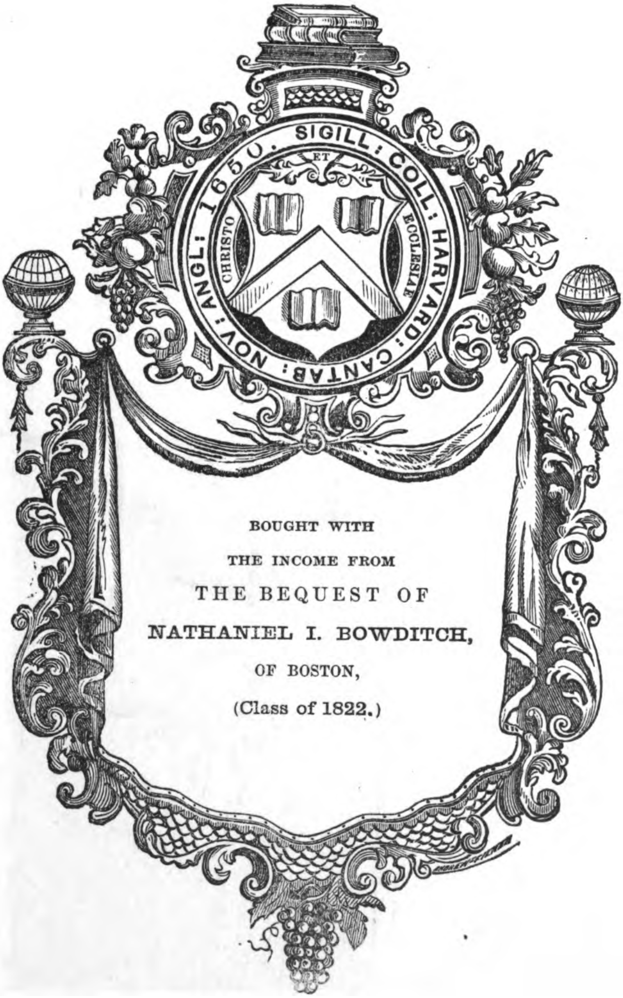
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CHRISTO ET ECCLESIAE

# THE

# MECHANICAL THEORY OF HEAT,

WITH ITS

## APPLICATIONS TO THE STEAM-ENGINE

AND TO THE

## PHYSICAL PROPERTIES OF BODIES.

BY

Rudolf [illegible]

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LONDON:
JOHN VAN VOORST, 1 PATERNOSTER ROW.
MDCCCLXVII.

PRINTED BY TAYLOR AND FRANCIS,
RED LION COURT, FLEET STREET.

# INTRODUCTION.

NEARLY seventeen years ago I translated for the Philosophical Magazine the first of this series of Memoirs, by Professor Clausius, on the Mechanical Theory of Heat. A short time afterwards the Essay of Professor Helmholtz, *Ueber die Erhaltung der Kraft,* was placed in my hands: I translated it, and had it published in the continuation of 'Taylor's Scientific Memoirs.' It was thus my fortune to introduce to the scientific public of England the earliest writings of two of the most celebrated contributors to the great theory in question. For many years subsequent to the period here referred to, I was careful to translate, or to have translated, every paper published by these two writers; and the fact that the following series of these Memoirs is thought worthy of being presented in a collected form to the English public, proves that I did not overestimate their importance. I have been asked by its publisher to write a line or two of introduction to the present volume. This I could not refuse to do, though I feel how superfluous it must be; for the name and fame of Professor Clausius stand as high in this country as in his own. My Introduction therefore shall be confined to this brief statement of my relationship to his writings. They fell into my hands at a time when I knew but little of the Mechanical Theory of Heat. In those days their author was my teacher; and in many respects I am proud to acknowledge him as my teacher still.

JOHN TYNDALL.

London, May 1867.

# AUTHOR'S PREFACE.

It has been repeatedly represented to me (and from very different quarters) that the memoirs on the Mechanical Theory of Heat which, since the year 1850, I have published from time to time, principally in Poggendorff's *Annalen*, are not easily accessible to all who wish to read them, the interest taken in the Mechanical Theory of Heat having in recent times greatly augmented in circles where physical Journals are not usually found. Accordingly I have thought it advisable to collect and republish those Memoirs. In so doing I have also sought to remedy certain defects which have hitherto diminished their utility.

My memoirs "On the Mechanical Theory of Heat" are of different kinds. Some are devoted to the development of the general theory and to the application thereof to those properties of bodies which are usually treated of in the doctrine of heat. Others have reference to the application of the mechanical theory of heat to electricity. The latter contain many expositions peculiar to the doctrine of electricity, and they form a separate group, the study of which is not requisite for understanding the former. Other memoirs, again, have reference to the conceptions I have formed of the molecular motions which we call heat. These conceptions, however, have no necessary connexion with the general theory, the latter being based solely on certain principles which may be accepted without adopting any particular view as to the nature of molecular motions. I have therefore kept the consideration of molecular motions quite distinct from the exposition of the general theory.

The memoirs constituting these three different groups did not, however, appear exactly in their present order; partly in consequence of the direction of my own studies, and partly for other reasons, I found it desirable to pass during their publication from one group to another. Hence has arisen the disadvantage that a reader desirous of becoming acquainted only with the theory, freed as much as possible from hypotheses, cannot know in advance which memoirs are requisite, and which are unnecessary for his purpose. This disadvantage is remedied in the present reprint by simply separating the memoirs into groups, as above explained.

The present collection contains the memoirs which belong to the first group; in them the mechanical theory of heat is developed from certain simple axiomatic principles, and is applied to a series of phenomena depending upon heat. I have also included the application of the theory to steam-engines, because this application may be conveniently associated with the expositions occurring in these memoirs, and especially with those which have reference to vapours*.

The memoirs which treat of the application to electricity, and those which relate to my conceptions of molecular motions, I intend subsequently to collect in like manner. The memoirs contained in this collection, however, are quite independent of the others, and form in themselves a complete and connected whole.

Another disadvantage which, as I frequently found, diminished the usefulness of my memoirs, arose from the fact that many passages therein were with difficulty understood. The mechanical theory of heat has introduced new ideas into science, differing from the earlier accepted views, and accordingly requiring special mathematical treatment. An instance of this, especially worthy of mention, is a certain kind of differential equations which I have used in my researches, and which differ from the ordinary ones in one essential point: misconception

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* [The ninth memoir of the present edition having been published in Germany subsequent to the appearance there of the First Part of the Collected Memoirs, was not included therein. It is now published for the first time in English; and, at the Author's suggestion, its appropriate place in the entire series of Memoirs is here assigned to it.—T. A. H.]

might easily arise if this difference were not sufficiently observed. The signification of, and the mode of treating these differential equations have, indeed, long been known to mathematicians through the researches of Monge; but, from the fact that an energetic attack on my theory originated in a misconception of the true nature of these equations, it would appear that they have not been sufficiently well studied. In order to avoid similar misunderstandings in future, I gave at the time a more detailed explanation of the subject; as this, however, was not published in Poggendorff's *Annalen*, in which my other memoirs appeared, but in Dingler's Polytechnic Journal (which contained that attack), it may possibly have been seen by few of my readers.

In order, once for all, to remove any difficulty of this nature, the present collection is preceded by a mathematical introduction, in which the treatment of the differential equations in question is discussed in a manner similar to that adopted in Dingler's Journal. I have also in many places added notes and appendices, in order to elucidate passages in the text.

The memoirs are reprinted *verbatim* in their original form. The mechanical theory of heat, to the establishment and development of which these memoirs have, as I believe, essentially contributed, is of so great importance that it has already frequently given rise to discussions on priority. Under these circumstances it appeared to me advisable to allow myself no alterations; for even unimportant ones, having reference solely to modes of expression, might possibly give rise to the thought that I intended thereby either to take credit, ultimately, for something which did not appear in the original memoirs, or to suppress something which was there inserted*.

The notes and appendices now given for the first time are plainly recognizable as such. In order to distinguish these notes from those which were previously published, the former

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* [It is scarcely necessary to state that in the present English edition this rule has not been adhered to. The translations of the original memoirs, which are here reprinted from the Philosophical Magazine, were made by different persons; and in order to secure the necessary uniformity in terminology, verbal alterations were frequently requisite. All such alterations, however, have been made with Prof. Clausius's sanction, to whom the proofs have all been submitted for revision.—T. A. H.]

are enclosed in square brackets; and to every note containing more than a mere reference is added the date. To the appendices also dates have been affixed.

Should apparently superfluous repetitions be here and there detected, it must be remembered that the memoirs were published at different times during the course of fourteen years, and that often, between two memoirs which directly follow each other in this edition, I had published several others bearing upon different subjects. It was necessary in such cases to recapitulate such portions of the antecedent memoirs as were deemed essential to the comprehension of the new one, or requisite for bringing the reader into the proper train of thought.

R. CLAUSIUS.

Zurich, August 1864.

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* [In Arts. 4 and 6 of this Introduction it is tacitly assumed that the functions $F(x, y)$ and $F(x, y, z)$ given in the equations (11) and (18) have each but one value for given values of the variables. It is easy to see what modifications will ensue on abandoning this assumption.—1867.]

† [Here and elsewhere Mayer's name has been incorrectly written Meyer.—T.A.H.]

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ON THE

# MECHANICAL THEORY OF HEAT.

◆

## MATHEMATICAL INTRODUCTION.

### ON THE TREATMENT OF DIFFERENTIAL EQUATIONS WHICH ARE NOT DIRECTLY INTEGRABLE*.

1. A differential equation of the form

$$dz=\phi\,(x,y)\,dx+\psi\,(x,y)\,dy \quad . \quad . \quad . \quad . \quad . \quad (1)$$

being given, we may, for brevity, introduce the letters M and N as representatives of the arbitrary functions $\phi\ (x,\ y)$ and $\psi\,(x,y)$ of the variables $x$ and $y$, and thus write that equation in the somewhat more convenient form

$$dz=\mathrm{M}dx+\mathrm{N}dy \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1^{a})$$

This equation indicates by how much the magnitude $z$ is increased, when $x$ and $y$ receive the infinitesimal increments represented by $dx$ and $dy$; a decrement being here, of course, considered as a negative increment. The above two functions, by which the differentials $dx$ and $dy$ are multiplied, represent the *partial differential coefficients* of $z$ according to $x$ and to $y$. Denoting, therefore, these partial differential coefficients by the fractional forms $\frac{dz}{dx}$ and $\frac{dz}{dy}$, we may write

$$\left.\begin{aligned}\frac{dz}{dx}&=\phi(x,y)=\mathrm{M},\\ \frac{dz}{dy}&=\psi(x,y)=\mathrm{N}.\end{aligned}\right\} \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

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* The principal part of this introduction is contained in a note, published by me, in Dingler's *Polytechnisches Journal*, vol. cl. p. 29 (1858).

This representation of partial differential coefficients by the simple fractions $\frac{dz}{dx}$, $\frac{dz}{dy}$ is, in a certain sense, objectionable. For if in the equation (1) or ($1^a$) we substitute these fractions for the functions in question, the equation

$$dz = \frac{dz}{dx}\,dx + \frac{dz}{dy}\,dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

is obtained, in which the same symbol $dz$ appears three times with three different meanings. On the right of the equation $dz$ denotes, *first*, the increment of $z$ when, $y$ remaining constant, $x$ alone is increased by $dx$; and *secondly*, the increment received by $z$ when, without changing $x$, $y$ is increased by $dy$; whilst on the left of the equation $dz$ represents the total increment of $z$ due to the simultaneous reception by $x$ and $y$ of the increments $dx$ and $dy$, respectively. This diversity in the interpretation of one and the same symbol, arising from the different combinations into which it enters, vitiates the expressiveness of the equation.

In consequence of this, various changes in the notation of partial differential coefficients have been proposed. In order to distinguish the partial differential coefficients from others, Euler enclosed the above simple fractions in brackets, and his method is still frequently adopted. In this notation the equation (3) assumes the form

$$dz = \left(\frac{dz}{dx}\right)dx + \left(\frac{dz}{dy}\right)dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3^a)$$

Other mathematicians give, as a suffix to the symbol $d$ in the numerators of the above fractions, the variable to whose variation the differential coefficient is due; in this notation the equation would be written thus:

$$dz = \frac{d_x z}{dx}\,dx + \frac{d_y z}{dy}\,dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3^b)$$

Others again, following the example of Jacobi, use the symbol $\partial$ in place of $d$ in the numerator as well as in the denominator of the fraction which represents a partial differential coefficient. In this manner our equation acquires the form

$$dz = \frac{\partial z}{\partial x}\,dx + \frac{\partial z}{\partial y}\,dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3^c)$$

Of these three notations that of ($3^b$), wherein suffixes are employed, is perhaps the most rational; for it is precisely the *numerators* of the representative fractions which admit of different interpretations, and the latter are clearly and unequivocally expressed by means of these suffixes. Nevertheless the incessant addition of a suffix constitutes an inconvenience, which, though trivial in individual cases, becomes much graver when partial differential coefficients are frequently employed. It must also be observed that, in the cases which most frequently occur, the original and most convenient notation gives rise to no ambiguity. For when $x$ and $y$ denote two mutually independent variables upon whose values that of $z$ depends, it is manifest that the $dz$ in the numerator of the fraction $\frac{dz}{dx}$ cannot be understood to denote other than that increment of $z$ which is due to the increment $dx$ of the variable $x$ which appears in the denominator. Any alteration which may simultaneously take place in the value of the other variable $y$ must, together with the consequent variation of $z$, be perfectly independent of the differential $dx$, so that the fraction $\frac{dz}{dx}$ would have no definite meaning whatever were the above variation of $z$ included in that of which $dz$ is here the symbol. It is consequently of little importance whether, in the representation of partial differential coefficients, we give preference to the ordinary fractional forms $\frac{dz}{dx}$, $\frac{dz}{dy}$, or, for the sake of greater clearness, to one of the above described modified forms of notation.

In one case only is it necessary to have recourse to a distinctive symbol in order to avoid misconception. It sometimes happens, for instance, that the magnitudes $x$ and $y$, upon whose values that of $z$ depends, are not independent of each other, but that the value of one is affected by that of the other; in other words, that the former may be regarded as a function of the latter. If $y$, for example, be considered as a function of $x$, then, in the event of $x$ increasing by $dx$, the simultaneous increment $dy$ of $y$ cannot be regarded as arbitrary, but must be treated as a magnitude whose value is also determined by the differential $dx$, and capable of representation by the expression $\frac{dy}{dx}\,dx$. By substitution, the differential equation (3) would now take the form

$$dz = \frac{dz}{dx} dx + \frac{dz}{dy} \cdot \frac{dy}{dx} dx.$$

Dividing throughout by $dx$ we obtain an equation which, if we also denote the quotient on the left by a simple fraction, would read thus:

$$\frac{dz}{dx} = \frac{dz}{dx} + \frac{dz}{dy} \cdot \frac{dy}{dx};$$

here, however, the fraction $\frac{dz}{dx}$ on the left has a very different meaning from that of the like fraction on the right.

In such cases the two fractions must in some way or other be distinguished. To do so, we may either employ, for the partial differential coefficients on the right, one of the three notations above described, or we may employ a different symbol for the fraction on the left. For the last purpose, mathematical authors have proposed to write, in place of $\frac{dz}{dx}$,

$$\text{either } \frac{1}{dx} dz, \text{ or } \frac{d(z)}{dx}, \text{ or } \frac{\mathbf{d}z}{\mathbf{d}x}.$$

Since cases of this kind however occur, comparatively speaking, but seldom, it is of little importance which of these methods of notation is adopted. In fact, whenever necessary, it will be easy to add an explanatory remark as to the meaning to be attached to any chosen symbol.

I have thought it necessary to enter into these details concerning the different systems of notation now in use, because it is precisely in investigations where familiar ideas are departed from, that a diversity of notation is most liable to give rise to misconceptions.

2. Returning to the differential equation

$$dz = \mathrm{M} dx + \mathrm{N} dy$$

given in (1) and ($1^a$), let us now inquire if, and how the magnitude $z$ can be determined therefrom.

Differential equations of this form cannot all be regarded as of like kind; according to the constitution of the functions M and N they are, on the contrary, divisible into two classes which differ from each other essentially, not only with respect to the treatment which they require, but also with reference to the results to which they lead. To the first class belong the cases where the functions in question satisfy the condition

$$\frac{dM}{dy}=\frac{dN}{dx}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the second class embraces all cases where this equation of condition is not satisfied by the two functions.

When the equation (4) is fulfilled, the expression on the right of the given differential equation (1) or ($1^a$) is integrable; that is to say, it is the complete differential of a function of $x$ and $y$, in which these two variables may be regarded as independent of each other; and by integration an equation can be obtained of the form

$$z=F(x, y)+\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

When the condition expressed by the equation (4) is not fulfilled, the expression on the right of the given differential equation is not integrable, whence we conclude *that z cannot be expressed as a function of x and y so long as these variables are regarded as independent, one of the other.* In fact, if we were to assume

$$z=F(x, y),$$

we should have

$$M=\frac{dz}{dx}=\frac{dF(x, y)}{dx},$$

$$N=\frac{dz}{dy}=\frac{dF(x, y)}{dy};$$

whence would result

$$\frac{dM}{dy}=\frac{d^2F(x, y)}{dx\,dy},$$

$$\frac{dN}{dx}=\frac{d^2F(x, y)}{dy\,dx}.$$

But since, when the two variables of a function are independent of each other, the result of differentiating, successively, according to both is not affected by the order in which these differentiations are effected, we have necessarily

$$\frac{d^2F(x, y)}{dx\,dy}=\frac{d^2F(x, y)}{dy\,dx};$$

so that from the two preceding equations the equation (4) follows as a consequence, and thus contradicts the hypothesis from which we started.

In such a case, therefore, the integration is impossible on the assumption that the variables $x$ and $y$ preserve their property of mutual independence. If, on the other hand, we assume any determinate relation whatever to exist between the two magnitudes, in consequence of which one may be represented as a function of the other, the integration of the given differential equation will be thereby rendered practicable. For if we put

$$f(x, y)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $f$ represents any function whatever, we can by means of this equation express either variable in terms of the other, and then eliminate the variable thus expressed, together with its differential, from the differential equation (1). The general form given in the equation (6) embraces, of course, the special case, where one of the magnitudes $x, y$ ceases to be variable; for then its differential, by becoming equal to zero, at once vanishes from the differential equation, and the magnitude itself becomes replaced by its constant value.

Let us now suppose one of the variables, say $y$, together with its differential, eliminated from the differential equation (1) by means of the equation (6), and the former thereby reduced to the form

$$dz=\Phi(x)\,dx\,;$$

the equation thus modified will obviously give, by integration, another of the form

$$z=\mathrm{F}(x)+\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Accordingly, the two equations (6) and (7) must together be regarded as constituting a solution of the given differential equation. Since the function $f(x, y)$ which appears in (6) is an arbitrary one, and to every different form of this function must correspond, in general, a different function $\mathrm{F}(x)$ in (7), it is manifest that there will be an infinite number of solutions of the kind under consideration.

The form of the equation (7), it is to be observed, is susceptible of several modifications. If, by means of the equation (6), $x$ had been expressed in terms of $y$; and then, together with its differential, eliminated from the given differential equation, the form in question would have been

$$dz = \Phi_1(y)\,dy;$$

from which, by integration, an equation of the form

$$z = F_1(y) + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7^a)$$

would have been obtained. Precisely the same equation would be arrived at by substituting for $x$, in the result (7) obtained by the first method, its value in $y$ as given by the equation (6). Again, $x$ might be only partially eliminated from (7). For instance, the function $F(x)$ will in general contain $x$ in two or more different combinations (or rather, it may be always made to do so, by substituting for $x$ equivalent expressions such as $(1-a)x + ax$, $\frac{x^{n+1}}{x^n}$, &c. . . .), and when this is the case the value of $x$ expressed in $y$ may always be substituted in some combinations, whilst others are allowed to remain unaltered. The equation would thereby assume the form

$$z = F_2(x, y) + \text{const.}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7^b)$$

which may be regarded as the more general one, embracing both the other forms as special cases.

It is obvious, however, that the three equations (7), ($7^a$), and ($7^b$), each of which only holds in combination with (6), do not constitute different solutions, but merely different expressions of one and the same solution.

3. In order clearly to appreciate the essential difference between the cases when the given differential equation belongs to the first, and when it belongs to the second class,—that is to say, when the condition (4) is, and when it is not fulfilled,—we will consider an example which, partly by its relation to an already well-known subject, and partly also by its susceptibility of geometrical representation, is well suited to furnish a clear conception of the matter.

Conceive a moveable point $p$ in a fixed plane, and let its position at any stated moment be determined by rectangular coordinates $x$ and $y$. Acting on the point, and tending to move it in the plane, is a force whose intensity and direction are different at different parts of the plane. Required the *work* done by this force when the point moves under its influence.

Let $ds$ be an element of the path described by the point, S the component of the force acting thereon which falls in the direction of this path, and $d\mathrm{W}$ the element of work performed by the force during this small motion. This last element will be determined by the equation

$$d\mathrm{W}=\mathrm{S}\,ds, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

to which, however, another form may be given more convenient for our present purpose. Let P be the whole force acting in the immediate neighbourhood of the arc-element $ds$, and $\phi$ the angle between this element and the direction of that force. Then, obviously,

$$\mathrm{S}=\cos\phi\,.\,\mathrm{P},$$

so that

$$d\mathrm{W}=\cos\phi\,.\,\mathrm{P}\,ds. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now if X and Y denote the two components of the force P in the directions of the coordinate axes, the cosines of the angles between these directions and that of P will be expressed by

$$\frac{\mathrm{X}}{\mathrm{P}} \text{ and } \frac{\mathrm{Y}}{\mathrm{P}}.$$

Moreover, if by $dx$ and $dy$ we understand the increments which the $x$ and $y$ of the point $p$ receive when the latter describes the arc-element $ds$, the cosines of the angles between the direction of this element and those of the coordinate axes will be expressed by

$$\frac{dx}{ds} \text{ and } \frac{dy}{ds}.$$

Hence for the cosine of the angle $\phi$ between the force P and the arc-element $ds$ we have the expression

$$\cos\phi=\frac{\mathrm{X}}{\mathrm{P}}\cdot\frac{dx}{ds}+\frac{\mathrm{Y}}{\mathrm{P}}\cdot\frac{dy}{ds},$$

which, when substituted in (9), gives the equation

$$d\mathrm{W}=\mathrm{X}\,dx+\mathrm{Y}\,dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This is a differential equation of the same form as those given in (1) and ($1^{\mathrm{a}}$), the notation alone being a little changed. Instead of $z$ the letter W is used, as more appropriate for the representation of work; and M and N, which before were abbreviated symbols for the functions $\phi(x, y)$ and $\psi(x, y)$, are now replaced by X and Y, the customary representatives of the components of the force P, and are again abbreviations for arbitrary functions of the coordinates $x$ and $y$; for, as already remarked, the force P varies in intensity and direction, according to some arbitrary law, with the position which the moveable point $p$, upon which it acts, occupies in the plane.

