

TRANSACTIONS
OF THE
ROYAL SOCIETY
OF
EDINBURGH.

VOL. XX.

EDINBURGH:
PUBLISHED BY ROBERT GRANT & SON, 82 PRINCES STREET.
AND WILLIAMS & NORGATE, 14 HENRIETTA STREET, COVENT GARDEN, LONDON.

MDCCCLIII.

XV.—*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.* By WILLIAM THOMSON, M.A., Fellow of St Peter's College, Cambridge, and Professor of Natural Philosophy in the University of Glasgow.

(Read 17th March 1851.)

INTRODUCTORY NOTICE.

1. SIR HUMPHREY 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 HUMPHREY 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 diathermane substances, consists of waves of transverse vibrations in an all-pervading medium.

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 HUMPHREY DAVY'S views.

* 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.

† 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.)

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, 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 connection with corresponding parts of the investigations at present laid before the Royal Society.

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

(1.) To shew what modifications of the conclusions arrived at by CARNOT, and by others who have followed his peculiar mode of reasoning regarding the motive

* "Annalen" of WÖHLER and LIEBIG, May 1842.

† British Association, August 1843, and Philosophical Magazine, September 1843.

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 shew that by taking these numbers (subject to correction when accurate experimental data regarding the density of saturated steam shall have been afforded), in connection 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 thermo-dynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.

10. The former proposition is shewn 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 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

* 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.

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 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 shew 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 connection 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 shewn that, although this and the axiom I have used are different

* "Account of CARNOT'S Theory," § 13.

† Ibid., § 6.

‡ POGGENDORFF'S *Annalen*, referred to above.

in form, either is a consequence of the other. The reasoning in each demonstration is strictly analogous to that which CARNOT originally 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 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 shewing how it may be proved that, 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 in from the source.

17. Lastly,‡ when a current produced by thermal agency is made to work an

* "There are [at present known] two, and only two, distinct ways in which 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 V.) 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 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).

† 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.

‡ This reasoning was suggested to me by the following passage contained in a letter which I

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 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 equality 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

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 shew 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 than is created at the cold soldering, 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 shew, 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 shew 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.

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, 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 shewed 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 temperature to $t + dt$. The quantity of work which it will produce will be

$$p dv;$$

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

$$M dv + N dt.$$

The mechanical equivalent of this is

$$J (M dv + N dt),$$

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

$$(p - J M) dv - J N dt.$$

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,

$$\int \{(p - J M) dv - J N dt\};$$

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

* "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.

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

$$(p - J M) dv - J N dt$$

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

$$\frac{d(p - J M)}{dt} = \frac{d(-J N)}{dv} \quad \dots \dots \dots (1),$$

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

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

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

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

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 refrigeration 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 farther, 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 $\frac{dp}{dt} \tau \cdot dv$ is obviously the whole work done in the complete cycle, and (by the definition of

M, in § 20) $M dv$ is the quantity of heat absorbed in the first operation. Hence the value of

$$\frac{\frac{dp}{dt} \tau \cdot dv}{M \cdot dv} \quad \text{or} \quad \frac{\frac{dp}{dt} \tau}{M}$$

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

$$\frac{d p}{d t} = \mu . \quad (4),$$

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

22. The very remarkable theorem that $\frac{d p}{d t}$ must be the same for all sub-

stances 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, and in the paper immediately following it in the Transactions, 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 shewn in Tables I. and II. of

and consequently, by (6),

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

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 find

$$W = \left(1 - \frac{\theta}{1.2} + \frac{\theta^2}{1.2.3} - \&c. \right) \cdot H \int_T^S \mu dt \quad (9).$$

where

$$\theta = \frac{1}{J} \int_T^S \mu dt$$

This shews 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) shews 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 $J H$, 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) shews 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

* "Account," &c., Equation 7, § 31.

† "Account," &c. Appendix, Section IV.

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.

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 $772\frac{2}{3}$ 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.

30. With regard to the determination of the values of μ for different temperatures, it is to be remarked that equation (4) shews 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 shewn in Part III. of this paper, the two expressions (6), given in § 30 of my former paper, 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° Fahrenheit, 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,

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

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.

