dv + \frac{dp}{dt}dt;$$

we have

$$Kdt = Mdv + Ndt.$$

Hence we find

$$M=\frac{-\frac{dp}{dv}}{\frac{dp}{dt}}(K-N)\dots\dots\dots\dots(15),$$

which merely shows the meaning in terms of the two specific heats, of what I have denoted by M. Using in this for M its value given by (3) of § 21, we find

$$K-N=\frac{\left(\frac{dp}{dt}\right)^2}{\mu\times-\frac{dp}{dv}}\dots\dots\dots\dots(16),$$

an expression for the difference between the two specific heats, derived without hypothesis from the second fundamental principle of the theory of the motive power of heat.

49. These results may be put into forms more convenient for use, in applications to liquid and solid media, by introducing the notation:—

$$\left.\begin{aligned}\kappa&=v\times-\frac{dp}{dv}\\ e&=\frac{1}{\kappa}\frac{dp}{dt}\end{aligned}\right\}\dots\dots\dots\dots(17),$$

where κ will be the reciprocal of the compressibility, and e the coefficient of expansion with heat.

Equations (14), (16) and (3), thus become

$$\frac{dN}{dv}=\frac{d\left(\frac{\kappa e}{\mu}\right)}{dt}-\frac{\kappa e}{J}\dots\dots\dots\dots(18),$$

$$K-N=v\frac{\kappa e^2}{\mu}\dots\dots\dots\dots(19),$$

$$M=\frac{1}{\mu}.\kappa e\dots\dots\dots\dots(20);$$

the third of these equations being annexed to show explicitly the quantity of heat developed by the compression of the substance kept at a constant temperature. Lastly, if θ denote the rise in temperature produced by a compression from $v+dv$ to v before any heat is emitted, we have

$$\theta = \frac{1}{N} \cdot \frac{\kappa e}{\mu} \cdot dv = \frac{\kappa e}{\mu K - v\kappa e^2} dv \text{............(21).}$$

50. The first of these expressions for θ shows that, when the substance contracts as its temperature rises (as is the case, for instance, with water between its freezing-point and its point of maximum density), its temperature would become lowered by a sudden compression. The second, which shows in terms of its compressibility and expansibility exactly how much the temperature of any substance is altered by an infinitely small alteration of its volume, leads to the approximate expression

$$\theta = \frac{\kappa e}{\mu K},$$

if, as is probably the case, for all known solids and liquids, e be so small that $e \cdot v\kappa e$ is very small compared with μK.

51. If, now, we suppose the substance to be a gas, and introduce the hypothesis that its density is strictly subject to the "gaseous laws," we should have, by Boyle and Mariotte's law of compression,

$$\frac{dp}{dv} = -\frac{p}{v} \text{..........................(22);}$$

and by Dalton and Gay-Lussac's law of expansion,

$$\frac{dv}{dt} = \frac{Ev}{1+Et} \text{..........................(23);}$$

from which we deduce

$$\frac{dp}{dt} = \frac{Ep}{1+Et}.$$

Equation (14) will consequently become

$$\frac{dN}{dv} = \frac{d\left\{\frac{Ep}{\mu(1+Et)} - \frac{p}{J}\right\}}{dt} \text{....................(24),}$$

a result peculiar to the dynamical theory and equation (16),

$$K - N = \frac{E^2 pv}{\mu(1-Et)^2} \text{........................(25),}$$

which agrees with the result of § 53 of my former paper.

If V be taken to denote the volume of the gas at the temperature 0° under unity of pressure, (25) becomes

$$K - N = \frac{E^2 V}{\mu(1 + Et)} \quad \text{.....................(26).}$$

52. All the conclusions obtained by Clausius, with reference to air or gases, are obtained immediately from these equations by taking

$$\mu = J \frac{E}{1 + Et},$$

which will make $\frac{dN}{dv} = 0$, and by assuming, as he does, that N, thus found to be independent of the density of the gas, is also independent of its temperature.

53. As a last application of the two fundamental equations of the theory, let the medium with reference to which M and N are defined consist of a weight $1 - x$ of a certain substance in one state, and a weight x in another state at the same temperature, containing more latent heat. To avoid circumlocution and to fix the ideas, in what follows we may suppose the former state to be liquid and the latter gaseous; but the investigation, as will be seen, is equally applicable to the case of a solid in contact with the same substance in the liquid or gaseous form.