Before proceeding, by the integration of this equation, to deduce the work corresponding to any finite motion, the question arises: does it satisfy the condition

$$\frac{dX}{dy}=\frac{dY}{dx},$$

analogous to the equation (4)? Should it do so, we may deduce at once an equation of the form

$$W=F(x, y)+\text{const.}; \quad . \quad . \quad . \quad . \quad . \quad (11)$$

but if it should *not* satisfy this condition, then in order to be able to integrate, we must first assume a relation to exist between the variables $x$ and $y$; so that finally we shall obtain a system of equations of the form

$$\left.\begin{array}{r} f(x, y)=0, \\ W=F(x, y)+\text{const.} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

4. The geometrical signification of these two different results is easily recognized.

Suppose the point $p$ to move from a given initial position $x_0, y_0$ to a given final one $x_1, y_1$. Then in the *first* case the work done by the acting force during this motion may be at once ascertained without the necessity of inquiring into the nature of the path thereby described. This work, in fact, is expressed by the difference

$$F(x_1, y_1)-F(x_0, y_0).$$

Although the point, therefore, may pursue very different paths when moving from one position to another, the quantity of work thereby performed by the acting force, being independent of the path, is perfectly determined so soon as the starting-point and the terminus are given.

In the *second* case it is otherwise. Of the two equations (12), which have reference thereto, the first is arbitrary, and the second can only be determined when the first is given, since the form of the function $F(x, y)$ varies obviously with that which is given to the function $f(x, y)$. The first equation is that of some curve, so that the above relation may be expressed, geometrically, by saying, in the present case, the work done by the acting force during the motion of the point $p$ can only be determined when the whole course of the curve on which it moves is known. The initial and final points of the motion being previously known, the first of the above equations must be chosen so that the curve thereby represented may pass through these two points; this curve, however, may have an infinity of different forms to which, notwithstanding the coincidence of the extremities, will correspond an infinity of different quantities of work.

If, for instance, the point $p$ be compelled to describe a closed curve, and thus to return to its initial position, the coordinates $x_1, y_1$ being respectively equal to $x_0, y_0$, the total work done, in the first case, will be zero; in the second, however, it need not be so, but may have any positive or negative value whatever.

The example here borrowed from analytical mechanics shows also very clearly how a magnitude which is incapable of expression as a function of $x$ and $y$ (so long as the latter are regarded as variables independent of each other) may still have, for partial differential coefficients according to $x$ and $y$, determinate functions of these variables. For it is manifest that, strictly speaking, the components X and Y must be termed *the partial differential coefficients, according to* x *and* y, *of the work* W; since, when $x$ increases by $dx$, $y$ remaining constant, the work increases by $Xdx$; and when $y$ increases by $dy$, $x$ remaining unaltered, the work augments by $Ydy$. Now whether W be a magnitude generally expressible as a function of $x$ and $y$, or whether it can only be determined on knowing the path described by the point, we may always employ the ordinary notation for the partial differential coefficients of W, and write,

$$\left.\begin{aligned}\frac{dW}{dx}&=X,\\ \frac{dW}{dy}&=Y.\end{aligned}\right\} \quad \dots\dots\dots\dots \quad (13)$$

5. When the functions $\phi(x,y)$ and $\psi(x,y)$, or M and N, which occur in the differential equation (1) or ($1^a$), fail to satisfy the condition (4), it has been shown that the integration may be

effected by assuming a relation to exist between the variables $x$ and $y$ of the form

$$f(x, y) = 0.$$

The same object is achieved in a more general manner, however, by assuming the existence of an equation, not merely between $x$ and $y$, but involving all the variables $x, y, z$, or rather any one or more of them, and therefore expressible in the form

$$f(x, y, z) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If by means of this equation one of the variables be eliminated from the given differential equation, another differential equation will be obtained which may always be integrated.

Indeed in order to exhaust all possible cases of complete differential equations of the first order in three variables, still further extensions of the above considerations would be necessary.

The differential equation (1) is itself a limited form of the kind in question, inasmuch as functions of all three variables, instead of the two variables $x, y$, might therein present themselves. When the differential equation has this more general form, which may be thus written:

$$\phi(x, y, z)dx + \psi(x, y, z)dy + \chi(x, y, z)dz = 0, \quad . \quad (15)$$

the condition to be satisfied in order that integration may be possible without the assumption of any further relation between the variables, assumes a more complicated form than that given in (4). It should, moreover, be observed that in the case of the non-fulfilment of this condition, and the consequent impossibility of actual integration, the relation which must be assumed, or be involved in some imposed condition, in order to be able to integrate, need not have the form of a primitive, but may itself be a differential equation. In the treatment of the equations, too, as well as in the manner of expressing the result, many modifications may present themselves.

It is not necessary, however, to enter here into all these extensions, since the preceding exposition will suffice to render intelligible the equations hereafter to be developed, as well as the operations to which such equations will be subjected.

6. I may mention, lastly, that the preceding considerations, relative to complete differential equations involving three variables, may be extended in a similar manner to complete differen-

tial equations in four or more variables, and that amongst the latter we are thereby led to the detection of corresponding differences. In illustration of this I will give but one simple special case, well known in mechanics, and closely related to the example already considered.

Let $p$ be a moveable point in space whose rectanglar coordinates at any particular moment are $x, y, z$. Conceive a force P to act on this point with an intensity and in a direction which may be different at different places in space. I propose to determine the quantity of work done by the force during any assigned motion.

Let $ds$ be an element of the path described by the point, and $\phi$ the angle at which this path is inclined to the direction of the force. The element of work $d\mathrm{W}$ will be again given by the equation

$$d\mathrm{W}=\cos\phi . \mathrm{P}ds.$$

In order to give another form to this expression, we may denote by X, Y, Z, the three components of P in the directions of the coordinate axes; in which case the fractions

$$\frac{\mathrm{X}}{\mathrm{P}}, \frac{\mathrm{Y}}{\mathrm{P}}, \frac{\mathrm{Z}}{\mathrm{P}}$$

will represent the cosines of the angles which the direction of the force makes with the directions of the three coordinate axes. If, further, $dx, dy, dz$ be the increments of the coordinates $x, y, z$, due to the description of the path-element $ds$, the cosines of the angle between the element $ds$, and the three coordinate axes will be expressed, respectively, by

$$\frac{dx}{ds}, \frac{dy}{ds}, \frac{dz}{ds}.$$

Hence is deduced, for the cosine of the angle $\phi$ between the directions of the path and the force, the value

$$\cos\phi=\frac{\mathrm{X}}{\mathrm{P}}\cdot\frac{dx}{ds}+\frac{\mathrm{Y}}{\mathrm{P}}\cdot\frac{dy}{ds}+\frac{\mathrm{Z}}{\mathrm{P}}\cdot\frac{dz}{ds}.$$

Substituting this value in the above expression for $d\mathrm{W}$, we have the differential equation

$$d\mathrm{W}=\mathrm{X}dx+\mathrm{Y}dy+\mathrm{Z}dz \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

for the determination of the work. The magnitudes X, Y, Z which here present themselves are perfectly arbitrary functions of $x, y, z$; for whatever values these three components may have at different points in space, a force P always results therefrom.

In treating this equation the following three conditions at once enter into consideration:

$$\frac{dX}{dy}=\frac{dY}{dx}, \quad \frac{dY}{dz}=\frac{dZ}{dy}, \quad \frac{dZ}{dx}=\frac{dX}{dz}; \quad . \quad . \quad . \quad (17)$$

and the question arises whether or not the functions X, Y, Z fulfil them.

When the three equations of condition are satisfied, the expression on the right of (16) is the complete differential of a function of $x, y, z$, wherein these three variables may be regarded as mutually independent. The integration therefore may be at once effected, and an equation thereby obtained of the form

$$W=F(x, y, z)+\text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If we now conceive the point $p$ to move from a given initial point $x_0, y_0, z_0$ to a given terminal point $x_1, y_1, z_1$, the work done by the force during the passage will be represented by the difference

$$F(x_1, y_1, z_1)-F(x_0, y_0, z_0).$$

This work, therefore, is completely determined by the positions of the extreme points between which motion has occurred, and hence it follows that the work done by the force is always the same whatever path may have been followed in passing from the one position to the other.

When the three conditions (17) are not fulfilled, the integration cannot be performed with the same generality. The integration will be rendered possible, however, so soon as the path pursued by the moving point $p$ is known. If between the extreme points we conceive several curves to be drawn, and the point $p$ compelled to move thereon, we shall obtain a definite amount of work corresponding to each curve, but these quantities of work need not, as in the previous case, be equal to one another; in fact they will, in general, have different values.

# FIRST MEMOIR.

## ON THE MOVING FORCE OF HEAT AND THE LAWS OF HEAT WHICH MAY BE DEDUCED THEREFROM*.

THE steam-engine having furnished us with a means of converting heat into a motive power, and our thoughts being thereby led to regard a certain quantity of work as an equivalent for the amount of heat expended in its production, the idea of establishing theoretically some fixed relation between a quantity of heat and the quantity of work which it can possibly produce, from which relation conclusions regarding the nature of heat itself might be deduced, naturally presents itself. Already, indeed, have many successful efforts been made with this view; I believe, however, that they have not exhausted the subject, but that, on the contrary, it merits the continued attention of physicists; partly because weighty objections lie in the way of the conclusions already drawn, and partly because other conclusions, which might render efficient aid towards establishing and completing the theory of heat, remain either entirely unnoticed, or have not as yet found sufficiently distinct expression.

The most important investigation in connexion with this subject is that of S. Carnot †.

Later still, the ideas of this author have been represented analytically in a very able manner by Clapeyron ‡.

Carnot proves that whenever work is produced by heat and a

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* Communicated in the Academy of Berlin, Feb. 1850, published in Poggendorff's Annalen, March–April 1850, vol. lxxix. pp. 368, 500, and translated in the Philosophical Magazine, July 1851, vol. ii. pp. 1, 102.

† *Reflexions sur la puissance motrice du feu, et sur les machines propres à développer cette puissance*, par S. Carnot. Paris, 1824. I have not been able to procure a copy of this work; I know it solely through the writings of Clapeyron and Thomson, from which latter are taken the passages hereafter cited. [At a later date I had an opportunity of studying the work itself, and of thus confirming the views, regarding its contents, which I had previously formed from a perusal of the writings referred to.—1864.]

‡ Journal de l'Ecole Polytechnique, vol. xiv. 1834; Pogg. Ann. vol. lix.; and Taylor's Scientific Memoirs, Part III. p. 347.

permanent alteration of the body in action does not at the same time take place, a certain quantity of heat passes from a warm body to a cold one; for example, the vapour which is generated in the boiler of a steam-engine, and passes thence to the condenser where it is precipitated, carries heat from the fireplace to the condenser. This *transmission* Carnot regards as the change of heat corresponding to the work produced. He says expressly, that *no heat is lost* in the process, that the quantity remains unchanged; and he adds, "This is a fact which has never been disputed; it is first assumed without investigation, and then confirmed by various calorimetric experiments. To deny it, would be to reject the entire theory of heat, of which it forms the principal foundation."

I am not, however, sure that the assertion, that in the production of work a loss of heat never occurs, is sufficiently established by experiment. Perhaps the contrary might be asserted with greater justice; that although no such loss may have been directly proved, still other facts render it exceedingly probable that a loss occurs. If we assume that heat, like matter, cannot be lessened in quantity, we must also assume that it cannot be increased; but it is almost impossible to explain the ascension of temperature brought about by friction otherwise than by assuming an actual increase of heat. The careful experiments of Joule, who developed heat in various ways by the application of mechanical force, establish almost to a certainty, not only the possibility of increasing the quantity of heat, but also the fact that the newly-produced heat is proportional to the work expended in its production. It may be remarked further, that many facts have lately transpired which tend to overthrow the hypothesis that heat is itself a body, and to prove that it consists in a motion of the ultimate particles of bodies. If this be so, the general principles of mechanics may be applied to heat; this motion may be converted into work, the loss of *vis viva* in each particular case being proportional to the quantity of work produced.

These circumstances, of which Carnot was also well aware, and the importance of which he expressly admitted, pressingly demand a comparison between heat and work, to be undertaken with reference to the divergent assumption that the production of work is not only due to an alteration in the *distribution* of heat, but to an actual *consumption* thereof; and inversely, that by the expenditure of work heat may be *produced*.

In a recent memoir by Holtzmann*, it seemed at first as if the author intended to regard the subject from this latter point of view. He says (p. 7), "the effect of the heat which has been communicated to the gas is either an increase of temperature combined with an increase of elasticity, or a mechanical work, or a combination of both; a mechanical work being the equivalent for an increase of temperature. Heat can only be measured by its effects; and of the two effects mentioned, mechanical work is peculiarly applicable here, and shall therefore be chosen as a standard in the following investigation. I name a unit of heat, the quantity which, on being communicated to any gas, is able to produce the quantity of work *a*; or to speak more definitely, which is able to raise *a* kilogrammes to a height of one metre." Afterwards, at page 12, he determines the numerical value of the constant *a*, according to the method of Meyer†, and obtains a number which exactly corresponds to that obtained in a totally different manner by Joule. In carrying out the theory, however, that is, in developing the equations by means of which his conclusions are arrived at, he proceeds in a manner similar to Clapeyron, so that the assumption that the quantity of heat is constant is still tacitly retained.

The difference between the two ways of regarding the subject has been seized with much greater clearness by W. Thomson, who has applied the recent investigations of Regnault, on the tension and latent heat of steam, to the completing of the memoir of Carnot‡. Thomson mentions distinctly the obstacles which lie in the way of an unconditional acceptance of Carnot's theory, referring particularly to the investigations of Joule, and dwelling on one principal objection to which the theory is liable. If it be even granted that the production of work, where the body in action remains in the same state after the production as before,

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* *Ueber die Wärme und Elasticität der Gase und Dämpfe*, von C. Holtzmann. Manheim, 1845. Also Poggendorff's Annalen, vol. lxxii. *a*; and Taylor's Scientific Memoirs, Part XIV. p. 189

† *Ann. der Chem. und Pharm.*, vol. xlii. p. 239.

‡ Transactions of the Royal Society of Edinburgh, vol. xvi.

is in all cases accompanied by a transmission of heat from a warm body to a cold one, it does not follow that by every such transmission work is produced, for the heat may be carried over by simple conduction; and in all such cases, if the transmission alone were the true equivalent of the work performed, an absolute loss of mechanical force must take place in nature, which is hardly conceivable. Notwithstanding this, however, he arrives at the conclusion, that in the present state of science the principle assumed by Carnot is the most probable foundation for an investigation on the moving force of heat. He says, "If we forsake this principle, we stumble immediately on innumerable other difficulties, which, without further experimental investigations, and an entirely new erection of the theory of heat, are altogether insurmountable."

I believe, nevertheless, that we ought not to suffer ourselves to be daunted by these difficulties; but that, on the contrary, we must look steadfastly into this theory which calls heat a motion, as in this way alone can we arrive at the means of establishing it or refuting it. Besides this, I do not imagine that the difficulties are so great as Thomson considers them to be; for although a certain alteration in our way of regarding the subject is necessary, still I find that this is in no case contradicted by *proved facts.* It is not even requisite to cast the theory of Carnot overboard; a thing difficult to be resolved upon, inasmuch as experience to a certain extent has shown a surprising coincidence therewith. On a nearer view of the case, we find that the new theory is opposed, not to the real fundamental principle of Carnot, but to the addition "no heat is lost;" for it is quite possible that in the production of work both may take place at the same time; a certain portion of heat may be consumed, and a further portion transmitted from a warm body to a cold one; and both portions may stand in a certain definite relation to the quantity of work produced. This will be made plainer as we proceed; and it will be moreover shown, that the inferences to be drawn from both assumptions may not only exist together, but that they mutually support each other.

## I. *Deductions from the principle of the equivalence of heat and work.*

We shall forbear entering at present on the nature of the motion which may be supposed to exist within a body, and shall assume generally that a motion of the particles does exist, and that heat is the measure of their *vis viva*. Or yet more generally, we shall merely lay down one maxim which is founded on the above assumption :—

*In all cases where work is produced by heat, a quantity of heat proportional to the work done is consumed ; and inversely, by the expenditure of a like quantity of work, the same amount of heat may be produced.*

Before passing on to the mathematical treatment of this maxim, a few of its more immediate consequences may be noticed, which have an influence on our entire notions as to heat, and which are capable of being understood, without entering upon the more definite proofs by calculation which are introduced further on.

We often hear of the *total heat* of bodies, and of gases and vapours in particular, this term being meant to express the sum of the sensible and latent heat. It is assumed that this depends solely upon the present condition of the body under consideration; so that when all other physical properties thereof, its temperature, density, &c. are known, the total quantity of heat which the body contains may also be accurately determined*. According to the above maxim, however, this assumption cannot be admitted. If a body in a certain state, for instance a quantity of gas at the temperature $t_0$ and volume $v_0$, be subjected to various alterations as regards temperature and volume, and brought at the conclusion into its original state, the sum of its sensible and latent heats must, according to the above assumption, be the same as before; hence, if during any portion of the process heat be communicated from without, the quantity thus received must be given off again during some other portion of

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* [The above may perhaps be more clearly expressed thus :—By *total heat* was formerly meant the total quantity of heat which must be imparted to a body in order, from any given initial condition, to bring it to any other, and it was thereby implied that, the initial condition being known, the quantity of heat in question is completely determined by the present condition of the body, no matter in what manner the body may have been brought to this condition.—1864.]

the process. With every alteration of volume, however, a certain quantity of work is either produced or expended by the gas; for by its expansion an outward pressure is forced back, and on the other hand, compression can only be effected by the advance of an outward pressure. If, therefore, alteration of volume be among the changes which the gas has undergone, work must be produced and expended. It is not, however, necessary that at the conclusion, when the original condition of the gas is again established, the entire amount of work produced should be exactly equal to the amount expended, the one thus balancing the other; an excess of one or the other will be present if the compression has taken place at a lower or a higher temperature than the expansion, as shall be proved more strictly further on. This excess of produced or expended work must, according to the maxim, correspond to a proportionate excess of expended or produced heat, and hence the amount of heat refunded by the gas cannot be the same as that which it has received.

There is still another way of exhibiting this divergence of our maxim from the common assumption as to the *total heat* of bodies. When a gas at $t_0$ and $v_0$ is to be brought to the higher temperature $t_1$ and the greater volume $v_1$, the quantity of heat necessary to effect this would, according to the usual hypothesis, be quite independent of the manner in which it is communicated. By the above maxim, however, this quantity would be different according as the gas is first heated at the constant volume $v_0$ and then permitted to expand at the constant temperature $t_1$, or first expanded at the temperature $t_0$ and afterwards heated to $t_1$, or expansion and heating alternated in any other manner, or even effected simultaneously; for in all these cases the work done by the gas is different.

In like manner, when a quantity of water at the temperature $t_0$ is to be converted into vapour of the temperature $t_1$ and the volume $v_1$, it will make a difference in the amount of heat necessary if the water be heated first to $t_1$ and then suffered to evaporate, or if it be suffered to evaporate by $t_0$ and the vapour heated afterwards to $t_1$ and brought to the volume $v_1$; or finally, if the evaporation take place at any intermediate temperature.

From this and from the immediate consideration of the maxim, we can form a notion as to the light in which *latent* heat must be regarded. Referring again to the last example, we distinguish in the quantity of heat imparted to the water during the change the *sensible* heat and the *latent* heat. Only the former of these, however, must we regard as present in the produced steam; the latter is, not only as its name imports, hidden from our perceptions, but has actually *no existence*; during the alteration it has been *converted into work.*

We must introduce another distinction still as regards the heat expended. The work produced is of a twofold nature. In the first place, a certain quantity of work is necessary to overcome the mutual attraction of the particles, and to separate them to the distance which they occupy in a state of vapour. Secondly, the vapour during its development must, in order to procure room for itself, force back an outer pressure. We shall name the former of these *interior work,* and the latter *exterior work,* and shall distribute the latent heat also under the same two heads.

With regard to the *interior* work, it can make no difference whether the evaporation takes place at $t_0$ or at $t_1$, or at any other intermediate temperature, inasmuch as the attraction of the particles must be regarded as invariable*. The *exterior* work, on the contrary, is regulated by the pressure, and therefore by the temperature also. These remarks are not restricted to the example we have given, but are of general application; and when it was stated above, that the quantity of heat necessary to bring a body from one condition into another depended, not upon the state of the body at the beginning and the end alone, but upon the manner in which the alterations had been carried on throughout, this statement had reference to that portion only of the *latent heat* which corresponds to the *exterior* work. The remainder

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* It must not be objected here that the cohesion of the water at $t_1$ is less than at $t_0$, and hence requires a less amount of work to overcome it. The lessening of the cohesion implies a certain work performed by the warming of the water as water, and this must be added to that produced by evaporation. Hence it follows, at once, that only part of the quantity of heat which water receives from without when heated, is to be regarded as heat in the free state, the rest being consumed in diminishing cohesion. This view is in accordance with the circumstance that water has so much higher a specific heat than ice, and probably also than steam. [The views briefly referred to in this note will receive full consideration in a subsequent memoir.—1864.]

of the latent heat and the entire amount of sensible heat are independent of the manner in which the alteration is effected.

When the vapour of water at $t_1$ and $v_1$ is reconverted into water at $t_0$, the reverse occurs. Work is here *expended,* inasmuch as the particles again yield to their attraction, and the outer pressure once more advances. In this case, therefore, heat must be produced; and the *sensible heat* which here exhibits itself does not come from any retreat in which it was previously concealed, but is *newly produced.* It is not necessary that the heat developed by this reverse process should be equal to that consumed by the other; that portion which corresponds to the *exterior* work may be greater or less according to circumstances.