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

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

(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 change of state defined 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 final 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

* 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 -1.5 (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.

remark, that the measurement actually made is of the quantity of heat emitted by a certain weight of water in passing through a calorimetric 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 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

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

consequently render considerable alterations in my results necessary, I shall still continue to use Table I. of that paper, which shews 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 centigrade 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 on 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 shews the values of $\int_0^t \mu dt$ for $t = 1, t = 2, t = 3, \dots t = 231$, 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 $J \dagger$ in the index of the exponential in 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 shew 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 $\int_0^t \mu dt$ 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 shews the assumed ranges.

Column II. shews 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 shewn in Column I.

Column III. shews 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 addi-

* I cannot see that any hypothesis, such as that adopted by CLAUSIUS fundamentally in his investigations on this subject, and leading, as he shews, 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.

† 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 $\frac{1}{20000}$ 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.

tions through the range, to compensate for the quantities converted into mechanical effect].

Column IV. shews the true duty of a unit of heat, and a comparison of the numbers in it with the corresponding numbers in Column III. shews 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 $\epsilon = 2.71828$, and for $\int_T^S \mu dt$ the successive values shewn in Column III. are used.

Column IV. is calculated by the formula

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

from the values of $1 - R$ shewn in Column V.

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

Range of Temperatures.				III.	IV.	V.	VI.
I.		II.		Duty of a Unit of Heat through the whole range.	Duty of a Unit of Heat supplied from the source.	Quantity of Heat converted into mechanical effect.	Quantity of Heat wasted.
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.	IV.	V.	VI.
I.		II.		Duty of a Unit of Heat through the whole range.	Duty of a Unit of Heat supplied from the source.	Quantity of Heat converted into mechanical effect.	Quantity of Heat wasted.
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 Col. III. of the supplementary Table, 377 ft.-lbs. as the corresponding duty of a unit of heat instead of 440, shewn in Col. 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 farther, that $\frac{1}{5.49}$, 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 shew the great advantage that may be anticipated from the perfecting of the air-engine, or any other kind of thermodynamic 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.

42. It was suggested to me by Mr JOULE, in a letter dated December 9, 1848,

subjected to a uniform pressure in all directions, which lead to various remarkable conclusions. Such 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 his assumption besides that which CARNOT gives regarding the motive power of heat through finite ranges of temperature, has yet been actually obtained and published.

45. The recent writings of CARNOT 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 $\frac{1}{10}^{\circ}$ 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

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

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

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

* See above, § 22.

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

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

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

$$K dt = M dv + N dt.$$

Hence we find

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

which merely shews 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

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

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:—

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

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

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

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

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

$$M = \frac{1}{\mu} \cdot \kappa e \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (20);$$

the third of these equations being annexed to shew 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

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

50. The first of these expressions for θ shews 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 shews, 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,

$$\frac{dp}{dv} = -\frac{p}{v} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (22);$$

and by DALTON and GAY LUSSAC's law of expansion,

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

from which we deduce

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

Equation (14) will consequently become

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

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

$$K - N = \frac{E^2 p v}{\mu(1+Et)^2} \quad (25),$$

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

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

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

$$\lambda(1-x) + \gamma x = v \quad (27),$$

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

$$M dv = L \frac{dx}{dv} dv$$

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

Now, by (27), we have

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

and

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

Hence

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

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

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

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

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,

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

$$\begin{aligned} \frac{dN}{dv} &= \left(h - c - L \frac{\frac{d\gamma}{dt} - \frac{d\lambda}{dt}}{\gamma - \lambda} \right) \frac{dx}{dv} \\ &= \left\{ \frac{h - c}{\gamma - \lambda} - \frac{L}{(\gamma - \lambda)^2} \right\} \frac{d(\gamma - \lambda)}{dt} \end{aligned}$$

Hence equation (2) of § 20 becomes

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

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

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

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

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

which shews 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 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 $\cdot 0075^\circ$ cent. by an additional atmosphere of pressure. CLAUSIUS, with the other data the same, obtains $\cdot 00733^\circ$ as the lowering of temperature produced 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 except h , which appears in equation (33), is known with tolerable accuracy 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 $\frac{1}{1693.5}$, 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 shewn in Table I. of my former paper. The values of $-h$ in the second column in the following table have been so calcu-