54. The volume and temperature of the whole medium being, as before, denoted respectively by v and t, we shall have

$$\lambda(1 - x) + \gamma x = v \quad \text{.......................(27),}$$

if λ and γ be the volumes of unity of weight of the substance in the liquid and the gaseous states respectively: and p, the pressure, may be considered as a function of t, depending solely on the nature of the substance. To express M and N for this mixed medium, let L denote the latent heat of a unit of weight of the vapour, c the specific heat of the liquid, and h the specific heat of the vapour when kept in a state of saturation. We shall have

$$Mdv = L \frac{dx}{dv} dv,$$

$$Ndt = c(1 - x) dt + hx dt + L \frac{dx}{dt} dt.$$

Now, by (27), we have

$$(\gamma-\lambda)\frac{dx}{dv}=1 \qquad (28),$$

and

$$(\gamma-\lambda)\frac{dx}{dt}+(1-x)\frac{d\lambda}{dt}+x\frac{d\gamma}{dt}=0 \qquad (29).$$

Hence

$$M=\frac{L}{\gamma-\lambda} \qquad (30),$$

$$N=c(1-x)+hx-L\frac{(1-x)\frac{d\lambda}{dt}+x\frac{d\gamma}{dt}}{\gamma-\lambda} \qquad (31).$$

55. The expression of the second fundamental proposition in this case becomes, consequently,

$$\mu=\frac{(\gamma-\lambda)\frac{dp}{dt}}{L} \qquad (32),$$

which agrees with Carnot's original result, and is the formula that has been used (referred to above in § 31) for determining μ by means of Regnault's observations on steam.

56. To express the conclusion derivable from the first fundamental proposition, we have, by differentiating the preceding expressions for M and N with reference to t and v respectively,

$$\frac{dM}{dt}=\frac{1}{\gamma-\lambda}\cdot\frac{dL}{dt}-\frac{L}{(\gamma-\lambda)^2}\cdot\frac{d(\gamma-\lambda)}{dt}$$

$$\frac{dN}{dv}=\left(h-c-L\frac{\frac{d\gamma}{dt}-\frac{d\lambda}{dt}}{\gamma-\lambda}\right)\frac{dx}{dv}$$

$$=\left\{\frac{h-c}{\gamma-\lambda}-\frac{L}{(\gamma-\lambda)^2}\right\}\frac{d(\gamma-\lambda)}{dt}.$$

Hence equation (2) of § 20 becomes

$$\frac{\frac{dL}{dt}+c-h}{\gamma-\lambda}=\frac{1}{J}\frac{dp}{dt} \qquad (33).$$

Combining this with the conclusion (32) derived from the second fundamental proposition, we obtain

$$\frac{dL}{dt}+c-h=\frac{L\mu}{J} \quad\text{.........................(34).}$$

The former of these equations agrees precisely with one which was first given by Clausius, and the preceding investigation is substantially the same as the investigation by which he arrived at it. The second differs from another given by Clausius only in not implying any hypothesis as to the form of Carnot's function μ.

57. If we suppose μ and L to be known for any temperature, equation (32) enables us to determine the value of $\frac{dp}{dt}$ for that temperature; and thence deducing a value of dt, we have

$$dt=\frac{\gamma-\lambda}{\mu L}\,dp \quad\text{.........................(35);}$$

which shows the effect of pressure in altering the "boiling-point" if the mixed medium be a liquid and its vapour, or the melting-point if it be a solid in contact with the same substance in the liquid state. This agrees with the conclusion arrived at [see pp. 156—164 above] by my elder brother in his "Theoretical Investigation of the Effect of Pressure in Lowering the Freezing-Point of Water." His result, obtained by taking as the value for μ that derived from Table I. of my former paper for the temperature 0°, is that the freezing-point is lowered by ·0075° Cent. by an additional atmosphere of pressure. Clausius, with the other data the same, obtains ·00733° as the lowering of temperature by the same additional pressure, which differs from my brother's result only from having been calculated from a formula which implies the hypothetical expression $J\frac{E}{1+Et}$ for μ. It was by applying equation (33) to determine $\frac{dL}{dt}$ for the same case that Clausius arrived at the curious result regarding the latent heat of water under pressure mentioned above (§ 45).

58. Lastly, it may be remarked that every quantity which appears in equation (33), except h, is known with tolerable ac-

curacy for saturated steam through a wide range of temperature; and we may therefore use this equation to find h, which has never yet been made an object of experimental research. Thus we have

$$-h = \frac{\gamma - \lambda}{J}\frac{dp}{dt} - \left(\frac{dL}{dt} + c\right).$$