We shall now turn to the mathematical treatment of the subject, confining ourselves, however, to the consideration of permanent gases, and of vapours at their maximum density; as besides possessing the greatest interest, our superior knowledge of these recommends them as best suited to the calculus. It will, however, be easy to see how the maxim may be applied to other cases also.

Let a certain quantity of *permanent gas,* say a unit of weight, be given. To determine its present condition, three quantities are necessary; the pressure under which it exists, its volume, and its temperature. These quantities stand to each other in a relation of mutual dependence, which, by a union of the laws of Mariotte and Gay-Lussac*, is expressed in the following equation:

$$pv = \mathrm{R}(a+t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(I)}$$

where $p$, $v$ and $t$ express the pressure, volume and temperature of the gas in its present state, $a$ a constant equal for all gases, and R also a constant, which is fully expressed thus, $\frac{p_0 v_0}{a+t_0}$, where $p_0$, $v_0$, and $t_0$ express contemporaneous values of the above three quantities for any other condition of the gas. This last constant is therefore different for different gases, being inversely proportional to the specific weight of each.

It must be remarked, that Regnault has recently proved, by a series of very careful experiments, that this law is not in all

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* This shall be expressed in future briefly thus—the law of M. and G.; and the law of Mariotte alone thus—the law of M.

strictness correct. The deviations, however, for the permanent gases are very small, and exhibit themselves principally in those cases where the gas admits of condensation. From this it would seem to follow, that the more distant, as regards pressure and temperature, a gas is from its point of condensation, the more correct will be the law. Whilst its accuracy, therefore, for permanent gases in their common state is so great, that in most investigations it may be regarded as perfect, for every gas a limit may be imagined, up to which the law is also perfectly true; and in the following pages, where the permanent gases are treated as such, we shall assume the existence of this ideal condition*.

The value $\frac{1}{a}$ for atmospheric air is found by the experiments both of Magnus and Regnault to be $=0\cdot003665$, the temperature being expressed by the centesimal scale reckoned from the freezing-point upwards. The gases, however, as already mentioned, not following strictly the law of M. and G., we do not always obtain the same value for $\frac{1}{a}$ when the experiment is repeated under different circumstances. The number given above is true for the case when the air is taken at a temperature of 0° under the pressure of *one* atmosphere, heated to a temperature of 100°, and the increase of expansive force observed. If, however, the pressure be allowed to remain constant, and the increase of volume observed, we obtain the somewhat higher value 0·003670. Further, the values increase when the experiments are made under a pressure exceeding that of the atmosphere, and decrease when the pressure is less. It is clear from this that the exact value for the ideal condition, where the differences pointed out would of course disappear, cannot be ascertained. It is certain, however, that the number 0·003665 is not far from the truth, especially as it very nearly agrees with the value found for hydrogen, which, perhaps of all gases, approaches nearest the ideal condition. Retaining, therefore, the above value for $\frac{1}{a}$, we have

$$a=273.$$

One of the quantities in equation (I), for instance $p$, may be re-

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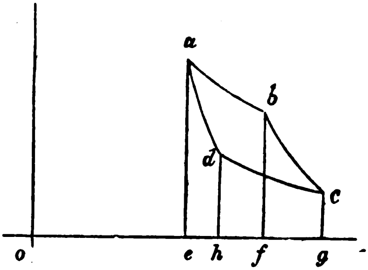
* [In my later memoirs the gases relative to which the existence of this ideal condition is assumed are termed *perfect* gases.—1864.]

garded as a function of the two others; the latter will then be the independent variables which determine the condition of the gas*.

We will now endeavour to ascertain in what manner the quantities which relate to the *amount of heat* depend upon $v$ and $t$.

When any body whatever changes its volume, the change is always accompanied by a mechanical work produced or expended. In most cases, however, it is impossible to determine this with accuracy, because an unknown *interior* work usually goes on at the same time with the *exterior*. To avoid this difficulty, Carnot adopted the ingenious contrivance before alluded to: he allowed the body to undergo various changes, and finally brought it into its primitive state; hence if by any of the changes *interior* work was produced, this was sure to be exactly nullified by some other change; and it was certain that the quantity of *exterior* work which remained over and above was the total quantity of work produced. Clapeyron has made this very evident by means of a diagram: we propose following his method with permanent gases in the first instance, introducing, however, some slight modifications rendered necessary by our maxim.

Fig. 1.



In the annexed figure let $oe$ represent the volume, and $ea$ the pressure of the unit-weight of gas when the temperature is $t$; let us suppose the gas to be contained in an expansible bag, with which, however, no exchange of heat is possible. If the gas be permitted to expand, no new heat

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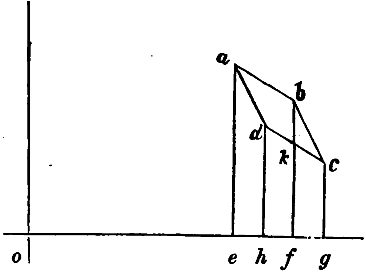
* [Clapeyron in his researches generally selected $v$ and $p$ for his two independent variables—a choice which accords best with the graphic representation, about to be described, wherein $v$ and $p$ constitute the coordinates. I have preferred, however, to consider $v$ and $t$ as the independent variables, and to regard $p$ as a function thereof; since in the theory of heat the temperature $t$ is especially important, and at the same time very suitable for determination by direct measurements, accordingly it is ordinarily regarded as a previously known magnitude upon which depend the several other magnitudes which there enter into consideration. For the sake of uniformity I have everywhere abided by this choice of independent variables; it need scarcely be remarked, however, that occasionally the equations thus established would assume a somewhat simpler form, if instead of $v$ and $t$, $v$ and $p$ or $t$ and $p$ were introduced therein as independent variables.—1864.]

being added, the temperature will fall. To avoid this, let the gas during the expansion be brought into contact with a body A of the temperature *t*, from which it shall receive heat sufficient to preserve it constant at the same temperature. While this expansion by constant temperature proceeds, the pressure decreases according to the law of M., and may be represented by the ordinate of a curve *a b*, which is a portion of an equilateral hyperbola. When the gas has increased in volume from *o e* to *o f*, let the body A be taken away, and the expansion allowed to proceed still further without the addition of heat; the temperature will now sink, and the pressure consequently grow less as before. Let the law according to which this proceeds be represented by the curve *b c*. When the volume of the gas has increased from *o f* to *o g*, and its temperature is lowered from *t* to $\tau$, let a pressure be commenced to bring it back to its original condition. Were the gas left to itself, its temperature would now rise; this, however, must be avoided by bringing it into contact with the body B at the temperature $\tau$, to which any excess of heat will be immediately imparted, the gas being thus preserved constantly at $\tau$. Let the compression continue till the volume has receded to *h*, it being so arranged that the decrease of volume indicated by the remaining portion *h e* shall be just sufficient to raise the gas from $\tau$ to *t*, if during this decrease it gives out no heat. By the first compression the pressure increases according to the law of M., and may be represented by a portion *c d* of another equilateral hyperbola. At the end the increase is quicker, and may be represented by the curve *d a*. This curve must terminate exactly in *a*; for as the volume and temperature at the end of the operation have again attained their original values, this must also be the case with the pressure, which is a function of both. The gas will therefore be found in precisely the same condition as at the commencement.

In seeking to determine the amount of work performed by these alterations, it will be necessary, for the reasons before assigned, to direct our attention to the *exterior* work alone. During the expansion, the gas *produces* a work expressed by the integral of the product of the differential of the volume into the corresponding pressure, which integral is represented geometrically by the quadrilaterals *e a b f*, and *f b c g*. During the compression, however, work will be *expended,* which is represented by the quadrilaterals $g\,c\,d\,h$ and $h\,d\,a\,e$. The excess of the former work above the latter is to be regarded as the entire work produced by the alterations, and this is represented by the quadrilateral $a\,b\,c\,d$.

If the foregoing process be reversed, we obtain at the conclusion the same quantity $abcd$ as the excess of the work *expended* over that *produced.*

Fig. 2.



In applying the foregoing considerations analytically, we will assume that the various alterations which the gas has undergone have been *infinitely small.* We can then consider the curves before mentioned to be straight lines, as shown in the accompanying figure. In determining its superficial content, the quadrilateral $a\,b\,c\,d$ may be regarded as a parallelogram, for the error in this case can only amount to a differential of the *third* order, while the area itself is a differential of the *second* order. The latter may therefore be expressed by the product $ef\,.\,b\,k$, where $k$ marks the point at which the ordinate $bf$ cuts the lower side of the parallelogram. The quantity $b\,k$ is the increase of pressure due to raising the temperature of the gas, at the constant volume $of$, from $\tau$ to $t$, that is to say, due to the differential $t-\tau=dt$. This quantity can be expressed in terms of $v$ and $t$ by means of equation (I.), as follows:

$$dp=\frac{\mathrm{R}dt}{v}.$$

If the increase of volume $ef$ be denoted by $d\,v$, we obtain the area of the quadrilateral, and with it

$$\textit{The work produced}=\frac{\mathrm{R}\,dv\,dt}{v}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

We must now determine the quantity of heat consumed during those alterations. Let the amount of heat which must be imparted during the transition of the gas in a definite manner from any given state to another, in which its volume is $v$ and its temperature $t$, be called Q; and let the changes of volume occurring in the process above described, which are now to be regarded separately, be denoted as follows: *ef* by $dv$, *hg* by $d'v$, *eh* by $\delta v$, and *fg* by $\delta' v$. During an expansion from the volume $oe = v$ to $of = v + dv$, at the constant temperature $t$, the gas must receive the quantity of heat expressed by

$$\left(\frac{dQ}{dv}\right)dv^{*};$$

and in accordance with this, during an expansion from $oh = v + \delta v$ to $og = v + \delta v + d'v$ at the temperature $t - dt$, the quantity

$$\left[\frac{dQ}{dv} + \frac{d}{dv}\left(\frac{dQ}{dv}\right)\delta v - \frac{d}{dt}\left(\frac{dQ}{dv}\right)dt\right]d'v.$$

In our case, however, instead of an expansion, a compression has taken place; hence this last expression must be introduced with the negative sign. During the expansion from *of* to *og*, and the compression from *oh* to *oe*, heat has been neither received nor given away; the amount of heat which the gas has

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* [In this memoir I have for the sake of greater clearness employed Euler's notation for partial differential coefficients in which the fractions which represent the latter are placed between brackets. This precaution was perhaps unnecessary, since in most cases, as was observed in the Introduction, no misconception can arise even when the brackets are omitted; nevertheless in the present reprint of the memoir the original notation has been retained. In accordance with the equation (3*a*) of the Introduction the complete differential equation of Q would here be

$$dQ = \left(\frac{dQ}{dt}\right)dt + \left(\frac{dQ}{dv}\right)dv.$$

For a given quantity of gas, and indeed for every other body whose condition is defined by its temperature and volume, the two partial differential coefficients $\left(\frac{dQ}{dt}\right)$, $\left(\frac{dQ}{dv}\right)$ must be regarded as perfectly determinate functions of $t$ and $v$, for the quantities of heat are perfectly defined which a body must receive when, from a given condition, its temperature is raised under constant volume, or its volume is increased without any alteration of temperature, a counter-pressure corresponding to its elastic force being thereby overcome. Whether Q itself, however, is also a magnitude which can be represented as a function of $t$ and $v$, in which these variables are independent of each other, or whether a further relation between these variables must be given in order to determine Q, depends upon the circumstance mentioned in the Introduction; viz., whether or not the condition (4), which in the present notation is thus written,

$$\frac{d}{dv}\left(\frac{dQ}{dt}\right) = \frac{d}{dt}\left(\frac{dQ}{dv}\right),$$

is satisfied; the object of the following development is to decide this question.—1864.]

received over and above that which it has communicated, or, in other words, *the quantity of heat consumed,* will therefore be

$$\left(\frac{dQ}{dv}\right)dv-\left[\left(\frac{dQ}{dv}\right)+\frac{d}{dv}\left(\frac{dQ}{dv}\right)\delta v-\frac{d}{dt}\left(\frac{dQ}{dv}\right)dt\right]d'v. \quad . \quad . \quad (2)$$

The quantities $\delta v$ and $d'v$ must now be eliminated; a consideration of the figure furnishes us with the following equation:

$$dv+\delta' v=\delta v+d'v.$$

During its compression from *o h* to *o e,* consequently during its expansion under the same circumstances from *o e* to *o h,* and during the expansion from *o f* to *o g,* both of which cause a decrease of temperature *dt,* the gas neither receives nor communicates heat: from this we derive the equations

$$\left(\frac{dQ}{dv}\right)\delta v-\left(\frac{dQ}{dt}\right)dt=0,$$

$$\left[\left(\frac{dQ}{dv}\right)+\frac{d}{dv}\left(\frac{dQ}{dv}\right)dv\right]\delta' v-\left[\left(\frac{dQ}{dt}\right)+\frac{d}{dv}\left(\frac{dQ}{dt}\right)dv\right]dt=0.$$

From these three equations and equation (2) the quantities $d'v$, $\delta v$, and $\delta' v$ may be eliminated; neglecting during the process all differentials of a higher order than the second, we obtain

$$\textit{The heat expended}=\left[\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)\right]dv\,dt^{*}. \quad . \quad (3)$$

Turning now to our maxim, which asserts that the production of a certain quantity of work necessitates the expenditure of a proportionate amount of heat, we may express this in the form of an equation, thus:

$$\frac{\text{The heat expended}}{\text{The work produced}}=A, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

*where* A *denotes a constant which expresses the equivalent of heat for the unit of work*†. The expressions (1) and (3) being introduced into this equation, we obtain

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* [With reference to the deduction of the equation (3), see also the *Appendix* A. at the end of the present memoir.]

† [This magnitude, which will often present itself in the sequel, may, in accordance with a modern custom, be briefly termed the *calorific equivalent of work.*—1864.]

$$\frac{\left[\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)\right]dv\,dt}{\frac{\mathrm{R}.dv\,dt}{v}}=\mathrm{A},$$

or

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)=\frac{\mathrm{A.R}}{v}. \quad . \quad . \quad . \quad . \quad \text{(II)}$$

This equation may be regarded as the analytical expression of the above maxim applicable to the case of permanent gases*. It shows that Q cannot be a function of $v$ and $t$ as long as the two latter are independent of each other. For otherwise, according to the known principle of the differential calculus, that when a function of two variables is differentiated according to both, the order in which this takes place is a matter of indifference, the right side of the equation must be equal 0.

The equation can be transformed to a *complete* differential equation *of the first order*† and of the following form:

$$dQ=d\mathrm{U}+\mathrm{A.R}\frac{a+t}{v}dv, \quad . \quad . \quad . \quad . \quad \text{(II}\,a\text{)}$$

where U denotes an arbitrary function of $v$ and $t$‡. This differ-

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* [The equation (II) may obviously be generalized so as to apply not only to a gas, but to any other body whatever whose condition is determined by its temperature and volume, and upon which the sole external forces which act consist of pressures normal to the surface, of equal intensity at all points of the latter, and differing so slightly from the body's force of expansion as to admit, in calculation, of being considered equal thereto. This generalization is effected by merely substituting for $\frac{\mathrm{R}}{v}$ the differential coefficient $\left(\frac{dp}{dt}\right)$; which latter, in the special case of gases, is equal to $\frac{\mathrm{R}}{v}$. The equation then becomes

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)=\mathrm{A}\left(\frac{dp}{dt}\right),$$

in which form it frequently presents itself in subsequent memoirs.—1864.]

† [By an oversight the *order* of this equation was not stated in the original edition.—1864.]

‡ [With respect to the manner in which, by integration, the equation (II $a$) may be deduced from the equation (II), see *Appendix* B to this Memoir.

That the differential equation (II $a$) of the first order actually corresponds to the differential equation (II) of the second order may moreover be easily shown, conversely, by differentiating (II $a$), and thence deducing (II). In fact, if for $d$U we write the complete expression

$$\left(\frac{d\mathrm{U}}{dt}\right)dt+\left(\frac{d\mathrm{U}}{dv}\right)dv,$$

ential equation is of course unintegrable until we find a second condition between the variables, by means of which $t$ may be expressed as a function of $v$. This is due, however, to the last member alone, and this it is which corresponds to the *exterior* work effected by the alteration; for the differential of this work is $pdv$, which, when $p$ is eliminated by means of (I), becomes

$$\frac{R(a+t)}{v}\,dv.$$

It follows, therefore, in the first place, from (II $a$), that the entire quantity of heat, Q, absorbed by the gas during a change of volume and temperature may be decomposed into two portions. One of these, U, which comprises the *sensible* heat and the heat necessary for *interior* work, if such be present, fulfils the usual assumption, it is a function of $v$ and $t$, and is therefore determined by the state of the gas at the beginning and at the end of the alteration; while the other portion, which comprises the heat expended on *exterior* work, depends, not only upon the state

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and similarly for $dQ$ the complete expression

$$\left(\frac{dQ}{dt}\right)dt+\left(\frac{dQ}{dv}\right)dv,$$

the equation (II. $a$.) becomes transformed to

$$\left(\frac{dQ}{dt}\right)dt+\left(\frac{dQ}{dv}\right)dv=\left(\frac{dU}{dt}\right)dt+\left[\left(\frac{dU}{dv}\right)+A.R\frac{a+t}{v}\right]dv,$$

whence, by comparison, the following equalities may be deduced:

$$\left(\frac{dQ}{dt}\right)=\left(\frac{dU}{dt}\right),$$

$$\left(\frac{dQ}{dv}\right)=\left(\frac{dU}{dv}\right)+A.R\,\frac{a+t}{v}.$$

On differentiating the first of these expressions according to $v$, and the second according to $t$, it is to be noticed that the magnitude U being, by a previous statement, a function of $t$ and $v$, the condition

$$\frac{d}{dv}\left(\frac{dU}{dt}\right)=\frac{d}{dt}\left(\frac{dU}{dv}\right)$$

is satisfied. Each of the quantities involved in the last equation, therefore, may be denoted by $\frac{d^2U}{dt\,dv}$; so that

$$\frac{d}{dv}\left(\frac{dQ}{dt}\right)=\frac{d^2U}{dt\,dv}$$

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right)=\frac{d^2U}{dt\,dv}+\frac{A.R}{v}.$$

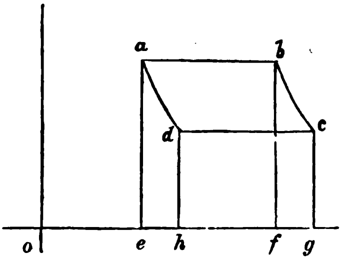
But the first of these two equations being subtracted from the second, leads at once to the equation (II).—1864.]

of the gas at these two limits, but also upon the manner in which the alterations have been effected throughout. It is shown above that the same conclusion flows directly from the maxim itself.

Before attempting to render this equation suitable for the deduction of further inferences, we will develope the analytical expression of the maxim applicable to *vapours at their maximum density.*

In this case we are not at liberty to assume the correctness of the law of M. and G., and must therefore confine ourselves to the maxim alone. To obtain an equation from this, we will again pursue the course indicated by Carnot, and reduced to a diagram by Clapeyron. Let a vessel impervious to heat be partially filled with water, leaving a space above for steam of the maximum density corresponding to the temperature *t*. Let the volume of both together be represented in the annexed figure by the abscissa *o e*, and the pressure of the steam by the ordinate *ea*. Let the vessel be now supposed to expand, while both the liquid and steam are kept in contact with a body A of the constant temperature *t*. As the space increases, more liquid is evaporated, the necessary amount of latent heat being supplied by the body A; so that the temperature, and consequently the pressure of the steam, may remain unchanged. When the entire volume is increased in this manner from *o e* to *o f*, an exterior work is produced which is represented by the rectangle *ea bf*. Let the body A be now taken away, and let the vessel continue to expand without heat being either given or received. Partly by the expansion of the steam already present, and partly by the formation of new steam, the temperature will be lowered and the pressure become less. Let the expansion be suffered to continue until the temperature passes from *t* to $\tau$, and let *o g* represent the volume at this temperature. If the decrease of pressure during this expansion be represented by the curve *b c*, the exterior work produced by it will be represented by *f b c g*.

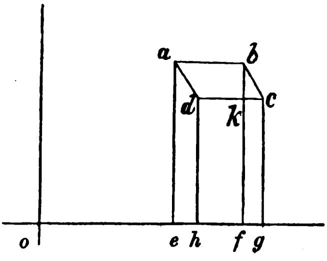
Fig. 3.



Let the vessel be now pressed together so as to bring the liquid and vapour to their original volume *o e*, and during a portion of the process let the vessel be in contact with a body, B, of the temperature $\tau$, to which any excess of heat shall be immediately imparted, and the temperature of the liquid and vapour kept constant at $\tau$. During the other portion of the process, let the body B be withdrawn so that the temperature may rise; let the first compression continue till the volume has been reduced to $o\,h$, it being so arranged that the remaining space $h\,e$ shall be just sufficient to raise the temperature from $\tau$ to $t$. During the first decrease of volume the pressure remains constant at $g\,c$, and the quantity of exterior work expended is equal to the rectangle $g\,c\,d\,h$. During the last decrease of volume the pressure increases, and may be represented by the curve $d\,a$, which must terminate exactly in the point $a$, as the original temperature $t$ must again correspond to the original pressure $e\,a$. The exterior work expended in this case is $=h\,d\,a\,e$.

At the end of the operation both fluid and vapour are in the same state as at the commencement, so that the excess of the *exterior* work produced over the amount expended expresses the *total amount* of work accomplished. This excess is represented by the quadrilateral $a\,b\,c\,d$, the content of which must therefore be compared with the *heat expended* at the same time.

Fig. 4.



For this purpose let it be assumed, as before, that the described alterations are infinitely small, and under this view let the process be represented by the annexed figure, in which the curves $a\,d$ and $b\,c$ shown in fig. 3 have passed into straight lines. With regard to the area of the quadrilateral $a\,b\,c\,d$, it may be again regarded as a parallelogram, the area of which is expressed by the product $ef.bk$. Now if, when the temperature is $t$, the pressure of the vapour at its maximum tension be equal to $p$, and the difference of temperature $t-\tau$ be expressed by $d\,t$, we have

$$bk=\frac{dp}{dt}\,dt\,*\,;$$

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* [In the equations corresponding to saturated vapour the differential coefficient $\frac{dp}{dt}$ is written without brackets, since the pressure is now no longer a function of the temperature and volume, but of the temperature solely.—1864.]