* Transactions, Vol. xvi., Part v. His paper was republished, with some slight modifications, in the Cambridge and Dublin Mathematical Journal, New Series, Vol. V.—Nov. 1850.

lated, with, besides, the following data afforded by REGNAULT from his observations on the total heat of steam, and the specific heat of water

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

$$L = 606\cdot 5 + \cdot 305 t - (\cdot 00002 t^2 + \cdot 0000003 t^3).$$

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

t	$-h$ according to Table I. of "Ac- count 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, and which has since been published in the Philosophical Magazine,*

* This explanation has been objected to as incorrect in principle by CLAUSIUS, in an article recently published in POGGENDORFF'S Annalen. I trust that, on reconsidering the subject (and, should this meet his eye, on reading the statement in the text, and the remarks in § 33 above), he will perceive that my explanation, as originally stated, is perfectly correct.

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 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 reduce it to the same state; and the issuing steam must, therefore, be above 100° in temperature, and dry.

XVI.—*On a Method of Discovering experimentally the Relation between the Mechanical Work spent, and the Heat produced by the Compression of a Gaseous Fluid.* By WILLIAM THOMSON, M.A., Fellow of St Peter's College, Cambridge, and Professor of Natural Philosophy in the University of Glasgow.

(Read 21st April 1851.)

1. 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 connection 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.

2. The Appendix to my Account of CARNOT'S Theory† contains a theoretical investigation of the heat developed by the compression of any fluid fulfilling the laws‡ of BOYLE and MARIOTTE and of DALTON and GAY LUSSAC. It has since been shown that that investigation requires no modification when the Dynamical Theory is adopted, and therefore the formula obtained as the result may be regarded as being established for a fluid of the kind assumed, independently of any hypothesis whatever. We may obtain a corresponding formula applicable to a fluid not fulfilling the gaseous laws of density, or to a solid pressed uniformly on all sides, in the following manner.

3. Let $M dv$ be the quantity of heat absorbed by a body kept at a constant temperature t , when its volume is increased from v to $v + dv$; let p be the uniform pressure which it experiences from without, when its volume is v and its temperature t ; and let $p + \frac{dp}{dt} dt$ denote the value p would acquire if the temperature were raised to $t + dt$, the volume remaining unchanged. Then, by equation (3) of

* Philosophical Magazine, May 1845, vol. xxvi., p. 369.

† Transactions, vol. xvi., part V.

‡ To avoid circumlocution these laws will, in what follows, be called simply, the *gaseous laws*, or the *gaseous laws of density*.

is not constant for all temperatures, unless CARNOT'S function for different temperatures vary inversely as $1 + Et$, and that it is not the simple mechanical equivalent of the heat, as it was unwarrantably* assumed by MAYER to be, unless this function have precisely the expression

$$\mu = J \cdot \frac{E}{1 + Et} \quad (I.)$$

This formula was suggested to me by Mr JOULE, in a letter dated December 9th, 1848, as probably a true expression for μ , being required to reconcile the expression derived from CARNOT'S theory (which I had communicated to him), for the heat evolved in terms of the work spent in the compression of a gas, with the hypothesis that the latter of these is exactly the mechanical equivalent of the former, which he had adopted in consequence of its being, at least approximately, verified by his own experiments. This, which will be called MAYER'S hypothesis, from its having been first assumed by MAYER, is also assumed by CLAUSIUS without any reason from experiment; and an expression for μ the same as the preceding, is consequently adopted by him as the foundation of his mathematical deductions from elementary reasoning regarding the motive power of heat. The preceding formulæ show that if it be true at a particular temperature for any one fluid fulfilling the gaseous laws, it must be true for every such fluid at the same temperature.