For the value of γ the best data regarding the density of saturated steam that can be had must be taken. If for different temperatures we use the same values for the density of saturated steam (calculated according to the gaseous laws, and Regnault's observed pressure from $\frac{1}{1698 \cdot 5}$, taken as the density at 100°), the values obtained for the first term of the second member of the preceding equation are the same as if we take the form

$$-h = \frac{L\mu}{J} - \left(\frac{dL}{dt} + c\right)$$

derived from (34), and use the values of μ shown in Table I. of my former paper. The values of $-h$ in the second column in the following table have been so calculated, with, besides, the following data afforded by Regnault from his observations on the total heat of steam, and the specific heat of water

$$\frac{dL}{dt} + c = \cdot 305.$$

$$L = 606 \cdot 5 + \cdot 305t - (\cdot 00002t^2 + \cdot 000000t^3). \quad \ldots \quad (?)$$

The values of $-h$ shown in the third column are those derived by Clausius from an equation which is the same as what (34) would become if $J\dfrac{E}{1+Et}$ were substituted for μ.

t.	$-h$ according to Table I. of "Account of Carnot's Theory."	$-h$ according to Clausius.
0	1·863	1·916
50	1·479	1·465
100	1·174	1·133
150	0·951	0·879
200	0·780	0·676

59. From these results it appears, that through the whole range of temperatures at which observations have been made, the

value of h is negative; and, therefore, if a quantity of saturated vapour be compressed in a vessel containing no liquid water, heat must be continuously abstracted from it in order that it may remain saturated as its temperature rises; and conversely, if a quantity of saturated vapour be allowed to expand in a closed vessel, heat must be supplied to it to prevent any part of it from becoming condensed into the liquid form as the temperature of the whole sinks. This very remarkable conclusion was first announced by Mr Rankine, in his paper communicated to this Society on the 4th of February last year. It was discovered independently by Clausius, and published in his paper in Poggendorff's *Annalen* in the months of April and May of the same year.

60. It might appear at first sight, that the well-known fact that steam rushing from a high-pressure boiler through a small orifice into the open air does not scald a hand exposed to it*, is inconsistent with the proposition, that steam expanding from a state of saturation must have heat given to it to prevent any part from becoming condensed; since the steam would scald the hand unless it were dry, and consequently above the boiling-point in temperature. The explanation of this apparent difficulty, given in a letter which I wrote to Mr Joule last October [Art. XLVII. above], and which has since been published in the *Philosophical Magazine*, is, that the steam in rushing through the orifice produces mechanical effect which is immediately wasted in fluid friction, and consequently reconverted into heat; so that the issuing steam at the atmospheric pressure would have to part with as much heat to convert it into water at the temperature 100° as it would have had to part with to have been condensed at the high pressure and then cooled down to 100°, which for a

[* *Note added June* 26, 1852, *in Phil. Mag. reprint.*—At present I am inclined to believe that the rapidity of the current exercises a great influence on the sensation experienced in the circumstances, by causing the steam to mix with the surrounding air; for I have found that the hand suffers pain when exposed to the steam issuing from a common kettle, and dried by passing through a copper tube surrounded by red-hot coals or heated by lamps. But although there may be uncertainty regarding the causes of the different sensations in the different circumstances, I believe there is no reason for doubting either the fact of the dryness of the steam issuing from a high-pressure boiler (except when there is "priming" to a considerable extent), or the correctness of the explanation of this fact which I have given in the letter referred to.]

pound of steam initially saturated at the temperature t is, by Regnault's modification of Watt's law, $\cdot 305\ (t - 100^{\circ})$ more heat than a pound of saturated steam at 100° would have to part with to be reduced to the same state; and the issuing steam must therefore be above 100° in temperature, and dry.

PART IV.

[Note of Dec. 30, 1881. The experimental method suggested in this Article, was carried out practically by Mr Joule and the author in successive years from 1852 to 1856. Extracts from their joint papers describing their work are included below [Art. XLIX.] in the present reprint.]

On a Method of discovering experimentally the Relation between the Mechanical Work spent, and the Heat produced by the Compression of a Gaseous Fluid.*

61. The important researches of Joule on the thermal circumstances connected with the expansion and compression of air, and the admirable reasoning upon them expressed in his paper† "On the Changes of Temperature produced by the Rarefaction and Condensation of Air," especially the way in which he takes into account any mechanical effect that may be externally produced, or internally lost, in fluid friction, have introduced an entirely new method of treating questions regarding the physical properties of fluids. The object of the present paper is to show how, by the use of this new method, in connexion with the principles explained in my preceding paper, a complete theoretical view may be obtained of the phenomena experimented on by Joule; and to point out some of the objects to be attained by a continuation and extension of his experimental researches.

62. The Appendix to my "Account of Carnot's Theory"‡ contains a theoretical investigation of the heat developed by the

* From the *Transactions of the Royal Society of Edinburgh*, Vol. xx. part 2. April 17, 1851.

† *Philosophical Magazine*, May, 1845. Vol. xxvi. p. 369.

‡ *Transactions*. Vol. xvi. part 5.