$ef$ is the increase of volume caused by the passing of a certain quantity of liquid represented by $dm$ into a state of vapour. Let the volume of the unit of steam at its maximum density for the temperature $t$ be called $s$, and the volume of the same quantity of liquid at the temperature $t$ be called $\sigma$; then is

$$ef = (s-\sigma)\, dm;$$

and hence the area of the rectangle, or

$$\textit{The work produced} = (s-\sigma)\frac{dp}{dt}\, dm\, dt. \quad . \quad . \quad . \quad (5.)$$

To express the amount of heat, we will introduce the following notation:—Let the quantity of heat rendered latent by the passage of a unit weight of liquid at the temperature $t$, and under a corresponding pressure into a state of vapour, be called $r$, and the specific heat of the liquid $c$; both of these quantities, as also the foregoing $s$, $\sigma$, and $\frac{dp}{dt}$, being functions of $t$. Finally, let the quantity of heat which must be communicated to a unit weight of vapour of water to raise it from the temperature $t$ to $t+dt$ (the vapour being preserved by pressure at the maximum density due to the latter temperature without precipitation) be called $hdt$, where $h$ likewise represents a function of $t$. We shall reserve the question as to whether its value is positive or negative for future consideration*.

If $\mu$ be the mass of liquid originally present in the vessel, and $m$ the mass of the vapour; further, $d\,m$ be the mass evaporated during the expansion from $o\,e$ to $o\,f$, and $d'm$ the mass precipitated by the compression from $o\,g$ to $o\,h$, we obtain in the first case the quantity

$$rdm$$

of latent heat which has been extracted from the body A; and in the second case, the quantity

$$\left(r-\frac{dr}{dt}dt\right)d'm$$

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* [The magnitude $h$ here introduced is precisely *the specific heat of the vapour at its maximun density*, or, in other words, *the specific heat of the saturated vapour*, which may be regarded as a peculiar kind of specific heat just as well as is the specific heat at a constant volume or the specific heat under constant pressure.—1864.]

of sensible heat which has been imparted to the body B. By the other expansion and compression heat is neither gained nor lost; hence at the end of the process we have

$$\textit{The heat expended} = rdm - \left(r - \frac{dr}{dt}dt\right)d'm. \quad . \quad . \quad (6)$$

In this equation the differential $d'm$ must be expressed through $dm$ and $dt$; the conditions under which the second expansion and the second compression have been carried out enable us to do this. Let the mass of vapour precipitated by the compression from *oh* to *oe*, and which therefore would develope itself by expansion from *oe* to *oh*, be represented by $\delta m$, and the mass developed by the expansion from *of* to *og* by $\delta' m$; then, as at the conclusion of the experiment the original mass of fluid and of vapour must be present, we obtain in the first place the equation

$$dm + \delta' m = d'm + \delta m.$$

Further, for the expansion from *oe* to *oh*, as the temperature of the liquid mass $\mu$ and the mass of vapour $m$ must thereby be lessened, the quantity $dt$ without heat escaping, we obtain the equation

$$r\delta m - \mu . cdt - m . hdt = 0;$$

and in like manner for the expansion from *of* to *og*, as here we have only to set $\mu - dm$ and $m + dm$ in the place of $\mu$ and $m$, and $\delta' m$ in the place of $\delta m$, we obtain

$$r\delta' m - (\mu - dm) cdt - (m + dm) hdt = 0. *$$

If from these three equations and equation (6.) the quantities $d'm$, $\delta m$, and $\delta' m$ be eliminated, and all differentials of a higher

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* [With respect to these two equations, whose use is to determine the relation which exists between $\delta m$ or $\delta' m$ and $dt$, a remark may be made of a similar kind to those contained in the *Appendix* A, which relate to the deduction of the equation (3). To be strictly accurate up to differentials of the second order, the expressions for $\delta m$ or $\delta' m$ ought to contain another term with the factor $dt^2$, just as do the expressions for $\delta v$ and $\delta' v$ in the equations ($m$) and ($n$) of *Appendix* A. Since this term would be the same in both equations, however, it would again disappear from the equation

$$d'm = dm + \delta' m - \delta m,$$

which determines $d'm$, and thus be wholly without influence on our result. Consequently it is unnecessary here to take this term into further consideration.—1864.]

order than the second be neglected, we have

$$\textit{The heat expended} = \left(\frac{dr}{dt} + c - h\right) dm\, dt. \quad . \quad . \quad . \quad (7)$$

The formulæ (7) and (5) must now be united, as in the case of permanent gases, thus:

$$\frac{\left(\frac{dr}{dt} + c - h\right) dm\, dt}{(s - \sigma)\frac{dp}{dm} dm\, dt} = \mathrm{A};$$

and hence we obtain, as the analytical expression of the maxim, applicable to vapours at their maximum density, the equation

$$\frac{dr}{dt} + c - h = \mathrm{A}(s - \sigma)\frac{dp}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{III})$$

If, instead of the above maxim, the assumption that the quantity of heat is *constant* be retained, then, according to (7), instead of equation (III) we must set

$$\frac{dr}{dt} + c - h = 0.^{*} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

And this equation, although not exactly in the same form, has been virtually used heretofore to determine the value of the quantity $h$. As long as the law of Watt is regarded as true, that the sum of the latent and sensible heat of a quantity of steam at its maximum density is the same for all temperatures, and consequently that

$$\frac{dr}{dt} + c = 0,^{\dagger}$$

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[*] [As before remarked, it would follow from this assumption that when a body suffers a series of changes such that it thereby returns finally to its initial state, the quantity of heat which it receives from without during one portion of these changes must be equal to the quantity which it gives off during the remaining changes. Now the difference between the received and imparted quantities of heat in the previously described cycle of infinitely small changes is, according to equation (7), represented by

$$\left(\frac{dr}{dt} + c - h\right) dm\, dt;$$

and this expression, equated to zero, leads at once to the equation

$$h = \frac{dr}{dt} + c,$$

which is another form of the equation (8).—1864.]

[†] [The law of Watt mentioned in the text, and formerly accepted as true,

it must be inferred that for this liquid $h$ also is equal 0; this, indeed, has often been asserted, by saying that when a quantity of vapour at its maximum density is compressed in a vessel impervious to heat, or suffered to expand in the same, it will remain at its maximum density. As, however, Regnault[*] has corrected the law of Watt so that we can set with tolerable accuracy

$$\frac{dr}{dt}+c=0·305,$$[†]

the equation (8) gives for $h$ also the value 0·305. It follows from this, that a portion of the steam in the impermeable vessel must be precipitated by compression, and that it cannot retain its maximum density after it has been suffered to expand, as its temperature does not decrease in a ratio corresponding to the decrease of density.

Quite otherwise is it if, instead of equation (8), we make use of equation (III). The expression on the right-hand side is from its nature always positive, and from this follows in the first place that $h$ is less than 0·305. It will be afterwards shown that the value of the said expression is so great that $h$ becomes even *negative*[‡]. Hence we must conclude that the above quan-

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asserts that the sum of the two quantities of heat required to raise the unit of weight of water from 0° to the temperature $t$, and then to convert it into vapour at this temperature, is independent of this temperature $t$. Accordingly we should have

$$r+\int_0^t c\,dt=\text{const.},$$

an equation which, by differentiation, leads to the equation

$$\frac{dr}{dt}+c=0,$$

given in the text.—1864.]

[*] *Mém. de l'Acad.* vol. xxi., 9th and 10th Memoirs.

[†] [Regnault has found that the sum of free and latent heat is not constant, as by the law of Watt it should be, but that with increasing temperature it increases in a manner approximately expressed by the equation

$$r+\int_0^t c\,dt=606·5+0·305\,t,$$

from which the equation

$$\frac{dr}{dt}+c=0·305$$

follows by differentiation.—1864.]

[‡] [In order to decide whether the equation

$$h=\frac{dr}{dt}+c-A(s-\sigma)\frac{dp}{dt},$$

tity of vapour will be partially precipitated, not by the *compression*, but by the *expansion*; when compressed, its temperature rises in a quicker ratio than that corresponding to the increase of density, so that it does not continue at its maximum density.

The result is indeed directly opposed to the notions generally entertained on this subject; I believe, however, that no experiment can be found which contradicts it. On the contrary, it harmonizes with the observations of Pambour better than the common notion. Pambour found* that the steam issuing from a locomotive after a journey always possesses the temperature for which the tension observed at the same time is a maximum. From this it follows that $h$ is either 0, as was then supposed, because this agreed with the law of Watt, which was considered correct at the time, or that $h$ is *negative*. If $h$ were positive, then the temperature of the issuing steam must have been too high in comparison with its tension, and this could not have escaped Pambour. If, on the contrary, in agreement with the above, $h$ be negative, too low a temperature cannot occur, but a portion of the vapour will be converted into water so as to preserve the remainder at its proper temperature. This portion is not necessarily large, as a small quantity of vapour imparts a comparatively large quantity of heat by its precipitation; the water thus formed is probably carried forward mechanically by the steam, and might remain unregarded; the more so, as, even if observed, it might have been imagined to proceed from the boiler†.

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deduced from (III), gives a positive or a negative value of $h$, the numerical value of A must be known; and since nothing has been said in the previous part of the memoir with respect to the numerical determination of this constant, I have not here entered into the determination of the magnitude $h$, but have referred the question to the sequel. In the second part of the memoir, an expression for the product $A(s-\sigma)\frac{dp}{dt}$ will be given which involves known magnitudes solely, and whose substitution in the foregoing equation leads to another, from which, not only the sign, but also the magnitude of $h$, as a function of the temperature, can be at once determined.—1864.]

* *Traité des locomotives*, 2nd edit., and *Théorie des machines à vapeur*, 2nd edit.

† [The process to which the observation of Pambour refers is too complicated to furnish a convenient and accurate comparison with the theoretical results obtained above. Accordingly the observation in question is cited, not with a view of supplying a reliable verification of those theoretical results, but

So far the consequences have been deduced from the above maxim alone, without any new assumption whatever being made. Nevertheless, by availing ourselves of a very natural incidental assumption, the equation for permanent gases (II $a$) may be rendered considerably more productive. Gases exhibit in their deportment, particularly as regards the relations of volume, temperature, and pressure expressed by the laws of M. and G., so much regularity as to lead us to the notion that the mutual attraction of the particles which takes place in solid and liquid bodies is in their case annulled; so that while with solids and liquids the heat necessary to effect an expansion has to contend with both an interior and an exterior resistance, the latter only is effective in the case of gases. If this be the case, then, by the expansion of a gas, only so much heat can be rendered *latent* as is necessary to *exterior* work. Further, there is no reason to suppose that a gas, after it has expanded at a constant temperature, contains more sensible heat than before. If this also be admitted, we obtain the proposition, *when a permanent gas expands at a constant temperature, it absorbs only as much heat as is necessary to the exterior work produced by the expansion*—a proposition which is probably true for each gas in the same degree as the law of M. and G is true for that gas*.

From this immediately follows

$$\left(\frac{dQ}{dv}\right)=A.R\frac{a+t}{v}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

for, as already mentioned, $R\frac{a+t}{v}dv$ represents the quantity of

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merely to show that it accords better with the latter than with the views previously entertained.—1864.]

* [Several authors before me regarded the heat which disappears during the expansion of a gas as simply equivalent to the work done in overcoming pressure. As far as I know, however, I was the first to enunciate the theorem in its complete form; according to which it is asserted that in general *exterior* and *interior* work are both simultaneously done when a body expands, but that in the special case of a permanent gas the law of M. and G. sanctions the assumption of an infinitesimal amount of *interior* work; further, that the degree of accuracy to which this assumption can lay claim, when applied to a certain gas, is the same as that which would attend the application thereto of the law of M. and G.; and, finally, that the theorem involves the additional assumption that the heat actually present in the gas is independent of its density.—1864.]

exterior work produced by the expansion $dv$. According to this, the function U, which appears in equation (II $a$), cannot contain $v$, and hence the equation changes to

$$dQ = c\,dt + AR\frac{a+t}{v}\,dv, \quad . \quad . \quad . \quad . \quad . \qquad \text{(II } b\text{)}$$

wherein $c$ can only be a function of $t$*; and it is even probable that the quantity $c$, which denotes the specific heat of the gas at a constant volume, is itself a constant.

To apply this equation to particular cases, the peculiar conditions of each case must be brought into connexion therewith, so as to render it integrable†. We shall here introduce only a few simple examples, which possess either an intrinsic interest, or obtain an interest by comparison with other results connected with this subject.

In the first place, if in equation (II $b$) we put, successively, $v=$ const. and $p=$ const., we shall obtain the specific heat of the gas at a constant volume, and its specific heat under a constant pressure. In the former case $dv=0$, and (II $b$) becomes

$$\frac{dQ}{dt} = c. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

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* [In fact, from the equation (II $a$), written in the form

$$dQ = \left(\frac{dU}{dt}\right) dt + \left[\left(\frac{dU}{dv}\right) + AR\,\frac{a+t}{v}\right] dv,$$

it follows immediately that

$$\left(\frac{dQ}{dv}\right) = \left(\frac{dU}{dv}\right) + AR\,\frac{a+t}{v}.$$

Now if, on the other hand, the equation (9), viz.

$$\left(\frac{dQ}{dv}\right) = AR\,\frac{a+t}{v},$$

be true, a necessary consequence of the coexistence of it and the previous equation is that

$$\left(\frac{dU}{dv}\right) = 0;$$

accordingly the function U, for perfect gases, must be independent of $v$. Substituting the symbol $c$ for the differential coefficient $\left(\frac{dU}{dt}\right)$, which of course shares with U the property of being independent of $v$, the equation (II $b$) is at once obtained.—1864.]

† [The equation (II $b$) belongs, in fact, to the class of equations, described in the Introduction, which only admit of being integrated on assuming a second equation to exist between the variables, whereby the sequence of the changes becomes determined.—1864.]

In the latter case, from the condition $p=$ const., we obtain with help of equation (I),

$$dv=\frac{\mathrm{R}dt}{p},$$

or

$$\frac{dv}{v}=\frac{dt}{a+t};$$

which by substitution in (II *b*), the specific heat under a constant pressure being denoted by $c'$, gives us

$$\frac{d\mathrm{Q}}{dt}=c'=c+\mathrm{AR}\,^{*} \quad . \quad . \quad . \quad . \quad . \quad (10\,a)$$

From this it may be inferred *that the difference of both specific heats for each gas is a constant quantity* AR†. But this quantity also expresses a simple relation for different gases. The complete expression for R is $\frac{p_0 v_0}{a+t_0}$, where $p_0$, $v_0$, and $t_0$ denote any

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* [It will be easily understood why the fraction $\frac{d\mathrm{Q}}{dt}$, in the equations (10) and (10 *a*), is written without the brackets which ordinarily enclose the fractions $\frac{d\mathrm{Q}}{dt}$ and $\frac{d\mathrm{Q}}{dv}$. For when, from the commencement, a condition is introduced which implies the constancy of $v$ or of $p$, the sequence of changes through which the gas can pass is thereby so far fixed, that the increment of Q is completely determined by the increment of one of the variables $t$. In such cases, therefore, the fraction $\frac{d\mathrm{Q}}{dt}$ does not represent the partial differential coefficient of a magnitude whose value depends upon those of two independent variables, but corresponds to the fraction $\frac{dz}{dx}$, treated at page 4 of the Introduction, which stands on the left of the differential equation wherein $y$ was considered as a function of $x$. In fact, it is obvious that, in the equations (10) and (10 *a*), the symbol $\frac{d\mathrm{Q}}{dt}$ has two different meanings, arising from the distinct conditions to which the equations have reference.—1864.]

† [The difference between the two specific heats $c$ and $c'$ being constant, the conclusion above arrived at, with reference to the specific heat at a constant volume, also holds for the specific heat under constant pressure, so that the latter is likewise independent of the density, and probably also of the temperature of the gas. At the time my memoir appeared, this conclusion was objected to on the ground of its being at variance with some of the observations of Suermann, and of De la Roche and Bérard, which at that time were pretty generally accepted as trustworthy; since then, however, it has been verified by the experiments which, in 1853, were published by Regnault.—1864.]

three contemporaneous values of $p$, $v$, and $t$ for a unit of weight of the gas in question; and from this it follows, as already mentioned in establishing equation (I), that R is inversely proportional to the specific gravity of the gas; the same must be true of the difference $c'-c=\mathrm{AR}$, as A is the same for all gases.

If it be desired to calculate the specific heat of the gas, not relative to the unit of *weight*, but (in accordance with the method more in use) to the unit of *volume*, say at the temperature $t_0$ and the pressure $p_0$, it is only necessary to divide $c$ and $c'$ by $v_0$. Let these quotients be expressed by $\gamma$ and $\gamma'$, and we obtain

$$\gamma'-\gamma=\frac{\mathrm{A}.\mathrm{R}}{v_0}=\mathrm{A}\frac{p_0}{a+t_0}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In this last expression nothing appears which is dependent on the peculiar nature of the gas; *the difference of the specific heats relative to the unit of volume is therefore the same for all gases.* This proposition has been deduced by Clapeyron from the theory of Carnot; but the result, that the difference $c'-c$ is constant, is there not arrived at; the expression found for it having still the form of a function of the temperature.

Dividing both sides of equation (11) by $\gamma$, we obtain

$$k-1=\frac{\mathrm{A}}{\gamma}\cdot\frac{p_0}{a+t_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

wherein, for brevity, $k$ is put in the place of $\frac{\gamma'}{\gamma}$. This is equal to the quotient $\frac{c'}{c}$; and through the theoretic labours of Laplace on the transmission of sound through air, has attained a peculiar interest in science. *For different gases, therefore, the excess of this quotient above unity is inversely proportional to the specific heat, at constant volume, the latter being calculated relative to the unit of volume.* This proposition has been proved experimentally by Dulong* to be so nearly correct, that its theoretic probability induced him to assume its entire truth, and to use it in an inverse manner in calculating the specific heats of various gases, the value of $k$ being first deduced from observation. It must, however, be remarked, that the proposition is theoretically safe only so far as the law of M. and G. holds

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* *Ann. de Chim. et de Phys.*, xli.; and *Pogg. Ann.*, xvi.

good; which, as regards the various gases examined by Dulong, was not always the case to a sufficient degree of accuracy.

Let us suppose that the specific heat $c$ at constant volume is constant for every gas; a supposition which we have already stated to be very probable; this will also be the case when the pressure is constant, and hence *the quotient of both specific heats* $\frac{c'}{c}=k$ *must be also constant.* This proposition, which Poisson, in agreement with the experiments of Gay-Lussac and Welter, has assumed to be correct, and made the basis of his investigations on the tension and heat of gases*, harmonizes very well with our present theory, while it is not possible to reconcile it with the theory of Carnot as heretofore treated.

In equation (II $b$) let $\mathrm{Q}=$const., we then obtain the following equation between $v$ and $t$:

$$cdt+\mathrm{A}.\mathrm{R}\frac{a+t}{v}dv=0; \quad . \quad . \quad . \quad . \quad . \quad (13)$$

from which, when $c$ is regarded as constant, we derive

$$v^{\frac{\mathrm{AR}}{c}}.(a+t)=\text{const.};$$

or, since according to equation (10 $a$), $\frac{\mathrm{AR}}{c}=\frac{c'}{c}-1=k-1$,

$$v^{k-1}(a+t)=\text{const.}$$

Let three corresponding values of $v$, $t$, and $p$ be denoted by $v_0$, $t_0$, and $p_0$; we obtain from this

$$\frac{a+t}{a+t_0}=\left(\frac{v_0}{v}\right)^{k-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

By means of equation (I) let the pressure $p$, first for $v$ and then for $t$, be introduced here, we thus obtain

$$\left(\frac{a+t}{a+t_0}\right)^k=\left(\frac{p}{p_0}\right)^{k-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\frac{p}{p_0}=\left(\frac{v_0}{v}\right)^k. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

These are the relations which subsist between volume, temperature, and pressure when a quantity of gas is compressed, or is

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* *Traité de Mécanique*, 2nd edit. vol. ii. p. 646.

suffered to expand in a holder impervious to heat. These equations agree completely with those developed by Poisson for the same case*, the reason being that he also regarded $k$ as constant.

Finally, in equation (II $b$) let $t=$const., the first member at the right-hand side disappears, and we have remaining

$$dQ=AR\frac{a+t}{v}dv; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

from which follows

$$Q=AR(a+t)\log v+\text{const.};$$

or when the values of $v, p, t,$ and Q, at the commencement of the experiment, are denoted by $v_0, p_0, t_0,$ and $Q_0$,

$$Q-Q_0=AR(a+t_0)\log\frac{v}{v_0} \quad . \quad . \quad . \quad . \quad (18)$$

From this, in the first place, we derive the proposition developed also by Carnot; *when a gas, without alteration of temperature, changes its volume, the quantities of heat developed or absorbed are in arithmetical progression, while the volumes are in geometrical progression.*

Further, let the complete expression for $R=\frac{p_0v_0}{a+t_0}$ be set in equation (18), and we obtain

$$Q-Q_0=Ap_0v_0\log\frac{v}{v_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

If we apply this equation to different gases, not directing our attention to equal weights of the same, but to such quantities as at the beginning embrace a common volume $v_0$, the equation will in all its parts be independent of the peculiar nature of the gas, and agrees with the known proposition to which Dulong, led by the above simple relation of the quantity $k-1$, has given expression: *that when equal volumes of different gases at the same pressure and temperature are compressed or expanded an equal fractional part of the volume, the same absolute amount of heat is in all cases developed or absorbed.* The equation (19) is, however, much more general. It says besides this, *that the quantity of heat is independent of the temperature at which the alteration of volume takes place,* if only the quantity of gas applied be always so determined that the original volumes $v_0$ at the different temperatures shall be equal; *further, that when the original pressure is in the different cases different, the quantities of heat are thereto proportional.*

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* *Traité de Mécanique*, vol. ii. 647.