6. Of the various experimental researches which might be suggested as suitable for testing MAYER'S hypothesis, it appears, from the preceding formula, that any which would give data for the determination of the values of μ through a wide range of temperatures, would, with a single accurate determination of J , afford a complete test. Thus an experimental determination of the density of saturated steam for temperatures from 0° to 230° cent., would complete the data, of which a part have been so accurately determined by REGNAULT, for the calculation of the values of μ between those wide limits, and would contribute more, perhaps, than any set of experimental researches that could at present be proposed, to advance the mechanical theory of heat.

7. The values of μ , given in Table I. of my Account of CARNOT'S Theory, which were calculated from REGNAULT'S observations on steam, with the assumption of $\frac{1}{1693.5}$, (the maximum density of water being unity) for the density of saturated steam at 100° cent., and of the gaseous laws for calculating it by means of REGNAULT'S observed pressures, at other temperatures, are far from verifying equation (I.), as appears from the Table of the values of $\frac{\mu(1 + Et)}{E}$, given in the preceding paper, § 51; or as the following comparative Table shows:—

* In violation of CARNOT'S important principle, that thermal agency and mechanical effect, or mechanical agency and thermal effect, cannot be regarded in the simple relation of cause and effect, when any other effect, such as the alteration of the density of a body, is finally concerned.

Col. 1. Temperature. t	Col. 2. Values of μ according to assumed density of saturated steam. $[\mu]$	Col. 3. Values of μ according to JOULE'S formula. $J \frac{E}{1 + Et}$	Col. 4. Values of μ according to modified assumption for density of saturated steam $\frac{1717.6}{1693.5} \times [\mu]$
0	4.967	5.087	5.038
10	4.832	4.908	4.901
20	4.703	4.740	4.769
30	4.578	4.584	4.643
40	4.456	4.438	4.519
50	4.337	4.300	4.399
60	4.221	4.171	4.281
70	4.114	4.050	4.172
80	4.013	3.935	4.070
90	3.921	3.827	3.977
100	3.833	3.724	3.887
110	3.753	3.627	3.806
120	3.679	3.535	3.731
130	3.611	3.447	3.662
140	3.546	3.364	3.596
150	3.487	3.284	3.536
160	3.432	3.209	3.481
170	3.382	3.136	3.430
180	3.335	3.067	3.382
190	3.289	3.001	3.336
200	3.247	2.937	3.293
210	3.208	2.876	3.254
220	3.171	2.818	3.216
230	3.135	2.762	3.179

Mr JOULE, when I pointed out these discrepancies to him in the year 1848, suggested that even between 0° and 100° , the inaccuracy of the data regarding steam might be sufficient to account for them. I think it will be generally admitted that there can be no such inaccuracy in REGNAULT'S part of the data, and there remains only the uncertainty regarding the density of saturated steam, to prevent the conclusion that μ cannot be expressed by $J \frac{E}{1 + Et}$; so that MAYER'S hypothesis would be confirmed if, and overturned unless, the density of saturated steam, instead of following the gaseous laws, were truly expressed by the equations

$$\left. \begin{aligned} \sigma &= \frac{\left(\frac{1}{E} + t\right) [\mu]}{J} \cdot [\sigma] \\ [\sigma] &= \frac{1}{1693.5} \cdot \frac{1 + E \times 100}{1 + Et} \cdot \frac{p}{\Pi} \end{aligned} \right\} \quad \dots \quad (II.)$$

where $[\mu]$ denotes the quantity tabulated for the temperatures $0^\circ, 1^\circ, 2^\circ, \dots 230^\circ$ in Table I. of my Account of CARNOT'S Theory; and $[\sigma]$ denotes the density of saturated steam which was assumed in the calculation of that Table, the values of $\frac{p}{\Pi}$

in the expression for it being obtained by dividing the numbers tabulated at the end of REGNAULT's eighth Mémoire by 760. The considerableness of the deviations from the gaseous laws which equation (II.) indicates, is seen at once by comparing the numbers in Col. 2 with those in Col. 3 of the preceding Table, and observing that the coefficient of $[\sigma]$ in (II.) is, for each temperature shown in that Table, obtained by dividing the corresponding number in Col. 2 by that in Col. 3. Col. 4 shows what the values of μ would be if the density of saturated steam at 100° were $\frac{1}{1717.6}$ instead of $\frac{1}{1693.5}$, and, for other temperatures, varied according to the gaseous laws.