## II. *Consequences of the principle of Carnot in combination with the preceding.*

Carnot, as already mentioned, has regarded *the production of work as the equivalent of a mere transmission of heat from a warm body to a cold one, the quantity of heat being thereby undiminished.*

The latter portion of this assumption, that the quantity of heat is undiminished, contradicts our maxim, and must therefore, if the latter be retained, be rejected. The former portion, however, may remain substantially as it is. For although we have no need of a peculiar equivalent for the produced work, after we have assumed as such an actual *consumption* of heat, it is nevertheless possible that the said transmission may take place *contemporaneously* with the consumption, and may likewise stand in a certain definite relation to the produced work. It remains therefore to be investigated whether this assumption, besides being possible, has a sufficient degree of probability to recommend it.

A transmission of heat from a warm body to a cold one certainly takes place in those cases where work is produced by heat, and the condition fulfilled that the body in action is in the same state at the end of the operation as at the commencement. In the processes described above, and represented geometrically in figs. 1 and 3, we have seen that the gas and the evaporating water, while the volume was increasing, received heat from the body A, and during the diminution of the volume yielded up heat to the body B, a certain quantity of heat being thus transmitted from A to B; and this quantity was so great in comparison with that which we assumed to be expended, that, in the infinitely small alterations represented in figs. 2 and 4, the latter was a differential of the second order, while the former was a differential of the first order. In order, however, to bring the transmitted heat into proper relation with the work, one limitation is still necessary. As a transmission of heat may take place by conduction without producing any mechanical effect when a warm body is in contact with a cold one, if we wish to obtain the greatest possible amount of work from the passage of heat between two bodies, say of the temperatures $t$ and $\tau$, the matter must be so arranged that two substances of different temperatures shall never come in contact with each other.

It is this *maximum* of work that must be compared with the transmission of the heat; and we hereby find that it may reasonably be assumed, with Carnot, that the work depends solely upon the quantity of heat transmitted, and upon the temperatures $t$ and $\tau$ of both bodies A and B, but not upon the nature of the substance which transmits it. This maximum has the property, that, by its *consumption*, a quantity of heat may be carried from the cold body B to the warm one A equal to that which passed from A to B during its *production*. We can easily convince ourselves of this by conceiving the processes above described to be conducted in a reverse manner; for example, that in the first case the gas shall be permitted to expand by itself until its temperature is lowered from $t$ to $\tau$, the expansion being then continued in connexion with B; afterwards compressed by itself until its temperature is again $t$, and the final compression effected in connexion with A. The amount of work expended during the compression will be thus greater than that produced by the expansion, so that on the whole a loss of work will take place exactly equal to the gain which accrued from the former process. Further, the same quantity of heat will be here taken away from the body B as in the former case was imparted to it, and to the body A the same amount will be imparted as by the former proceeding was taken away from it; from which we may infer, both that the quantity of heat formerly consumed is here produced, and also that the quantity which formerly passed from A to B now passes from B to A.

Let us suppose that there are two substances, one of which is able to produce more work by the transmission of a certain amount of heat, or what is the same, that in the performance of a certain work requires a less amount of heat to be carried from A to B than the other; both these substances might be applied alternately; by the first work might be produced according to the process above described, and then the second might be applied to consume this work by a reversal of the process. At the end both bodies would be again in their original state; further, the work expended and the work produced would exactly annul each other, and thus, in agreement with our maxim also, the quantity of heat would neither be increased nor diminished. Only with regard to the *distribution* of the heat would a difference occur, as more heat would be brought from B to A than from A to B, and thus on the whole a transmission from B to A would take place. Hence by repeating both these alternating processes, without expenditure of force or other alteration whatever, any quantity of heat might be transmitted from a *cold* body to a *warm* one; and this contradicts the general deportment of heat, which everywhere exhibits the tendency to annul differences of temperature, and therefore to pass from a *warmer* body to a *colder* one*.

From this it would appear that we are *theoretically* justified in retaining the first and really essential portion of the assumption of Carnot, and to apply it as a second maxim in connexion with the former. It will be immediately seen that this procedure receives manifold corroboration from its *consequences*.

This assumption being made, we may regard the maximum work which can be effected by the transmission of a unit of heat from the body A at the temperature $t$ to the body B at the temperature $\tau$, as a function of $t$ and $\tau$. The value of this function must of course be so much smaller the smaller the difference $t-\tau$ is; and must, when the latter becomes infinitely small $(=dt)$, pass into the product of $dt$ with a function of $t$ alone. This latter being our case at present, we may represent the work under the form

$$\frac{1}{C}\cdot dt,$$

wherein C denotes a function of $t$ only†.

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* [The principle here assumed, *that heat cannot of itself pass from a colder to a warmer body*, and by means of which I have theoretically established the relation between the work gained and the heat transmitted, is to be regarded as a principle of the same importance as the one, in virtue of which it is assumed that neither work nor heat can be produced from nothing. In consequence of the different opinions of other authors I afterwards thought it necessary to make this principle the subject of a special memoir, which will be found in the sequel.—1864.]

† [It will perhaps be well to illustrate somewhat further what is here stated in the text.

When any substance whatever undergoes a complete cycle of changes, heat being thereby withdrawn from a body A of the temperature $t$, and when of this heat a portion is consumed by the production of work and the remaining portion transmitted to a body B of the temperature $\tau$, then, according to the

To apply this result to the case of permanent gases, let us once more turn to the process represented by fig. 2. During the first expansion in that case the amount of heat,

$$\left(\frac{dQ}{dv}\right).dv,$$

above principles, the latter portion, that is to say the quantity of heat transmitted from A to B, must bear to the amount of work produced (provided the latter be the above-mentioned maximum) a certain definite ratio which will depend upon the temperatures of the two bodies A and B, but not upon the nature of the interposed substance or upon that of its changes. Consequently an equation of the following form must exist:

$$\frac{\textit{Work produced}}{\textit{Heat transmitted}}=\phi(t,\tau), \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(a)}$$

wherein $\phi(t,\tau)$ denotes a generally true function of the two temperatures $t$ and $\tau$; it is, in fact, the function which, as stated in the text, represents the maximum of the produced work corresponding to the unit of transmitted heat.

Let the temperature $t$ of the body A be now regarded as given, the temperature $\tau$ of the body B being at the same time susceptible of any values whatever. It is readily seen that when the difference $t-\tau$ is smaller, the work which corresponds to the transmission of the unit of heat will also be smaller, and that when the difference of temperature is infinitesimal, in which case it may be represented by $dt$, the work will also be an infinitesimal quantity of the same order. Imagine then $t-dt$ to be substituted for $\tau$ in the function $\phi(t,\tau)$ which represents the work, and this function to be subsequently expanded in a series arranged according to increasing powers of $dt$. No term of this series will contain a power of $dt$ lower than the first, so that, neglecting terms which contain higher powers of $dt$, we may write

$$\phi(t, t-dt)=\psi(t)dt,$$

where the function $\psi(t)$ is likewise a generally true one. On proceeding to further calculations it is found that the equations assume a somewhat more convenient form when, in place of writing the function $\psi(t)$ itself, a new symbol is introduced for its reciprocal $\frac{1}{\psi(t)}$; the letter C having already been employed by Clapeyron for this purpose I have provisionally retained it. Accordingly,

$$\phi(t,t-dt)=\frac{1}{C}.dt,$$

the equation (a), in the case where the bodies A and B have the temperatures $t$ and $t-dt$, becomes thus transformed:

$$\frac{\textit{Work produced}}{\textit{Heat transmitted}}=\frac{1}{C}dt. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(b)}$$

The function of the temperature denoted by C is frequently called Carnot's function. An opportunity will present itself in the course of this memoir of determining the form of this function. Its expression will then be found sufficiently simple to admit of direct introduction into the equations, and that done the symbol C will of course become superfluous.—1864.]

passed from A to the gas; and during the first compression the following portion thereof was yielded to the body B:

$$\left[\left(\frac{dQ}{dv}\right)+\frac{d}{dv}\left(\frac{dQ}{dv}\right)\delta v-\frac{d}{dt}\left(\frac{dQ}{dv}\right)dt\right]d'v,$$

or

$$\left(\frac{dQ}{dv}\right)dv-\left[\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)\right]dv\,dt.$$

The latter quantity is therefore the amount of heat transmitted. As, however, we can neglect the differential of the second order in comparison with that of the first, we retain simply

$$\left(\frac{dQ}{dv}\right)dv.$$

The quantity of work produced at the same time was

$$\frac{R\,dv\,.\,dt}{v},$$

and from this we can construct the equation

$$\frac{R\,\dfrac{dv\,.\,dt}{v}}{\left(\dfrac{dQ}{dv}\right)dv}=\frac{1}{C}\,.\,dt,$$

or

$$\left(\frac{dQ}{dv}\right)=\frac{R\,.\,C}{v}{}^{*}\;.\;.\;.\;.\;.\;.\;.\;.\;.\quad (IV)$$

Let us now make a corresponding application to the process of evaporation represented by fig. 4. The quantity of heat in that case transmitted from A to B was

$$\left(r-\frac{dr}{dt}\,dt\right)d'm,$$

or

$$rdm-\left(\frac{dr}{dt}+c-h\right)dm\,dt;$$

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* [This equation may be generalized in the same way as was the equation (II) in a previous note. In fact, replacing the fraction $\frac{R}{v}$ by the differential coefficient $\left(\frac{dp}{dt}\right)$, which for gaseous bodies has the same value, the more general equation

$$\left(\frac{dQ}{dv}\right)=C\left(\frac{dp}{dt}\right)$$

is obtained.—1864.]

for which, neglecting the differentials of the second order, we may simply put

$$rdm.$$

The quantity of work thereby produced was

$$(s-\sigma)\frac{dp}{dt}dm\,dt,$$

and hence is obtained the equation

$$\frac{(s-\sigma)\frac{dp}{dt}\,.\,dm\,.\,dt}{rdm}=\frac{1}{C}\,.\,dt,$$

or

$$r=C\,.\,(s-\sigma)\frac{dp}{dt}{}^*. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (V.)$$

These, although not in the same form, are the two analytical expressions of the principle of Carnot as given by Clapeyron. In the case of vapours, the latter adheres to equation (V.), and contents himself with some immediate applications thereof. For gases, on the contrary, he makes equation (IV.) the basis of a further development; and in this development alone does the partial divergence of his result from ours make its appearance†.

We will now bring both these equations into connexion with the results furnished by the first fundamental principle, commencing with those which have reference to permanent gases.

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* [This equation also is merely a special form of the equation

$$\left(\frac{dQ}{dv}\right)=C\left(\frac{dp}{dt}\right);$$

for in the present case we may put

$$\left(\frac{dQ}{dv}\right)=\frac{r}{s-\sigma},$$

since the heat which must be imparted to the body under consideration, consisting of liquid and vapour, during its increase of volume is precisely the heat rendered latent by the production of vapour.

The differential coefficient $\frac{dp}{dt}$ is written in the equation (V) without brackets, for the manifest reason before alluded to.—1864.]

† [Clapeyron, in fact, when treating the equation (IV) and the more general one given in a previous note, starts from the hypothesis that the magnitude Q is completely determined by the state of the body at the moment under consideration, and consequently that it can be at once represented by a function of the two variables ($p$ and $v$ in his case) upon which the condition of the body depends. In this sense he effected the integration.—1864.]

Confining ourselves to that deduction which has the maxim alone for basis, that is to equation (II $a$), the quantity U which stands therein as an arbitrary function of $v$ and $t$ may be more fully determined by (IV); the equation thus becomes

$$dQ=\left[B+R\left(\frac{dC}{dt}-A\right)\log v\right]dt+\frac{R.C}{v}.dv, \qquad \text{(II } c\text{)}$$

in which B remains as an arbitrary function of $t$ alone*.

If, on the contrary, we regard the incidental assumption also as correct, the equation (IV) will thereby be rendered unnecessary for the nearer determination of (II $a$), inasmuch as the same object is arrived at in a much more complete manner by equation (9), which flowed immediately from the combination of the said assumption with the original maxim. The equation (IV), however, furnishes us with a means of submitting both principles to a reciprocal test. The equation (9) was thus expressed,

$$\left(\frac{dQ}{dv}\right)=\frac{R.A(a+t)}{v};$$

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* [This equation is obtained in the following manner. From the equation (II $a$), that is from

$$dQ=dU+AR\frac{a+t}{v}dv,$$

may be deduced

$$\left(\frac{dQ}{dv}\right)=\left(\frac{dU}{dv}\right)+AR\frac{a+t}{v}.$$

Hence, replacing $\left(\frac{dQ}{dv}\right)$ by its value given in (IV), we have

$$\frac{R.C}{v}=\left(\frac{dU}{dv}\right)+AR.\frac{a+t}{v},$$

or

$$\left(\frac{dU}{dv}\right)=[C-A(a+t)]\frac{R}{v}.$$

This, integrated according to $v$, gives

$$U=[C-A(a+t)]R\log v+\phi(t),$$

where $\phi(t)$ denotes an arbitrary function of $t$. Differentiating the last equation completely, and putting B in place of the differential coefficient $\frac{d\phi(t)}{dt}$, which, like $\phi(t)$ itself, is also to be regarded as an arbitrary function of $t$, we have

$$dU=\left[\left(\frac{dC}{dt}-A\right)R\log v+B\right]dt+\left[C-A(a+t)\right]\frac{R}{v}dv.$$

But if this expression for $dU$ be substituted in the equation (II $a$) the term $AR\frac{a+t}{v}$ will disappear, and the equation (II $c$) of the text will remain.—1864.]

and when we compare this with equation (IV), we find that both of them express the same thing; with this difference only, that one of them expresses it more definitely than the other. In (IV.) the function of the temperature is expressed in a general manner merely, whereas in (9) we have instead of C the more definite expression $A(a+t)$.

To this surprising coincidence the equation (V) adds its testimony, and confirms the result that $A(a+t)$ is the true expression for the function C. This equation is used by Clapeyron and Thomson in determining the values of C for particular temperatures. The temperatures chosen by Clapeyron were the boiling-points of æther, of alcohol, of water, and of oil of turpentine. He employed the values of $\frac{dp}{dt}$, $s$ and $r$, determined by experiment for these liquids at their boiling-points; and setting these values in equation (V), he obtained for C the numbers contained in the second column of the following Table. Thomson, on the contrary, limited himself to the vapour of *water*; but considered it at various temperatures, and in this way calculated the value of C for every single degree from 0° to 230° Cent. The observations of Regnault had furnished him with a secure basis as regards the quantities $\frac{dp}{dt}$ and $r$; but for other temperatures than the boiling-point, the value of $s$ is known with much less certainty. In this case, therefore, he felt compelled to make an assumption which he himself regarded as only approximately correct, using it merely as a preliminary help until the discovery of more exact data. The assumption was, that the vapour of water at its maximum density follows the law of M. and G. The numbers thus found for the temperatures used by Clapeyron, as reduced to the French standard, are exhibited in the third column of the following table:—

TABLE I.

| 1.<br>$t$ in Cent. degrees. | 2.<br>C according to Clapeyron. | 3.<br>C according to Thomson. |
|---|---|---|
| ° | | |
| 35·5 | 0·733 | 0·728 |
| 78·8 | 0·828 | 0·814 |
| 100 | 0·897 | 0·855 |
| 156·8 | 0·930 | 0·952 |

We see that the values of C found in both cases increase, like those of $A(a+t)$, slowly with the temperature. They bear the same ratio to each other as the numbers of the following series :

1 ; 1·13 ; 1·22 ; 1·27 ;
1 ; 1·12 ; 1·17 ; 1·31 ;

and when the ratio of the values of $A(a+t)$ (obtained by setting $a=273$) corresponding to the same temperatures are calculated, we obtain

1 ; 1·14 ; 1·21 ; 1·39.

This series of *relative* values deviates from the former only so far as might be expected from the insecurity of the data from which those are derived : the same will also exhibit itself further on in the determination of the *absolute* value of the constant A.

Such a coincidence of results derived from two entirely different bases cannot be accidental. Rather does it furnish an important corroboration of both, and also of the additional incidental assumption.

Let us now turn again to the application of equations (IV) and (V) ; the former, as regards *permanent gases*, has merely served to substantiate conclusions already known. For *vapours*, however, and for other substances to which we might wish to apply the principle of Carnot, the said equation furnishes the important advantage, that by it we are justified in substituting everywhere for the function C the definite expression $A(a+t)$ *.

The equation (V) changes by this into

$$r=A(a+t)\,.\,(s-\sigma)\,\frac{dp}{dt}\,; \qquad . \quad . \quad . \quad . \qquad (\mathrm{V}a)$$

we thus obtain for the vapour a simple relation between the temperature at which it is formed, the pressure, the volume, and

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* [In this manner we arrive at the definite and simple expression for the function C of the temperature to which allusion was made in a previous note (p. 46), and which when first introduced had no determined form. Since this function, in virtue of its signication, must have a general validity, it is obvious that the expression for it which has been found on considering specially the expansion of a perfect gas, may also be applied to all other substances, and to all kinds of changes whereby these substances are able to produce work through the expenditure of heat. Whenever, therefore, by the interposition of any variable substance, heat is transferred from a body A of

the latent heat, and can make use of it in drawing still further conclusions.

Were the law of M. and G. true for vapours at their maximum density*, we should have

$$ps = R(a+t) \qquad (20)$$

By means of this equation let $s$ be eliminated from (V $a$); neglecting the quantity $\sigma$, which, when the temperature is not very high, disappears in comparison with $s$, we obtain

$$\frac{1}{p}\frac{dp}{dt} = \frac{r}{AR(a+t)^2}.$$

If the second assumption, that $r$ is constant, be here made, we obtain by integration

$$\log\frac{p}{p_1} = \frac{r(t-100)}{AR(a+100)\ (a+t)},$$

where $p_1$ denotes the tension of the vapour at 100°. Let

$$t-100=\tau, \quad a+100=\alpha, \text{ and } \frac{r}{AR(a+100)}=\beta;$$

we have then

$$\log\frac{p}{p_1} = \frac{\beta\,.\,\tau}{\alpha+\tau}. \qquad (21)$$

This equation cannot of course be strictly correct, because the two assumptions made during its development are not so. As

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the temperature $t$ to a body B of the temperature $t-dt$, the relation between the transmitted heat and the maximum of the work possibly produced thereby may be expressed by the equations

$$\frac{\textit{Work produced}}{\textit{Heat transmitted}} = \frac{dt}{A(a+t)}.$$

In a similar manner the general equation given in the note to equation (IV) (p. 47), can now be written thus:—

$$\left(\frac{dQ}{dv}\right) = A(a+t)\left(\frac{dp}{dt}\right),$$

whereby the quantity of heat is completely determined which a body must absorb when, at a constant temperature, it changes its volume under the influence of an external pressure equal to its own force of expansion.—1864.]

* [The sole object of the inaccurate assumptions made, merely *en passant*, in this paragraph is to elucidate further the formula for the tension of vapours which was established by Roche, and considered, from theoretical points of view, by Holtzmann and other authors; and to show, on the one hand, why the formula is approximately correct, and on the other, why it is not strictly so.—1864.]

however the latter approximate at least in some measure to the truth, the formula $\frac{\beta . \tau}{\alpha + \tau}$ expresses in a rough manner, so to speak, the route of the quantity $\log \frac{p}{p_1}$; and from this it may be perceived how it is, when the constants $\alpha$ and $\beta$ are regarded as arbitrary, instead of representing the definite values which their meaning assigns to them, that the above may be used as an empirical formula for the calculation of the tension of vapours, without however considering it, as some have done, to be *completely* true theoretically.

Our next application of equations (V $a$) shall be to ascertain how far the vapour of water, concerning which we possess the most numerous data, *diverges in its state of maximum density from the law of M. and G.* This divergence cannot be small, as carbonic acid and sulphurous acid gas, long before they reach their points of condensation, exhibit considerable deviations.

The equation (V $a$) can be brought to the following form:

$$\mathrm{A}p(s-\sigma)\frac{a}{a+t}=\frac{ar}{(a+t)^2\frac{1}{p}\frac{dp}{dt}}. \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

Were the law of M. and G. strictly true, the expression at the left-hand side must be very nearly constant, as the said law would, according to (20), immediately give

$$\mathrm{A} . ps\frac{a}{a+t}=\mathrm{A} . \mathrm{R}a,$$

where instead of $s$ we can, with a near approach to accuracy, set the quantity $s-\sigma$. By a comparison with its true values calculated from the formula at the right-hand side of (22), this expression becomes peculiarly suited to exhibit every divergence from the law of M. and G. I have carried out this calculation for a series of temperatures, using for $r$ and $p$ the numbers given by Regnault*.

In the first place, with regard to the *latent heat*, the quantity of heat $\lambda$ necessary, according to Regnault †, to raise a unit of weight of water from 0° to $t°$, and then to evaporate it at this

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* *Mém. de l'Acad. de l'Inst. de France*, vol. xxi. (1847).

† *Ibid. Mém.* IX.; also Pogg. *Ann.*, vol. lxxviii.

temperature, may be represented with tolerable accuracy by the following formula:

$$\lambda = 606{\cdot}5 + 0{\cdot}305t. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (23)$$

In accordance, however, with the meaning of $\lambda$, we have

$$\lambda = r + \int_0^t c\,dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (23\,a)$$

For the quantity $c$, which is here introduced to denote the specific heat of the water, Regnault* has given, in another investigation, the following formula:

$$c = 1 + 0{\cdot}00004\,.\,t + 0{\cdot}0000009\,.\,t^2. \quad . \quad . \quad . \qquad (23\,b)$$

By means of these two equations we obtain from (23) the following expression for the latent heat:

$$r = 606{\cdot}5 - 0{\cdot}695\,.\,t - 0{\cdot}00002\,.\,t^2 - 0{\cdot}0000003\,.\,t^3\dagger. \quad . \qquad (24)$$

Further, with regard to the pressure, Regnault‡ has had recourse to a diagram to obtain the most probable values from his numerous experiments. He has constructed curves in which the abscissæ represent the temperature, and the ordinates the pressure $p$, taken at different intervals from −33° to 230°. From 100° to 230° he has drawn another curve, the ordinates of which

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* *Mém. de l'Acad. de l'Inst. de France,* Mem. X.