8. This subject has been very carefully examined by CLAUSIUS, who has indicated the great deviations from the gaseous laws of density that MAYER's hypothesis requires in saturated steam, and has given an empirical formula for the density of saturated steam founded on that hypothesis, and on REGNAULT's observations on the pressure and latent heat. In this direction theory can go no farther, for want of experimental data, although, from what we know of gases and saturated vapours, it may be doubted whether such excessive deviations, in the case of steam, from the laws of a "perfect gas" are rendered probable by a hypothesis resting on no experimental evidence whatever.*

9. To JOULE we are indebted for a most important series of experimental researches on the relation between the thermal effects, the external mechanical effects, and the internal mechanical effects (*vis viva* destroyed by fluid friction) due to compressions and expansions of air in various circumstances.† These researches afford actual tests which, so far as they go, are verifications of the truth of MAYER's hypothesis for temperatures between 50° and 60° Fahr., founded on two distinct methods, either of which is perfect in principle, and might be made the foundation of experiments at any temperature whatever.

10. The first of these methods consists simply in determining, by direct experiment, the heat evolved by the expenditure of a given amount of work in compressing air, and comparing it with the quantity of heat created by the same amount of work in JOULE's original experiments on the heat developed by magneto-electricity, and by the friction of fluids in motion.

11. The second method is especially remarkable, as affording, in each experiment, an independent test of the truth of MAYER's hypothesis for air at the temperature used, without requiring any knowledge of the absolute value of the mechanical equivalent of heat. In JOULE's actual experiments, the test is simply

* JOULE's experimental verification of MAYER's law for temperatures of from 50° to 60° Fahr., shews, if rigorously exact, that the density of saturated steam at about 10° centigrade must be $\frac{1693.5}{1717.6}$ of what was assumed for it in the calculations of my former paper, but does not go towards indicating any deviation from the gaseous laws of variation in the density of saturated steam at different temperatures.

† Philosophical Magazine, May 1845.

this:—The total external thermal effect is determined when air is allowed to expand, through a small orifice, from one vessel into another previously exhausted by an air-pump. Here the first mechanical effect produced by the expanding gas, is *vis viva* generated in the rushing of the air. By the time equilibrium is established, all this mechanical effect has been lost in fluid friction (there being no appreciable mechanical effect produced externally in sound, which is the only external mechanical effect, other than heat, that can be produced by the motions of a fluid within a fixed rigid vessel); and no truth in physical science can be more certain than that by the time thermal as well as mechanical equilibrium is established at the primitive temperature, the contents of the two vessels must have parted with just as much more heat than they would have parted with, had the air in expanding pushed out a piston against an external resisting force, as is equivalent to the mechanical effect thus produced externally. Hence, if the two vessels and the tube connecting them be immersed (as they are in JOULE's first set of experiments with this apparatus) in one vessel of water, and if, after time is allowed for the pressure and temperature of the air to become the same in the two vessels, the water be found to have neither gained nor lost heat (it being understood, of course, that the air and all other matter external to the water are at an absolutely constant temperature during the experiment), then, for the temperature of the experiment, MAYER's hypothesis is perfectly confirmed; but any final elevation or depression of temperature in the water, would show that the work due to the expansion is either greater than or less than the absolute equivalent of the heat absorbed.

12. Mr JOULE's second experiment on the same apparatus, in which he examined separately the external thermal effects round each of the two vessels, and round a portion of the tube containing the small orifice (a stop-cock) has suggested to me a method which appears still simpler, and more suitable for obtaining an excessively delicate test of MAYER's hypothesis for any temperature. It consists merely in dispensing with the two vessels in JOULE's apparatus, and substituting for them two long spirals of tube (instead of doing this for only one of the vessels, as JOULE does in his third experiment with the same apparatus); and in forcing air continuously through the whole. The first spiral portion of the tube, up to a short distance from the orifice, ought to be kept as nearly as possible at the temperature of the atmosphere surrounding the portion containing the orifice, and serves merely to fix the temperature of the entering air. The following investigation shows what conclusions might be drawn by experimenting on the thermal phenomena of any fluid whatever treated in this manner.

13. Let p be the uniform pressure of the fluid in the first spiral, up to a short distance from the orifice, and let p' be the pressure a short distance from the orifice on the other side, which will be uniform through the second spiral. Let t be the constant external temperature, and let the air in both spirals be kept as

closely as possible at the same temperature. If there be any elevation or depression of temperature of the fluid in passing through the orifice, it may only be after passing through a considerable length of the second spiral that it will again arrive sensibly at the temperature, t , and the spiral must be made at least so long that the fluid issuing from the open end of it, when accurately tested, may be found not to differ appreciably from the primitive temperature, t .

14. Let H be the total quantity of heat emitted from the portion of the tube containing the orifice, and the second spiral, during the passage of a volume u through the first spiral, or of an equivalent volume u' through the parts of the second where the temperature is sensibly t . This will consist of two parts; one (positive) the heat produced by the fluid friction, and the other (negative) the heat emitted by that portion of the fluid which passes from one side to the other of the orifice, in virtue of its expansion. To find these two parts, let us first suppose the transference of the fluid to take place without loss of mechanical effect in fluid friction, as it would do if, instead of the partition with a small orifice, there were substituted a moveable piston, and if a volume u of fluid, on the side where the pressure is higher (p), were enclosed between that and another piston, and allowed to slide through the tube till the second piston should take the place of the first, and to expand till its volume should be u' . If we adopt the same notation with reference to the volume, v , of the substance between the pistons, kept at a constant temperature, t , as has been used uniformly in this and the preceding paper; we shall have, for the quantity of heat absorbed during the motion of the piston,

$$\int_u^{u'} M dv;$$

or, by the second fundamental equation of the theory, (3) of § 21 of the preceding paper,

$$\frac{1}{\mu} \int_u^{u'} \frac{d\varpi}{dt} dv,$$

where ϖ denotes the actual pressure (intermediate between p and p') of the substance when its volume is v . Again, the work done by the pistons will be given by the equation

$$W = \int_u^{u'} \varpi dv + p u - p' u' \quad (e).$$

If now the transference of the substance from the one portion of the tube, where the pressure is p , to the other, where the pressure is p' , take place through a small orifice, exactly that amount, W , of work will be lost as external mechanical effect, and will go to generate thermal *vis viva*. The quantity of heat thus produced will be

$$\frac{1}{J} \left\{ \int_u^{u'} \varpi dv + p u - p' u' \right\}.$$

Hence the total quantity of heat emitted will be the excess of this above the amount previously found to be absorbed when the mechanical effect is all external; and therefore we have

$$H = \frac{1}{J} \left\{ \int_u^{u'} \varpi dv + p u - p' u' \right\} - \frac{1}{\mu} \int_u^{u'} \frac{d\varpi}{dt} dv \quad . \quad . \quad (f).$$

Whatever changes of temperature there may actually be of the air in or near the orifice, this expression will give rigorously the total quantity of heat emitted by that portion of tube which contains the orifice and the whole of the second spiral during the passage of a volume u through the first spiral, or u' through any portion of the second spiral where the temperature is sensibly t .

15. To apply this result to the case of a gas fulfilling the gaseous laws, we may put

$$p u = p' u'.$$

Hence (e) becomes

$$W = \int_u^{u'} \varpi dv = p u \log \frac{u'}{u} = p' u' \log \frac{p}{p'} \quad . \quad . \quad (5),$$

and, by (3), we have

$$\frac{dW}{dt} = \frac{E p u}{1 + E t} \log \frac{u'}{u} = \frac{E W}{1 + E t}.$$

Hence the expression (f) for the heat emitted becomes

$$H = \left\{ \frac{1}{J} - \frac{E}{\mu(1 + E t)} \right\} W \quad . \quad . \quad . \quad (6).$$