† In the greater number of his experiments Regnault has observed, not so much the heat which becomes *latent* during evaporation, as that which becomes *sensible* by the precipitation of the vapour. Since, therefore, it has been shown, that if the maxim regarding the equivalence of heat and work be correct, the heat developed by the precipitation of a quantity of vapour is not necessarily equal to that which it had absorbed during evaporation, the question may occur whether such differences may not have occurred in Regnault's experiments also, the given formula for $r$ being thus rendered useless. I believe, however, that a negative may be returned to this question; the matter being so arranged by Regnault, that the precipitation of the vapour took place at the same pressure as its development, that is, nearly under the pressure corresponding to the maximum density of the vapour at the observed temperature; and in this case the same quantity of heat must be produced during condensation as was absorbed by evaporation.

[In a subsequent memoir I have proposed to employ, instead of the equation (24), the following equation for the latent heat:

$$r = 607 - 0{\cdot}708\,.\,t.$$

It is more convenient for calculation, and gives very nearly the same value for $r$ as the equation (24) itself.—1864.]

‡ *Ibid. Mém.* VIII.

represent, not *p* itself, but the logarithms of *p*. From this diagram the following values are obtained; these ought to be regarded as the most immediate results of his observations, while the other and more complete tables which the memoir contains are calculated from formulæ, the choice and determination of which depend in the first place upon these values.

### TABLE II.

| *t* in Cent. degrees of the air-thermometer. | *p* in millimetres. | *t* in Cent. degrees of the air-thermometer. | *p* in millimetres, | |
|---|---|---|---|---|
| | | | according to the curve of the numbers. | according to the curve of the logarithms *. |
| −20° | 0·91 | 110° | 1073·7 | 1073·3 |
| −10 | 2·08 | 120 | 1489·0 | 1490·7 |
| 0 | 4·60 | 130 | 2029·0 | 2030·5 |
| 10 | 9·16 | 140 | 2713·0 | 2711·5 |
| 20 | 17·39 | 150 | 3572·0 | 3578·5 |
| 30 | 31·55 | 160 | 4647·0 | 4651·6 |
| 40 | 54·91 | 170 | 5960·0 | 5956·7 |
| 50 | 91·98 | 180 | 7545·0 | 7537·0 |
| 60 | 148·79 | 190 | 9428·0 | 9425·4 |
| 70 | 233·09 | 200 | 11660·0 | 11679·0 |
| 80 | 354·64 | 210 | 14308·0 | 14325·0 |
| 90 | 525·45 | 220 | 17390·0 | 17390·0 |
| 100 | 760·00 | 230 | 20915·0 | 20927·0 † |

To carry out the intended calculations from these data, I have first obtained from the Table the values of $\frac{1}{p} \cdot \frac{dp}{dt}$ for the temperatures −15°, −5°, 5°, 15°, &c. in the following manner. As the quantity $\frac{1}{p} \cdot \frac{dp}{dt}$ decreases but slowly with the increase of temperature, I have regarded the said decrease for intervals of 10°, that is, from −20° to −10°, from −10° to 0°, &c. as uniform,

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* This column contains, instead of the logarithms derived immediately from the curve and given by Regnault, the corresponding numbers, so that they may be more readily compared with the values in the column preceding.

† [It would have been more convenient to employ the values of vapour-tensions, calculated by Regnault, from degree to degree, by help of an empirical formula, and collected in his well-known larger table. On attempting to do so, however, I found that it would be more appropriate for my present object to return to the values here tabulated, and which were obtained without the aid of an empirical formula, from immediate measurements of the curves drawn according to observations; for these values represent with the greatest purity the results of observations, and are consequently particularly well adapted for comparison with theoretical results.—1864.]

so that the value due to 25° might be considered as a mean between that of 20° and that of 30°. As $\frac{1}{p}\cdot\frac{dp}{dt}=\frac{d(\log p)}{dt}$, I was by this means enabled to use the following formula:

$$\left(\frac{1}{p}\cdot\frac{dp}{dt}\right)_{25^\circ}=\frac{\log p_{30^\circ}-\log p_{20^\circ}}{10},$$

or

$$\left(\frac{1}{p}\cdot\frac{dp}{dt}\right)_{25^\circ}=\frac{\mathrm{Log}\, p_{30^\circ}-\mathrm{Log}\, p_{20^\circ}}{10\,.\,\mathrm{M}}, \quad . \quad . \quad . \quad (25)$$

wherein, by Log, is meant Briggs's logarithms, and by M, the modulus of his system. With the assistance of these values of $\frac{1}{p}\cdot\frac{dp}{dt}$, and those of $r$ given by equation (24), as also the value 273 of $a$, the values assumed by the formula at the right-hand side of (22) are calculated, and will be found in the second column of the following Table. For temperatures above 100°, the

TABLE III.

| 1. $t$ in Cent. degrees of the air-thermometer. | $Ap(s-\sigma)\frac{a}{a+t}$. | | | 4. Differences. | |
|---|---|---|---|---|---|
| | 2. According to the values observed. | | 3. According to equation (27). | | |
| −15° | 30·61 | | 30·61 | 0·00 | |
| − 5 | 29·21 | | 30·54 | +1·33 | |
| 5 | 30·93 | | 30·46 | −0·47 | |
| 15 | 30·60 | | 30·38 | −0·22 | |
| 25 | 30·40 | | 30·30 | −0·10 | |
| 35 | 30·23 | | 30·20 | −0·03 | |
| 45 | 30·10 | | 30·10 | 0·00 | |
| 55 | 29·98 | | 30·00 | +0·02 | |
| 65 | 29·88 | | 29·88 | 0·00 | |
| 75 | 29·76 | | 29·76 | 0·00 | |
| 85 | 29·65 | | 29·63 | −0·02 | |
| 95 | 29·49 | | 29·48 | −0·01 | |
| 105 | 29·47 | 29·50 | 29·33 | −0·14 | −0·17 |
| 115 | 29·16 | 29·02 | 29·17 | +0·01 | +0·15 |
| 125 | 28·89 | 28·93 | 28·99 | +0·10 | +0·06 |
| 135 | 28·88 | 29·01 | 28·80 | −0·08 | −0·21 |
| 145 | 28·65 | 28·40 | 28·60 | −0·05 | +0·20 |
| 155 | 28·16 | 28·25 | 28·38 | +0·22 | +0·13 |
| 165 | 28·02 | 28·19 | 28·14 | +0·12 | −0·05 |
| 175 | 27·84 | 27·90 | 27·89 | +0·05 | −0·01 |
| 185 | 27·76 | 27·67 | 27·62 | −0·14 | −0·05 |
| 195 | 27·45 | 27·20 | 27·33 | −0·12 | +0·13 |
| 205 | 26·89 | 26·94 | 27·02 | +0·13 | +0·08 |
| 215 | 26·56 | 26·79 | 26·68 | +0·12 | −0·11 |
| 225 | 26·64 | 26·50 | 26·32 | −0·32 | −0·18 |

two series of numbers given above for $p$ are made use of singly, and the results thus obtained are placed side by side. The signification of the third and fourth columns will be more particularly explained hereafter.

We see directly from this Table that $Ap(s-\sigma)\frac{a}{a+t}$ is not constant, as it must be if the law of M. and G. were valid, but that it decidedly decreases with the temperature. Between 35° and 95° this decrease is very uniform. Before 35°, particularly in the neighbourhood of 0°, considerable irregularities take place; which, however, are simply explained by the fact, that here the pressure $p$ and its differential quotient $\frac{dp}{dt}$ are very small, and hence the trifling inaccuracies which might attach themselves to the observations can become *comparatively* important. It may be added, further, that the curve by means of which, as mentioned above, the single values of $p$ have been obtained, was not drawn continuously from −33° to 100°, but to save room was broken off at 0°, so that the route of the curve at this point cannot be so accurately determined as within the separate portions above and below 0°. From the manner in which the divergences show themselves in the above Table, it would appear that the value assumed for $p$ at 0° is a little too great, as this would cause the values of $Ap(s-\sigma)\frac{a}{a+t}$ to be too small for the temperatures immediately under 0°, and too large for those above it*. From 100° upwards the values of this expression do not decrease with the same regularity as between 35° and 95°. They

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* [It must be remembered that the values of

$$Ap(s-\sigma)\frac{a}{a+t}$$

are calculated by the formula

$$\frac{ar}{(a+t)^2\frac{1}{p}\cdot\frac{dp}{dt}}$$

given in equation (22). If now the value of $p$, and consequently also the value of log $p$, corresponding to 0° be too great, we must assume that the values of the differential coefficient of log $p$, that is to say of $\frac{1}{p}\cdot\frac{dp}{dt}$, will be too great immediately under 0°, and too small immediately above 0°, in consequence of show, however, a *general* correspondence; and particularly when a diagram is made, it is found that the curve which, within those limits, connects almost exactly the points, as determined from the numbers contained in the foregoing Table, may be carried forward to 230°, so that the points are uniformly distributed on both sides of it.

Taking the entire Table into account, the route of this curve may be expressed with tolerable accuracy by the equation

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which the values of the above formula which contains $\frac{1}{p}\frac{dp}{dt}$ in the denominator will necessarily be incorrect in an opposite sense. With reference to temperatures under 0° another circumstance must also be mentioned. For temperatures under 0° I have, in my calculations, applied the values of the vapour-tension $p$, given by Regnault's observations, also to the case when the vapour is in contact with liquid water, as of course it may be, since under certain conditions water may remain liquid at a temperature far below 0°. Accordingly I have considered the magnitude $r$ in the numerator of the formula to be, at all temperatures, the quantity of heat consumed in the evaporation of liquid water. If, on the contrary, we assume that those values of $p$ given by observation have reference, for temperatures under 0°, to the case where vapour is in contact with ice; then, for these temperatures, $r$ must be understood to denote the quantity of heat which is consumed in the evaporation of ice. For the temperature 0° itself the latter quantity of heat is obtained by simply adding to the heat consumed in the evaporation of liquid water the latent heat of fusion, that is to say $606{\cdot}5+79=685{\cdot}5$. For temperatures under 0° this method, it is true, is not quite accurate; nevertheless it must be very nearly so when, in applying it, the differences in the latent heat of fusion are considered which correspond to different temperatures. The value of

$$\mathrm{A}p(s-\sigma)\,\frac{a}{a+t},$$

corresponding to the temperature −5°, when calculated in this manner according to the above formula, gives the number 32·93, instead of 29·21, as found by the previous calculation. Comparing this number 32·93 with the series of numbers which correspond to the positive temperatures 5°, 15°, &c., we find that its deviation from the course of the latter is of an opposite kind to, and indeed somewhat greater than, the deviation of the previously calculated number 29·21. Regnault's values, therefore, regarded in either of the ways, lead to irregularities in the course of the numbers. The occurrence of such irregularities at low temperatures, is explained, as has already been observed, by the fact that the vapour-tensions are then so small, that errors of observation, though absolutely small, may become relatively great; less weight, therefore, must be attached to the numbers in the above Table which refer to low temperatures, than to those which correspond to the mean and to the higher temperatures.—1864.]

$$\mathrm{A}p(s-\sigma)\frac{a}{a+t}=m-ne^{kt}; \quad . \quad . \quad . \quad . \quad (26)$$

in which $e$ denotes the base of the Napierian logarithms, and $m$, $n$, and $k$ are constants. When the latter are determined from the values given by the curve for 45°, 125° and 205°, we obtain

$$m=31{\cdot}549;\ n=1{\cdot}0486;\ k=0{\cdot}007138; \quad . \quad . \quad (26\,a)$$

and when, for the sake of convenience, we introduce the logarithms of Briggs, we have

$$\mathrm{Log}\left[31{\cdot}549-\mathrm{A}p(s-\sigma)\frac{a}{a+t}\right]=0{\cdot}0206+0{\cdot}003100\,t. \quad (27)$$

From this equation the numbers contained in the third column are calculated, and the fourth column contains the differences between these numbers and those contained in the second.

From the data before us we can readily deduce a formula which will enable us more definitely to recognize the manner in which the deportment of the vapour diverges from the law of M. and G. Assuming the correctness of the law, if $ps_0$ denote the value of $ps$ for 0°, we must put, in agreement with (20),

$$\frac{ps}{ps_0}=\frac{a+t}{a},$$

and we thereby obtain for the differential quotients $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$ a constant quantity, that is to say, the known coefficient of expansion $\frac{1}{a}=0{\cdot}003665$. Instead of this we derive from (26), when in the place of $s-\sigma$ we set $s$ itself simply, the equation

$$\frac{ps}{ps_0}=\frac{m-n\,.\,e^{kt}}{m-n}\cdot\frac{a+t}{a}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and from this follows

$$\frac{d}{dt}\left(\frac{ps}{ps_0}\right)=\frac{1}{a}\cdot\frac{m-n[1+k(a+t)]e^{kt}}{m-n}. \quad . \quad . \quad . \quad (29)$$

The differential quotient is therefore not a constant, but a function which decreases with the increase of temperature; and which, when the numbers given by (26 $a$) for $m$, $n$ and $k$, are introduced, assumes among others the following values:—

### TABLE IV.

| $t$. | $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$. | $t$. | $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$. | $t$. | $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$. |
|---|---|---|---|---|---|
| 0° | 0·00342 | 70° | 0·00307 | 140° | 0·00244 |
| 10 | 0·00338 | 80 | 0·00300 | 150 | 0·00231 |
| 20 | 0·00334 | 90 | 0·00293 | 160 | 0·00217 |
| 30 | 0·00329 | 100 | 0·00285 | 170 | 0·00203 |
| 40 | 0·00325 | 110 | 0·00276 | 180 | 0·00187 |
| 50 | 0·00319 | 120 | 0·00266 | 190 | 0·00168 |
| 60 | 0·00314 | 130 | 0·00256 | 200 | 0·00149 |

We see from this that the deviations from the law of M. and G. are small at low temperatures; at high temperatures, however, for example at 100° and upwards, they are no longer to be neglected.

It may, perhaps, at first sight appear strange that the values found for $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$ are *less* than 0·003665, as it is known that for those gases which deviate most from the law of M. and G., as carbonic acid and sulphurous acid, the coefficient of expansion is not *smaller* but *greater*. The differential quotients before calculated must not however be regarded as expressing *literally* the same thing as the coefficient of expansion, which latter is obtained either by suffering the volume to expand under a *constant pressure*, or by heating a *constant volume*, and then observing the increase of expansive force; but we are here dealing with a third particular case of the general differential quotient $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$, where the pressure increases with the temperature in the ratio due to the vapour of water which retains its maximum density. To establish a comparison with carbonic acid, the same case must be taken into consideration.

At 108° steam possesses a tension of 1 metre, and at 129½° a tension of 2 metres. We will therefore inquire how carbonic acid acts when its temperature is raised 21½°, and at the same time the pressure increased from 1 to 2 metres. According to Regnault*, the coefficient of expansion for carbonic acid at a constant pressure of 760 millims. is 0·003710, and at a pressure of 2520 millims. it is 0·003846. For a pressure of 1500 millims. (the mean between 1 metre and 2 metres) we obtain, when we regard the in-

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* *Mém de l'Acad.*, vol. xxi. Mem. I.

crease of the coefficient of expansion as proportional to the increase of pressure, the value 0·003767. If therefore carbonic acid were heated under this mean pressure from 0 to 21½°, the quantity $\frac{pv}{pv_0}$ would be thus increased from 1 to $1+0{\cdot}003767\times 21{\cdot}5 = 1{\cdot}08099$. Further, it is known from other experiments of Regnault*, that when carbonic acid at a temperature of nearly 0°, and a pressure of 1 metre, is loaded with a pressure of 1·98292 metre, the quantity $pv$ decreases at the same time in the ratio of 1 : 0·99146; according to which, for an increase of pressure from 1 to 2 metres, the ratio of the decrease would be 1 : 0·99131. If now both take place at the same time, the increase of temperature from 0 to 21½, and the increase of pressure from 1 metre to 2 metres, the quantity $\frac{pv}{pv_0}$ must thereby increase very nearly from 1 to $1{\cdot}08099\times 0{\cdot}99131 = 1{\cdot}071596$; and from this we obtain, as the mean value of the differential quotient $\frac{d}{dt}\left(\frac{pv}{pv_0}\right)$,

$$\frac{0{\cdot}071596}{21{\cdot}5} = 0{\cdot}00333.$$

We see, therefore, that for the case under contemplation a value is obtained for carbonic acid also which is less than 0·003665; and it is less to be wondered at if the same result should occur with the vapour *at its maximum density.*

If, on the contrary, the real coefficient of expansion for the vapour were sought, that is to say, the number which expresses the expansion of a certain quantity of vapour taken at a definite temperature in the state of maximum density, and then heated under a constant pressure, we should certainly obtain a value *greater*, and perhaps *considerably* greater, than 0·003665.

From the equation (26) the *relative* volumes of a unit weight of steam at its maximum density for the different temperatures, as referred to the volume at a fixed temperature, is readily estimated. To calculate from these the *absolute* volumes with sufficient exactitude, the value of the constant A must be established with greater certainty than is at present the case†.

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* *Mém. de l'Acad.*, vol. xxi. Mem. VI.

† [At the time I wrote this Joule had not stated which value of the me-

The question now occurs, whether a single volume may not be accurately estimated in some other manner, so as to enable us to infer the absolute values of the remaining volumes from their relative values. Already, indeed, have various attempts been made to determine the specific gravity of water vapour; but I believe for the case in hand, where the vapour is at its maximum density, the results are not yet decisive. The numbers usually given, particularly that found by Gay-Lussac, 0·6235, agree pretty well with the theoretic value obtained from the assumption, that two measures of hydrogen and one of oxygen give by their combination two measures of vapour, that is to say, with the value

$$\frac{2\times 0{\cdot}06926+1{\cdot}10563}{2}=0{\cdot}622.$$

These numbers, however, refer to observations made, not at those temperatures where the pressure used was equal to the maximum expansive force, but at higher ones. In this state the vapour might nearly agree with the law of M. and G., and hence may be explained the coincidence of experiment with the theoretic values. To make this, however, the basis from which, by application of the above law, the condition of the vapour at its maximum density might be inferred, would contradict the results before obtained; as in Table IV. it is shown that the divergence at the temperatures to which these determinations refer are too considerable. It is also a fact, that those experiments where the vapour at its maximum density was observed have in most cases given larger numbers; and Regnault* has convinced himself, that even at a temperature a little above 30°, when the vapour was developed *in vacuo*, a satisfactory coincidence was first observed when the tension of the vapour was 0·8 of that which corresponded to the maximum density due to the temperature existing at the time; with proportionately greater tension, the

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chanical equivalent of heat he considered to be most in accordance with the results of all his experiments. Taking experimental difficulties into consideration, the values yielded by his various methods of observation agreed sufficiently well with each other to leave no doubt in the mind as to the accuracy of the theorem relative to the equivalence of heat and work, but not well enough to enable me to deduce therefrom a value capable of being employed with safety in the calculation of vapour-volumes.—1864.]

* *Ann. de Chim. et de Phys.*, ser. 3, vol. xv. p. 148.

numbers were too large. The case, however, is not finally set at rest by these experiments; for, as remarked by Regnault, it is doubtful whether the divergence is due to the too great specific gravity of the developed vapour, or to a quantity of water condensed upon the sides of the glass balloon. Other experiments, wherein the vapour was not developed *in vacuo* but saturated a current of air, gave results which were tolerably free* from these irregularities; but from these experiments, however important they may be in other respects, no safe conclusion can be drawn as to the deportment of the vapour *in vacuo*.

The following considerations will perhaps serve to fill up to some extent the gap caused by this uncertainty. The Table (IV.) shows that the lower the temperature of the vapour at its maximum density, the more nearly it agrees with the law of M. and G.; and hence we must conclude that the specific gravity for low temperatures approaches more nearly the theoretic value than for high ones. If therefore, for example, the value of 0·622 for 0° be assumed to be correct, and the corresponding values $d$ for higher temperatures be calculated from the following equation, deduced from (26),

$$d=0{\cdot}622\,\frac{m-n}{m-ne^{kt}}\dagger, \quad \ldots\ldots\ldots \quad (30)$$

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* *Ann. de Chim. et de Phys.*, ser. 3, vol. xv. p. 158.

† [The magnitude $d$ denotes the density of the vapour compared with that of atmospheric air of the same temperature, and under the same pressure. Now if $s$ represent, as before, the volume of a unit of weight of the vapour, and $v$ the volume of an equal weight of atmospheric air of the same temperature, and under the same pressure, we may put

$$d=\frac{v}{s}.$$

But, according to the law of M. and G.,

$$v=\frac{p_0v_0}{p}\cdot\frac{a+t}{a},$$

where $p_0$ and $v_0$ have reference to the temperature 0°; and again, according to the equation (26), $\sigma$ being neglected therein,

$$s=\frac{1}{\mathrm{A}p}\cdot\frac{a+t}{a}(m-ne^{kt}).$$

Now these values of $v$ and $s$ being substituted in the above fraction, we have

$$d=\frac{\mathrm{A}p_0v_0}{m-ne^{kt}},$$

we shall obtain far more probable values than if we had made use of 0·622 for all temperatures. The following Table gives some of these.

TABLE V.

| $t$. | 0°. | 50°. | 100°. | 150°. | 200°. |
|---|---|---|---|---|---|
| $d$. | 0·622 | 0·631 | 0·645 | 0·666 | 0·698 |

Strictly speaking, however, we must proceed still further. In Table III. it is seen that the values of $Ap(s-\sigma)\dfrac{a}{a+t}$, as the temperature decreases, approach a limit which is not attained even by the lowest temperatures in the Table; and not until this limit be reached can we really admit the validity of the law of M. and G., or assume the specific gravity to be 0·622. The question now occurs, what is this limit? Could we regard the formula (26) to be true for temperatures under −15° also, it would only be necessary to take that value to which it approaches as an asymptote, $m=31{\cdot}549$, and we could then replace (30) by the equation

$$d=0{\cdot}622\,.\,\frac{m}{m-ne^{kt}}. \qquad \ldots\ldots\ldots \qquad (31)$$

From this we should derive for 0° the specific gravity 0·643 instead of 0·622, and the other numbers of the above Table would have to be increased proportionately. But we are not justified in making so wide an application of the formula (26), as it has been merely derived empirically from the values contained in Table III.; and among these, the values belonging to the lowest temperatures are insecure. We must therefore for the present regard the limit of $A(s-\sigma)\dfrac{a}{a+t}$ as unknown, and con-

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and hence, for the temperature 0°,

$$d_0=\frac{Ap_0v_0}{m-n}.$$

Eliminating $p_0v_0$ from these equations, we arrive at the equation

$$d=d_0\frac{m-n}{m-ne^{kt}},$$

from which, on replacing $d_0$ by its value 0·622, the equation (30) is at once obtained.—1864.]

tent ourselves with an approximation similar to that furnished by the numbers in the foregoing Table; so much however we may conclude, that these numbers are rather too small than too large*.

By combining (V$a$) with the equation (III), which was derived from the first fundamental principle, we can eliminate $A(s-\sigma)\frac{dp}{dt}$, and thus obtain the equation

$$\frac{dr}{dt}+c-h=\frac{r}{a+t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

by means of which, the quantity $h$, described above as negative, can be more nearly determined. For $c$ and $r$ let the expressions in (23$b$) and (24) be substituted, and for $a$ the number 273; we then obtain

$$h=0{\cdot}305-\frac{606{\cdot}5-0{\cdot}695t-0{\cdot}00002t^2-0{\cdot}0000003t^3}{273+t}\dagger; \quad . \quad (33)$$

and from this we derive among others the following values for $h$:

TABLE VI.‡

| $t$. | 0°. | 50°. | 100°. | 150°. | 200°. |
|---|---|---|---|---|---|
| $h$. | −1·916 | −1·465 | −1·133 | −0·879 | −0·676 |

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* [For a comparison of the theoretical determination of the density of vapour, as here expounded, with more recent results of observations, see *Appendix* C.]

† [When we employ the simplified formula

$$r=607-0{\cdot}708\,.\,t,$$

given in the note to equation (24), and retain the value 0·305 given by Regnault for the sum $\frac{dr}{dt}+c$, the equation for $h$ assumes the simpler form

$$h=0{\cdot}305-\frac{607-0{\cdot}708\,.\,t}{273+t},$$

which may also be written thus:

$$h=1{\cdot}013-\frac{800{\cdot}3}{273+t}.$$

This formula for $h$ is a still more convenient one.—1864.]

‡ [The conclusion, that $h$ is a negative magnitude, was also drawn by Rankine, in a memoir published almost at the same time as my own, in the Transactions of the Royal Society of Edinburgh (vol. xx.), wherein the magnitude itself is represented by $K_r$. The above equation (32), however, which serves for the exact numerical calculation of $h$, was not established by Rankine, since he was not then in possession of the necessary second fundamental theorem of the mechanical theory of heat. The equation employed by

In a manner similar to that already pursued in the case of aqueous vapour, the equation (V$a$) might be applied to the vapours of other fluids, and the results thus obtained compared with each other, as is done in Table I. with the numbers calculated by Clapeyron. We will not, however, enter further upon this application*.

We must now endeavour to determine, at least approximately, the numerical value of the constant A, or, what is more usual, the value of the fraction $\frac{1}{A}$; in other words, to determine the *equivalent of work for the unit of heat*†.

Pursuing the same course as that of Meyer and Holtzmann, we can in the first place make use of equation (10$a$), developed for permanent gases. This equation was

$$c' = c + AR;$$

and when for $c$ the equivalent expression $\frac{c'}{k}$ is introduced, we have

$$\frac{1}{A} = \frac{k.R}{(k-1).c'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

For atmospheric air, the number 0·267, as given by De Laroche and Bérard, is generally assumed for $c'$; and for $k$, as given by Dulong, 1·421. For the determination of $R = \frac{p_0 v_0}{a + t_0}$, we know that the pressure of one atmosphere (760 millims.) on a square metre amounts to 10333 kils.; and the volume of 1 kil. of atmospheric air under the said pressure and at the temperature of the

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him for the determination of this magnitude, numbered (30) in his memoir, would agree with my equation (III), deduced from the first fundamental theorem, had not Rankine, contrary to myself, assumed the law of M. and G. to be true for saturated vapours.—1864.]

* [The experimental data when this was written being too incomplete and unsafe, further pursuit of the subject appeared inappropriate. Regnault, however, having now published the second series of his extremely valuable investigations (*Rélations des Expériences*, t. ii.), in which the vapour-tension, the latent heat of evaporation, and the specific heat for a considerable number of liquids are determined in the same manner as was done for aqueous vapour in the first series, it would be easy to extend to vapours of other liquids the calculations which above have reference to aqueous vapour.—1864.]

† [Now called, more briefly, *the mechanical equivalent of heat.*—1864.]

freezing-point is $=0{\cdot}7733$ of a cubic metre. From this follows

$$R=\frac{10333.0{\cdot}7733}{273}=29{\cdot}26,$$

and hence

$$\frac{1}{A}=\frac{1{\cdot}421\times 29{\cdot}26}{0{\cdot}421\times 0{\cdot}267}=370;$$

that is to say, by the expenditure of one unit of heat (the quantity which raises 1 kil. of water from 0° to 1°) a weight of 370 kils. can be raised to a height of 1 metre. This value, however, on account of the uncertainty of the numbers 0·267 and 1·421, is deserving of little confidence. Holtzmann gives as the limits between which he is in doubt the numbers 343 and 429*.

The equation (V*a*) developed for *vapours* can be made use of for the same purpose. If we apply it to the vapour of *water*, the foregoing determinations, whose result is expressed in equation (26), may be used. If, for example, the temperature 100° be chosen, and for $p$ the corresponding pressure of one atmosphere $=10333$ kils. be substituted in the above equation, we obtain

$$\frac{1}{A}=257\,.\,(s-\sigma).\dagger \quad \ldots\ldots\ldots \quad (35)$$

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* [The remark in the text on the uncertainty of the experimental data employed in this calculation, has been recently verified by Regnault's finding that the specific heat of atmospheric air is represented by 0·2375, instead of by the number 0·267, which was previously considered to be the most trustworthy. By introducing the former into the above calculation the value 416, instead of 370, is obtained for the mechanical equivalent of heat. If moreover we replace the number 1·421 by 1·410, which probably more nearly expresses the true proportion between the two specific heats, we obtain 424 as the result of the calculation. I may also here remark that the number 29·26 of the text requires changing to 29·27: this, however, has no influence upon the given result, since the latter is calculated only to three figures.—1864.]

† [This equation may obviously be directly deduced from the equation (V *a*); for the latter gives at once

$$\frac{1}{A}=\frac{(a+t)\frac{dp}{dt}}{r}(s-\sigma).$$

The differential coefficient $\frac{dp}{dt}$, here involved, has, according to Regnault, at 100°, the value 27·200, expressed in millimetres of mercury, and when this number is reduced to the measure of pressure above employed, *i. e.* to kilo-

If it be now assumed with Gay-Lussac that the specific gravity of aqueous vapour is 0·6235, we obtain $s=1{\cdot}696$, and hence

$$\frac{1}{A}=437.$$

Similar results are obtained from the values of C contained in Table I., which Clapeyron and Thomson have calculated from equation (V). If these be regarded as the values of $A(a+t)$ corresponding to the adjacent temperatures, a series of numbers are obtained for $\frac{1}{A}$, all of which lie between 416 and 462.

It has been mentioned above, that the specific gravity of aqueous vapour at its maximum density given by Gay-Lussac is probably a little too small, and the same may be said of the specific gravities of vapours generally. Hence the value of $\frac{1}{A}$ derived from these must be considered a little too large. If the number 0·645 given in Table V. for the vapour of water, and from which we find $s=1{\cdot}638$, be assumed, we obtain

$$\frac{1}{A}=421;$$

which value is perhaps still too great, though probably not much. As this result is preferable to that obtained from the atmospheric air, we may conclude *that the equivalent of work for the unit of heat is the raising of something over* 400 *kils. to a height of* 1 *metre.*

With this theoretic result, we can compare those obtained by Joule from direct observation. From the heat produced by magneto-electricity he found

$$\frac{1}{A}=460^{*}.$$

From the quantity of heat absorbed by atmospheric air during its expansion,

$$\frac{1}{A}=438\dagger;$$

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logrammes on a square metre, becomes 369·8. On substituting further, for $a+t$ and $r$, the values 373 and 536·5, corresponding to the temperature 100°, the equation (35) is obtained.—1864.]

* Phil. Mag. vol. xxiii. p. 441. The English measure has been reduced to the French standard.

† Ibid. vol. xxvi. p. 381.

and as mean of a great number of experiments in which the heat developed by the friction of water, of mercury, and of cast iron was observed,

$$\frac{1}{A}=425^*.$$

The coincidence of these three numbers with each other, notwithstanding the difficulty of the experiments, dispels all doubt as to the correctness of the principle which asserts the equivalence of heat and work; and the agreement of the same with the number 421 corroborates in like manner the truth of Carnot's principle in the form which it assumes when combined with our first fundamental principle.

## APPENDICES TO FIRST MEMOIR [1864].

### APPENDIX A. (Page 27.)

### COMPLETED DEDUCTION OF THE EXPRESSION FOR THE EXPENDED HEAT GIVEN IN EQUATION (3).

In developing the expression for the expended heat given in the equation (3) of the text, certain magnitudes have been left unconsidered which have no influence on the result, and which in order to simplify the calculus are usually disregarded in all similar cases. One disadvantage of this procedure, however, is that to the reader doubts may thereby arise as to the accuracy of the result. On this account I deem it desirable to supply here a somewhat more complete deduction of the equation (3).

In doing so it must be remembered that the following development, as well as that given in the text, holds not only for a gas, but also for every other body whose condition is determined by its temperature and its volume, and whose variations of volume occur in such a manner that force and resistance differ so little from one another as to justify, in calculation, the assumption of their equality. We shall assume, moreover, that the sole

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* Phil. Mag. vol. xxxv. p. 534.

exterior force which influences the changes of volume acts everywhere normally and equally upon the surface, so that in general it may be termed a pressure, inasmuch as any pull which may possibly take place may be regarded as a negative pressure.

Let us consider the quantity of heat $dQ$ which a body must receive during an increase of temperature equal to $dt$, and an augmentation of volume equal to $dv$. For a differential which depends, as $dQ$ does, on the differentials of two independent variables, it is customary to employ the equation

$$dQ=\left(\frac{dQ}{dt}\right)dt+\left(\frac{dQ}{dv}\right)dv, \quad . \quad . \quad . \quad . \quad . \quad \text{(a)}$$

which by the introduction of simple symbols for the partial differential coefficients, that is to say by putting

$$\left.\begin{array}{l}\left(\dfrac{dQ}{dt}\right)=M,\\[2ex] \left(\dfrac{dQ}{dv}\right)=N,\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(b)}$$

may be thus written:

$$dQ=Mdt+Ndv. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(c)}$$

Strictly speaking, however, this equation is incomplete. The complete expression for $dQ$ contains an infinity of terms, of the successive orders one, two, three, &c., in reference to the differentials $dt$ and $dv$. By actually introducing the terms of the second order, and merely indicating the remaining ones, the equation for $dQ$ becomes

$$dQ=Mdt+Ndv+\frac{1}{2}\left\{\left(\frac{dM}{dt}\right)dt^2+\left[\left(\frac{dM}{dv}\right)+\left(\frac{dN}{dt}\right)\right]dt\,dv\right.$$
$$\left.+\left(\frac{dN}{dv}\right)dv^2\right\}+\&c.\ldots \quad . \quad . \quad . \quad . \quad \text{(d)}$$

Now it is clear that when an expression contains terms of the first order in the differentials, all accompanying terms of the second or of higher order may be neglected. Accordingly the two first terms on the right of the above equation are the only ones which are usually written. When in any calculation, however, the terms of the first order cancel each other, so that among the terms of the final result those of the second are the lowest in order, then from the commencement all terms of the second order must be taken into consideration, and it is only those of the third and higher orders which can be neglected. This occurs in the case under consideration, since the expression for the expended heat, containing the product $dv\,dt$ as a factor, is necessarily of the second order. The calculation, given in the text, was conducted, it is true, in such a manner that only those terms of the second order were neglected which were without influence on the final result, nevertheless for the sake of completeness and rigour, these terms in the following calculation shall also be written.

When any relation whatever is given between the variables $t$ and $v$, in virtue of which the one may be regarded as a function of the other, the equation (d) may be written so that the terms on the right proceed simply according to ascending powers of a single variable. If $t$, for instance, be regarded as a function of $v$, and the following symbols be introduced for the differential coefficients of $t$ according to $v$,

$$\frac{dt}{dv}=\xi;\quad \frac{d^2t}{dv^2}=\xi';\ \text{\&c.}\ldots$$

then we shall have

$$dt=\xi dv+\xi'\frac{dv^2}{2}+\text{\&c.}\ldots\ldots, \qquad \text{(e)}$$

whereby the equation (d) will become

$$dQ=(M\xi+N)dv+\left\{\left(\frac{dM}{dt}\right)\xi^2+\left[\left(\frac{dM}{dv}\right)+\left(\frac{dN}{dt}\right)\right]\xi+\left(\frac{dN}{dv}\right)+M\xi'\right\}\frac{dv^2}{2}+\text{\&c.} \qquad \text{(f)}$$

If, on the other hand, $v$ be regarded as a function of $t$ and we introduce the symbols

$$\frac{dv}{dt}=\eta;\quad \frac{d^2v}{dt^2}=\eta';\ \text{\&c.}\ldots$$

we shall have

$$dv=\eta dt+\eta'\frac{dt^2}{2}+\text{\&c.}\ldots, \qquad \text{(g)}$$

and accordingly

$$dQ=(M+N\eta)dt+\left\{\left(\frac{dM}{dt}\right)+\left[\left(\frac{dM}{dv}\right)+\left(\frac{dN}{dt}\right)\right]\eta+\left(\frac{dN}{dv}\right)\eta^2+N\eta'\right\}\frac{dt^2}{2}+\text{\&c.}\ldots\ldots \qquad \text{(h)}$$

These equations are to be applied to the four changes to which the gas or the body under consideration is to be subjected, and which are to proceed according to two different laws.

We consider first the changes of volume which occur at a constant temperature. In this case the differential coefficients of $t$ according to $v$, that is to say, the magnitudes $\xi$, $\xi'$, &c., must be put equal to zero. Consequently in order to determine the quantity of heat which the body must receive during an expansion $dv$ from its initial state without change of temperature, we may employ the equation (f) in a simplified form; the terms which contain the factors $\xi$, $\xi'$, &c. . . being omitted. Stopping at terms of the second order, we thus arrive at the equation

$$dQ = N dv + \left(\frac{dN}{dv}\right)\frac{dv^2}{2}.$$

In order to express, in a similar manner, the quantity of heat which the body must receive when at the temperature $t-dt$ it expands from the volume $v+\delta v$ to the volume $v+\delta v+d'v$, we must replace $dv$ in the foregoing equation by $d'v$, and in place of N and $\left(\frac{dN}{dv}\right)$ introduce the values which these magnitudes possess at the slightly changed temperature $t-dt$, and the somewhat altered volume $v+\delta v$. Assuming these values to be expressed in series proceeding according to powers of $dt$ and $dv$, we need only retain terms of the first order in the case of N, since the latter quantity is multiplied by a differential in the above equation, and all subsequent terms in N would merely lead, in $dQ$, to terms of a higher order than the second. Accordingly in place of N we have to put

$$N + \left(\frac{dN}{dv}\right)\delta v - \left(\frac{dN}{dt}\right)dt.$$

In the value of $\left(\frac{dN}{dv}\right)$, which in the above equation is multiplied by the square of a differential, we may for the same reason omit terms of the first order, and simply retain the original value $\left(\frac{dN}{dv}\right)$. Accordingly if we represent the quantity of heat received during this expansion by $d'Q$, we have the equation

$$d'Q = \left[N + \left(\frac{dN}{dv}\right)\delta v - \left(\frac{dN}{dt}\right)dt\right]d'v + \left(\frac{dN}{dv}\right)\frac{d'v^2}{2}.$$

Subtracting this quantity of heat from the former, we obtain the *heat expended* during the whole process, that is

$$\left.\begin{aligned} dQ-d'Q=Ndv-\left[N+\left(\frac{dN}{dv}\right)\delta v-\left(\frac{dN}{dt}\right)dt\right]d'v \\ +\left(\frac{dN}{dv}\right)\frac{dv^2-d'v^2}{2}. \end{aligned}\right\} \quad . \quad . \quad . \quad \text{(i)}$$

This expression differs only in the last term from the one numbered (2) in the text, and this term is easily recognized to be only apparently of the second order, for the differentials $dv$ and $d'v$ can only differ from one another by a magnitude infinitely small relative to their own proper values, so that the difference $dv^2-d'v^2$ is an infinitesimal of an order higher than the second.

We proceed now to changes of volume of another description, —to changes produced without either communicating heat to the body or abstracting it therefrom. In this case the temperature must change with the volume, and one of these magnitudes being chosen as the independent variable, we have to determine the differential coefficients of the other. We shall consider $v$ as a function of $t$, and determine the differential coefficients $\eta$, $\eta'$ &c. of the former. To this end we must employ the equation (h), and put therein $dQ=0$, whereby we shall have

$$\left.\begin{aligned} 0=(M+N\eta)dt+\left\{\left(\frac{dM}{dt}\right)+\left[\left(\frac{dM}{dv}\right)+\left(\frac{dN}{dt}\right)\right]\eta \right. \\ \left. +\left(\frac{dN}{dv}\right)\eta^2+N\eta'\right\}\frac{dt^2}{2}+\&c. \end{aligned}\right\} \quad . \quad . \quad . \quad \text{(k)}$$

Since this equation must hold for any value of $dt$, the factor of each power of $dt$ must vanish. Equating to zero the factor of the first power of $dt$, we have

$$M+N\eta=0,$$

whence we deduce

$$\eta=-\frac{M}{N}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(l)}$$

The magnitude $\eta$ is thereby determined as a function of $t$ and $v$. The next differential coefficient $\eta'$ might be similarly determined by equating to zero the factor of the second power of $dt$; it is not necessary, however, actually to perform this calculation, since $\eta'$ may also be found by differentiating the expression for $\eta$, already found completely, according to $t$; that is to say we may differentiate according to $t$ and $v$, and regarding $v$ as a function of $t$, put $\frac{dv}{dt}=\eta$. The succeeding differential coefficients of $v$ according to $t$, if required, would have to be calculated in a similar manner.

Now to determine the magnitude $\delta v$ by which the volume of the body must increase from its initial value, in order that the temperature may sink from $t$ to $t-dt$, we must employ the equation (g), and write therein $\delta v$ in place of $dv$, and $-dt$ in place of $dt$. By so doing and contenting ourselves with terms whose order does not exceed the second, we obtain the equation

$$\delta v=-\eta dt+\eta'\frac{dt^2}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(m)}$$

Similarly, to find the value of $\delta' v$, that is to say how much the body, starting from the volume $v+dv$, must expand in order that the temperature may fall from $t$ to $t-dt$, we must replace $\eta$ in the foregoing expression by its changed value $\eta+\left(\frac{d\eta}{dv}\right)dv$. The corresponding change of $\eta'$ need not be considered, since the only terms which could arise therefrom would be of an order higher than the second. We have therefore

$$\delta' v=-\left[\eta+\left(\frac{d\eta}{dv}\right)dv\right]dt+\eta'\frac{dt^2}{2}. \quad . \quad . \quad . \quad \text{(n)}$$

Besides these equations for $\delta v$ and $\delta' v$, another must exist involving the four changes of volume which the body suffers successively, during the process. This is the equation which expresses the condition that the body ultimately returns to its initial volume, and which is thus written:

$$dv+\delta' v=\delta v+d' v. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(o)}$$

From this it follows that

$$d' v=dv+\delta' v-\delta v,$$

an equation which, on substituting for $\delta v$ and $\delta' v$ their respective values as already found, becomes

$$d' v=dv-\left(\frac{d\eta}{dv}\right)dv\,dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(p)}$$

We now return to equation (i), which represents the *heat expended* during the whole process, and substitute therein the values of $\delta v$ and $d'v$ as given by the equations (m) and (p). Neglecting all terms of an order higher than the second, we thus find

$$dQ-d'Q=\left[\left(\frac{dN}{dt}\right)+\left(\frac{dN\eta}{dv}\right)\right]dv\,dt\,; \quad . \quad . \quad . \quad . \quad \text{(q)}$$

and if in this we replace $\eta$ by its value given in (l), we have

$$dQ-d'Q=\left[\left(\frac{dN}{dt}\right)-\left(\frac{dM}{dv}\right)\right]dv\,dt, \quad . \quad . \quad . \quad . \quad . \quad \text{(r)}$$

which, by introducing in place of M and N the original symbols for partial differential coefficients, becomes

$$dQ-d'Q=\left[\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)\right]dv\,dt. \quad . \quad . \quad . \quad \text{(s)}$$

This is the equation (3) given in the text, to re-establish which, in a somewhat more rigorous manner, was the object of the present Appendix.

## APPENDIX B. (Page 28.)

### INTEGRATION OF THE DIFFERENTIAL EQUATION (II).

It will perhaps be useful to elucidate somewhat more fully the manner of obtaining the equation (II$a$) from the equation (II).