16. Lastly, if MAYER'S hypothesis be fulfilled for the gas used in the experiment, the coefficient of W vanishes, by (I.), and therefore

$$H = 0 \quad . \quad . \quad . \quad . \quad . \quad (III.)$$

17. From equation (III.) it follows that, if MAYER'S hypothesis be true, there is neither emission nor absorption of heat, on the whole, required to reduce the temperature of the air after passing through the orifice, to its primitive value, t . Hence, although no doubt those portions of the air in the intermediate neighbourhood of the orifice, which are communicating, by their expansion, *vis viva* to those contiguous to them, will be becoming colder, and those which are the means of occasioning the portions contiguous to them to lose *vis viva*, through fluid friction, will be becoming warmer at each instant; yet very near the orifice on each side, where the motion of the air is uniform, the temperature would be constantly equal to t . Hence the simplest conceivable test of the truth of MAYER'S hypothesis would be to try whether the temperature of the air is exactly the same on the two sides of the orifice. This might be done by very delicate thermometers adjusted in the tube at sufficient distances on each side of the orifice to be quite out of the *rush* which there is of air in the immediate neighbourhood of the orifice; but it might be done in a still more refined manner by means of a deli-

cate galvanometer, and a small thermo-electric battery arranged so that one set of the solderings might be within the tube on the side of the entering current of air, and the other set within the tube on the side of the current from the orifice. The tube on each side of the orifice would need to be bent so as to bring two parts of it, at small distances from the orifice on each side, near enough one another to admit of the battery being so placed. The only difficulty I can perceive in the way of making the necessary arrangements is what might be experienced in fitting the two ends of the battery air-tight into the two parts of the tube. It first occurred to me that the little battery itself might be placed entirely within the tube, and the difference of pressure kept up in the two parts by the middle of the battery being fitted nearly air-tight in the tube, by means of wax, or otherwise; but this arrangement would not be satisfactory, as portions of the bars of the battery, if not the ends themselves directly, would be altered in temperature, even if MAYER'S hypothesis were rigorously true, on account of the rushing of the air among them. No part of the battery ought to be exposed to the rushing of the air in the neighbourhood of the orifice, and therefore the middle of the battery would have to be external to the tube, the ends being cemented into the tube by some indulating cement sufficiently strong and compact to hold perfectly air-tight on the side where the pressure is different from the atmospheric pressure. By such means as these I think a very satisfactory series of experiments might easily be performed to test MAYER'S hypothesis for air through a very wide range of temperatures.

18. Should the differential method of experimenting just described indicate any difference of temperature whatever on the two sides of the orifice, MAYER'S hypothesis would be shown to be not exactly fulfilled, and, according as the air leaving the orifice is found to be warmer or colder than the entering air, we should infer that the heat absorbed, when air expands at a constant temperature, is less than or greater than the mechanical effect produced by the expansion.

19. Calorimetrical methods, like those used by JOULE, might then be followed for actually determining the heat emitted or absorbed by the air in the neighbourhood of the orifice, or in the second spiral, in acquiring the temperature of the air in the entering stream, and by careful experimenting, it is probable that excessively accurate results might be thus obtained for a wide range of temperature.

20. The result of each experiment would be a value of μ , in terms of JOULE'S mechanical equivalent; to be calculated by the following expression, derived from equations (5) and (6).

$$\mu = \frac{\frac{J E}{1 + E t}}{1 - J \cdot \frac{H}{p' u' \log \frac{p}{p'}}} \quad \dots \quad (7).$$

In the second member of this equation p' denotes the pressure of the air through the second spiral, which would be the atmospheric pressure, or excessively near it, if, as in JOULE'S third experiment, mentioned above (described by the author in p. 378 of the volume* containing his paper), the air leaving the second spiral be measured by means of a pneumatic trough: p denotes the pressure in the first spiral, which ought to be constant, and must be carefully measured; u' denotes the volume of air which leaves the apparatus in any time; and H denotes the quantity of heat emitted in the same time. The experiment might be continued for any length of time, and each one of these four quantities might be determined with great accuracy, so that probably very accurate direct results of observations might be obtained. If so, no way of experimenting could be better adapted than this to the determination of CARNOT'S function, for different temperatures, in terms of JOULE'S mechanical equivalent of heat.

* Phil. Mag., vol. xxvi.