The equation (II), which in the text is thus written,

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)=\frac{A.R}{v}, \quad . \quad . \quad . \quad . \quad \text{(II)}$$

may be called *a partial differential equation of the second order*, although it differs somewhat from the ordinary equations of this kind, since in the latter it is usual to assume, tacitly, the fulfilment of the condition

$$\frac{d}{dv}\left(\frac{dQ}{dt}\right)=\frac{d}{dt}\left(\frac{dQ}{dv}\right).$$

In order to pass, by integration, from the equation (II) to a differential equation of the first order, we may proceed as follows. In the first place we take any function whatever of $t$ and $v$ as a representative of one of the two partial differential coefficients $\left(\frac{dQ}{dt}\right)$ and $\left(\frac{dQ}{dv}\right)$. For instance, M being any such function, we put

$$\left(\frac{dQ}{dt}\right)=\mathrm{M}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(a)}$$

and introduce this value into the equation (II). The substituted term being then removed from the left to the right of the equation, we have

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right)=\left(\frac{d\mathrm{M}}{dv}\right)+\frac{\mathrm{AR}}{v}.$$

Integrating this equation according to $t$, and under the hypothesis that $v$ remains constant, we find

$$\left(\frac{dQ}{dv}\right)=\int\left(\frac{d\mathrm{M}}{dv}\right)dt+\mathrm{AR}\,\frac{t}{v}+\phi(v), \quad . \quad . \quad . \qquad \text{(b)}$$

where $\phi(v)$ denotes an arbitrary function of $v$. Having thus obtained an expression for the partial differential coefficient $\left(\frac{dQ}{dv}\right)$, we next form the *complete differential equation of the first order*,

$$dQ=\left(\frac{dQ}{dt}\right)dt+\left(\frac{dQ}{dv}\right)dv,$$

and substitute therein the assumed function M for $\left(\frac{dQ}{dt}\right)$, and the expression just obtained for $\left(\frac{dQ}{dv}\right)$. We thus arrive at the equation

$$dQ=\mathrm{M}dt+\left[\int\left(\frac{d\mathrm{M}}{dv}\right)dt+\mathrm{AR}\frac{t}{v}+\phi\,(v)\right]dv. \quad . \quad . \quad . \qquad \text{(c)}$$

The expression

$$\mathrm{M}dt+\left[\int\left(\frac{d\mathrm{M}}{dv}\right)\,dt+\phi(v)\right]dv,$$

which forms a constituent part of the right-hand side of this equation, is at once seen to be the complete differential of a function of $t$ and $v$; for the factor of $dt$, when differentiated according to $v$, gives the same result, $\left(\frac{d\mathrm{M}}{dv}\right)$, as does the differentiation, according to $t$, of the factor of $dv$. For this expression, therefore, we may introduce the symbol $d$S; and since M represents an arbitrary function of $t$ and $v$, and $\phi(v)$ an arbitrary function of $v$, S itself must be regarded as a perfectly arbitrary function of $t$ and $v$. The introduction of the symbol into the equation (c) gives

$$dQ=dS+AR\frac{t}{v}\,dv. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

For the further treatment of this equation it will be convenient to introduce, in place of the simple magnitude $t$ in the last term, the sum $a+t$, where $a$ is the constant defined in the text. To do this the last equation may be written in the form

$$dQ=dS-AR\frac{a}{v}\,dv+AR\,\frac{a+t}{v}\,dv;$$

or rather thus:

$$dQ=d(S-ARa\log v)+AR\,\frac{a+t}{v}\,dv, \quad . \quad . \quad (e)$$

which latter may be simplified by putting

$$S-ARa\log v=U, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (f)$$

where U is again an arbitrary function of $t$ and $v$, since an algebraical sum which consists of an arbitrary, and of a known function of the same variables must itself be regarded as an arbitrary function of these variables. By introducing this new symbol U into the equation (e), we obtain the equation (II$a$) of the text, that is to say,

$$dQ=dU+AR\frac{a+t}{v}\,dv. \quad . \quad . \quad . \quad . \quad (IIa)$$

The object of the introduction of the sum $a+t$ in place of the quantity $t$, is to render the last term susceptible of a simple mechanical meaning. In fact, from the equation

$$pv=R(a+t),$$

which applies to permanent gases, it follows that

$$AR\,\frac{a+t}{v}\,dv=Apdv; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (g)$$

and since $pdv$ denotes the exterior work done during the expansion $dv$, the last term of the equation (II$a$) obviously represents the heat-equivalent of the exterior work.

The more general differential equation of the second order,

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)=A\left(\frac{dp}{dt}\right), \quad . \quad . \quad . \quad . \quad (II')$$

given in the first note on p. 28, may be treated in the same manner as we have just treated the equation (II), and thereby the following complete differential equation of the first order obtained,

$$dQ=dU+Apdv. \qquad . \ . \ . \ . \ . \ . \ . \qquad (\text{II}'a)$$

The function U, here introduced, is of great importance in the theory of heat; it will frequently come under discussion in the following memoirs. As stated in the text, it involves two of the three quantities of heat which enter into consideration when a body changes its condition; these are the augmentation of the so-called *sensible* or *actually present* heat, and the heat *expended in interior work*.

## APPENDIX C. (Page 65.)

### ON THE DENSITY OF SATURATED AQUEOUS VAPOUR.

The conclusions drawn in the text, relative to the deviation from the law of M. and G. presented by saturated vapours, and which at that time stood isolated, inasmuch as it was the universal custom to apply the law in question also to vapours, have since been experimentally verified by Fairbairn and Tate*. The following summary of a note communicated by me to the Academy of Sciences at Paris †, will show how far these results of observation agree with my formula.

Under (30), in the text, is given the equation

$$d=0{\cdot}622\,\frac{m-n}{m-ne^{kt}},$$

wherein $d$ denotes the density of the saturated aqueous vapour, in comparison with atmospheric air at the same temperature and under the same pressure, and $m, n, k$ are three constants having the values

$$m=31{\cdot}549, \quad n=1{\cdot}0486, \quad k=0{\cdot}007138.$$

By means of this equation the values of $d$ were calculated which are contained in Table V. of the text (p. 64). If $s$ be the volume of a kilogramme of saturated vapour, and $v$ that of a kilogramme of atmospheric air at the same temperature and pressure, the fraction $\frac{v}{s}$ may be put instead of $d$. The reciprocal fraction, therefore, will, according to the foregoing equation, have the value

$$\frac{s}{v}=\frac{m-ne^{kt}}{0{\cdot}622.(m-n)}.$$

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* Proceedings of the Royal Society, 1860; and Phil. Mag. Fourth Series, vol. xxi. p. 230.

† *Comptes Rendus*, vol. lii. p. 706 (April 1861).

This equation may be written in the more convenient form

$$\frac{s}{v}=M-N\alpha^{t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where the constants M, N, $\alpha$ have the following values, dependent on the values of $m$, $n$, $k$ previously given,

$$M=1{\cdot}6630, \quad N=0{\cdot}05527, \quad \alpha=1{\cdot}007164.$$

Strictly speaking the difference $s-\sigma$, where $\sigma$ is the volume of a kilogramme of water, should enter into the foregoing equations instead of the quantity $s$, since this difference occurs in the equation (26), from which (30) is deduced. The volume of water being very small, however, when compared with that of vapour, the quantities $s$ and $s-\sigma$ may, in an approximate calculation, be regarded as equal to one another.

In the following Table the values of $s$, calculated from the above formula for $\frac{s}{v}$, are placed side by side with those deduced by Fairbairn and Tate from their observations, and with the values formerly assumed as corresponding to the equation

$$\frac{s}{v}=\frac{1}{0{\cdot}622}.$$

| Temperature in degrees Centigrade. | Volumes of a kilogramme of saturated aqueous vapour in cubic metres according to | | |
|---|---|---|---|
| | the former assumption. | the equation (a). | observation. |
| 58°·21 | 8·38 | 8·23 | 8·27 |
| 68·52 | 5·41 | 5·29 | 5·33 |
| 70·76 | 4·94 | 4·83 | 4·91 |
| 77·18 | 3·84 | 3·74 | 3·72 |
| 77·49 | 3·79 | 3·69 | 3·71 |
| 79·40 | 3·52 | 3·43 | 3·43 |
| 83·50 | 3·02 | 2·94 | 3·05 |
| 86·83 | 2·68 | 2·60 | 2·62 |
| 92·66 | 2·18 | 2·11 | 2·15 |
| 117·17 | 0·991 | 0·947 | 0·941 |
| 118·23 | 0·961 | 0·917 | 0·906 |
| 118·46 | 0·954 | 0·911 | 0·891 |
| 124·17 | 0·809 | 0·769 | 0·758 |
| 128·41 | 0·718 | 0·681 | 0·648 |
| 130·67 | 0·674 | 0·639 | 0·634 |
| 131·78 | 0·654 | 0·619 | 0·604 |
| 134·87 | 0·602 | 0·569 | 0·583 |
| 137·46 | 0·562 | 0·530 | 0·514 |
| 139·21 | 0·537 | 0·505 | 0·496 |
| 141·81 | 0·502 | 0·472 | 0·457 |
| 142·36 | 0·495 | 0·465 | 0·448 |
| 144·74 | 0·466 | 0·437 | 0·432 |

From this Table it will be seen that the observed values agree much better with those calculated from my equation than with the formerly assumed values; and further, that the differences which still exist between the observed values and those of my formula are generally of such a character that the observed values differ from the formerly assumed ones still more than do the values of my formula.

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## ON THE INFLUENCE OF PRESSURE UPON THE FREEZING OF LIQUIDS*.

Mr. William Thomson has described an experimental investigation, conducted by himself†, and originating in a theoretic view entertained by his brother, James Thomson. The latter had concluded, from the known principle of Carnot, that by an increase of pressure the freezing-point of water must be lowered, which view was completely verified by experiment.

Some time ago I published a theoretic memoir ‡, in which the principal part of Carnot's law is retained, but altered in one minor particular. This alteration rendered certain of the conclusions heretofore deduced from the principle impossible, while others remained valid; the latter being those whose correctness or high probability had been demonstrated by experiment. Now as the above conclusion regarding the freezing-point of fluids has also been substantiated experimentally, and thus in a scientific point of view has obtained a greater significance than one would be inclined at first sight to attribute to so small a difference, I feel myself called upon, in behalf of my theory, to show that my alteration of Carnot's principle is in no way opposed to this result§. Moreover, by a simultaneous ap-

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* Note published in Poggendorff's Annalen, September 1850, vol. lxxxi. p. 168; and translated in the Philosophical Magazine, S. 4. vol. ii. p. 548.

† Proceedings of the Royal Society of Edinburgh, February 1850; and Phil. Mag. S. 3. vol. xxxvii. p. 123.

‡ [First Memoir of this collection.]

§ I need hardly mention that I have here no thought of disputing with Mr. J. Thomson the *priority* of his ingenious application of the principle of Carnot.

plication of the first fundamental principle which I have assumed, a new conclusion is arrived at which, although practically unimportant on account of the smallness of the numbers which it involves, nevertheless deserves expression on account of its theoretic interest.

A lengthened analysis of the subject is not here necessary. The considerations dwelt upon in my former paper regarding the evaporation*, may be applied almost *verbatim* to the freezing of a liquid. We have only to conceive the vessel impervious to heat to be filled with the body partly in the solid and partly in the liquid state, instead of, as in the former case, partly in the liquid and partly in the vaporiform state; and then, instead of permitting a fresh portion of the liquid to evaporate, to allow a portion of it to freeze, &c.

One of the two principal equations deduced therefrom was

$$r = A(a+t)\,(s-\sigma)\,\frac{dp}{dt}; \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(Va)}$$

and this holds good for the freezing also, $p$ and $t$ again denoting the pressure and temperature, and $\sigma$ the volume of a unit of weight of the liquid, whereas $s$ denotes the volume of a unit of weight of a solid body (instead of vapour, as in the former case), and $r$ the latent heat of the freezing (instead of the evaporation). The latter, however, must be here taken as negative, because by freezing, heat will be *liberated*, and not rendered *latent*. We have therefore

$$\frac{dt}{dp} = -\frac{A(a+t)\ (s-\sigma)}{r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let the value of $\frac{1}{A}$, given by Joule in his last investigation† as the most probable result of all his experiments, that is 423·55 (772 English), be here substituted, as also for $a$ the number 273; further, with regard to the water, $t=0$, $r=79$, $\sigma=0·001$, and $s=0·001087$; and, finally, let $p$ be expressed in atmospheres, instead of in kilogrammes, pressing upon a square metre, we then obtain

$$\frac{dt}{dp} = -0·00733,$$

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* [First Memoir, pp. 30 and 47.]

† Phil. Trans. of the Royal Society of London for the year 1850, part 1. p. 61.

which may be regarded as equal to the value calculated by James Thomson, and corroborated by William Thomson, namely $-0{\cdot}0075$.

The other principal equation deduced from the principle of the equivalence of heat and work was

$$\frac{dr}{dt}+c-h=\mathrm{A}(s-\sigma)\frac{dp}{dt}. \quad . \quad . \quad . \quad . \quad . \quad \text{(III)}$$

To apply this to the case of freezing, we must regard $c$ and $h$ as two quantities which differ from the specific heats of the liquid and solid body only so far as they express, not the heat which must be imparted to a body when it is simply warmed, but that which is necessary when the pressure varies with the temperature in the manner indicated by equation (1). This difference, however, cannot be considerable, since Regnault* has found that water, by an additional pressure of 10 atmospheres, does not increase $\frac{1}{50}$th of a degree Cent. in temperature; besides this, as the differences for $c$ and $h$ take place both in the same sense, and hence in the difference $c-h$ are subtracted, we can set with a near approach to accuracy for $c-h$ the difference of both specific heats simply†. If the value of $\frac{dp}{dt}$ estimated from (1) be substituted in (III), and if the sign of $\frac{dr}{dt}$ be changed like that of $r$ in the former case, we have

$$\frac{dr}{dt}=c-h+\frac{r}{a+t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this we must conclude, that when the freezing-point changes, the latent heat must also change; for *water* $c=1$, and, according to Person‡, $h=0{\cdot}48$. Hence we have

$$\frac{dr}{dt}=0{\cdot}52+0{\cdot}29=0{\cdot}81;$$

that is to say, when the freezing-point of water is lowered by pressure, the latent heat decreases 0·81 for every degree.

We must not confound this result with that already expressed by Person§. From the circumstance that the specific heat of

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* *Mém. de l'Acad. de l'Inst. de France*, vol. xxi. Mém. VII.

† [In one of the following Memoirs a more accurate determination will be given.—1866.]

‡ *Comptes Rendus*, vol. xxx. p. 526.

§ Ibid. vol. xxiii. p. 336, and Poggendorff's *Annalen*, vol. lxx. p. 302.

ice is less than that of water, the latter concluded with great probability, that when the freezing-point, without increasing the pressure, is simply lowered by preserving the fluid perfectly motionless, the latent heat must then be less than at 0°. This decrease may be expressed by the equation

$$\frac{dr}{dt}=c-h\,;$$

the above equation (2) therefore shows that, when the freezing-point is lowered by pressure, the latent heat, besides the change due to the last-mentioned cause, suffers a still further diminution expressed by the quantity $\frac{r}{a+t}$; this in the case of water is $=0{\cdot}29$, and it is this quantity which corresponds, as equivalent, to the exterior work accomplished.

The recent observation of Person*, that ice does not melt completely at a definite temperature, but becomes softer immediately before it reaches the melting-point, I have left unnoticed, as its introduction would merely render the development more difficult, without serving any important end; for the decrease of latent heat, which corresponds, as equivalent, to the produced work, must be independent of the little irregularities which may take place during the melting.

## APPENDIX TO PRECEDING NOTE (1864).

### ON THE DIFFERENCE BETWEEN THE LOWERING OF THE FREEZING-POINT WHICH IS CAUSED BY CHANGE OF PRESSURE AND THAT WHICH MAY OCCUR WITHOUT ANY SUCH CHANGE.

It will not, perhaps, be without advantage to examine somewhat more closely what has been said at the end of the preceding Note. Allusion was there made to the well-known phenomenon of the lowering of the freezing-point of water brought about, not by increasing the pressure, but by protecting the water from all agitation; and it was asserted that in this case the latent heat, or rather the heat rendered sensible on solidification, must change according to a law different from that which obtains when the

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* *Comptes Rendus*, vol. xxx. p. 526.

freezing-point is lowered by pressure. The correctness of this assertion, and of the equation relative thereto, will be rendered manifest by the following considerations.

It was fully demonstrated in the First Memoir that the heat which must be imparted to (or abstracted from) a body in order to bring it from a given initial condition to another determinate one, may be divided into three parts; these are the quantity of heat which serves to increase that which is actually present in the body (the so-called sensible heat), the quantity expended on interior work, and the quantity expended on exterior work. It was stated that the two first parts are completely determined by the initial and final conditions of the body, and that for this determination it is not necessary to know in what manner the changes of the body have occurred, in other words, what path has been pursued by the body in passing from one condition to the other. If, therefore, we include both these quantities of heat in one symbol U, as was done in the First Memoir, we shall thereby obtain a magnitude which, on the supposition that the initial condition of the body is known, depends only upon its present condition, and not at all upon the manner in which it has been brought into this condition. The third quantity of heat, however, that expended on exterior work, depends not only upon the initial and final states of the body, but also upon the whole series of changes which it has undergone. The exterior work being represented by W, the heat expended in its production will be AW, and on adding to the latter the other two quantities of heat, we obtain the sum

$$U + AW$$

as the representative of the total heat which must be imparted to the body during its several changes.

Now let us conceive a unit of weight of water to be given at the temperature 0°, and let it be required to convert it into ice at a certain temperature $t_1$ below zero, the pressure remaining constantly equal to that of the atmosphere, and to express the quantity of heat which must be withdrawn from the mass in order to do so.

The simplest way of producing this change would be to allow the water to freeze at 0°, and then to cool the ice so formed to the temperature $t_1$. The process, however, may be also conducted in another way. We will allow the water, in its liquid state, to be cooled to a temperature $t$ between 0° and $t_1$, and then at this temperature to be solidified. When water which has been cooled to a temperature below zero freezes, a considerable quantity solidifies suddenly, and the heat thereby produced or rendered sensible raises the whole mass to 0° again, after which the further solidification proceeds gradually at the latter temperature. Nevertheless, although not actually feasible, we will conceive the sensible heat to be withdrawn from the mass during its solidification just as quickly as it is generated, so that the whole mass may freeze at one and the same temperature $t$. The ice thus produced shall then be subjected to a further cooling down to the temperature $t_1$.

In finding an expression for the quantity of heat which must be withdrawn from the mass during this process, we shall employ the following symbols :—

$r'$ the heat rendered sensible during gelation,
$c'$ the specific heat of the water,
$h'$ the specific heat of the ice,
$\sigma'$ the volume of a unit of weight of water,
$s'$ the volume of a unit of weight of ice.

The *letters*, it will be observed, are the same as in the foregoing Note, they are here accented because they have now slightly different values. In the preceding Note, in fact, they had reference to the case where the pressure increased according to a certain law with the diminution of temperature, whereas now the pressure is supposed to remain constantly equal to one atmosphere.'

Accordingly the heat which serves to bring the water from the temperature 0° to the temperature $t$ will be represented by the integral

$$\int_0^t c'dt.$$

Now the temperature $t$ being, by hypothesis, lower than 0°, $t$ is a negative quantity, and with it the value of the integral also; this expresses the fact that the heat in question is not imparted to, but withdrawn from the body. In a similar manner the quantity of heat which serves to depress the temperature of the ice thus formed from $t$ to $t_1$ is expressed by the integral

$$\int_t^{t_1} h'dt.$$

Lastly, $r'$ represents the heat rendered sensible during solidification, and to it a negative sign must be affixed in order to indicate that this quantity of heat must also be withdrawn from the body.

The algebraical sum of these three quantities constitutes the required expression for the total heat under consideration, and since this latter quantity is also expressible by the sum previously determined, we have the equation

$$-r'+\int_0^t c'dt+\int_t^{t_1} h'dt=\mathrm{U}+\mathrm{AW}. \quad . \quad . \quad . \quad . \quad \text{(a)}$$

The exterior work W still remains to be determined. The initial volume of the mass coincides with that of a unit of weight of water at the temperature 0°, and its final volume is that of a unit of weight of ice at the temperature $t_1$. These two volumes, as special values of $\sigma'$ and $s'$, being represented by $\sigma_0'$ and $s_1'$, the increment of volume will be expressed by $s_1'-\sigma_0'$. Since this increment of volume takes place under the constant pressure $p_0$ of one atmosphere, the corresponding work will be expressed by the product $p_0(s_1'-\sigma_0')$ simply, and the temperature at which freezing may have taken place is here a matter of indifference. By substituting this expression for W in the preceding equation, the latter takes the form

$$-r'+\int_0^t c'dt+\int_t^{t_1} h'dt=\mathrm{U}+\mathrm{A}p_0(s_1'-\sigma_0'). \quad . \quad \text{(b)}$$

We will next differentiate this equation according to the intermediate temperature $t$ at which freezing took place. Since now the magnitude U, in every case, depends solely upon the initial and final conditions, and since, in the special case now under consideration, the heat expended on exterior work is likewise independent of the intermediate temperature $t$, we may, in differentiating, consider the whole of the right-hand side of the equation as constant. The result, therefore, will be

$$-\frac{dr'}{dt}+c'-h'=0,$$

or

$$\frac{dr'}{dt}=c'-h'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(c)}$$

This is, in reality, the last equation of the preceding Note; the notation alone is slightly different, inasmuch as the accents which, for the sake of better definition, have been here introduced were not there employed; it being assumed that the different significations of the several quantities, due to the peculiar circumstances, were self-evident, even in the absence of distinguishing marks.

In order to render perfectly manifest the essential points of difference between the case just considered, where the lowering of the freezing-point is occasioned solely by protecting the water from agitation, and the case where the freezing-point is lowered by increasing the pressure, I will here also re-establish the equation (2) of the preceding Note, and in so doing retain the same method of reasoning which has just led to the equation (c).

Given, once more, a unit of weight of water at 0° to be converted into ice of the temperature $t_1$, but in such a manner that during the diminution of the temperature the pressure shall increase according to the law expressed by the equation (1) of the preceding Note. Since, under these circumstances, the diminution of the temperature $t$ likewise represents the depression of the freezing-point of the water, every temperature $t$ between 0° and $t_1$ may be assumed as that at which freezing takes place. Conceive the water, therefore, to be cooled in the liquid condition from 0° to $t$, then to be frozen at this temperature $t$, and finally to be cooled, in its solid state, from $t$ to $t_1$. The quantity of heat which must be withdrawn from the mass during this process will, on again calculating abstracted heat as a negative quantity imparted to the mass, be represented by the algebraical sum

$$-r+\int_0^t cdt+\int_t^{t_1} hdt.$$

Equating this sum to the expression $U+AW$, which applies generally to all changes, we have, corresponding to (a), the following equation:

$$-r+\int_0^t cdt+\int_t^{t_1} hdt=U+AW. \quad . \quad . \quad . \quad (d)$$

The exterior work W must here be determined anew, and its determination under the present assumed circumstances will not be so simple as in the previously considered case, since the pressure, instead of being constant, is now dependent upon the temperature. During the cooling of the water from 0° to $t$ the volume changes from $\sigma_0$ to $\sigma$ under variable pressure; during the process of gelation the volume changes from $\sigma$ to $s$ under constant pressure; and as the ice finally cools from $t$ to $t_1$ the volume changes from $s$ to $s_1$ again under variable pressure. The total work therefore is

$$\mathrm{W}=p(s-\sigma)+\int_{\sigma_0}^{\sigma} p\,d\sigma+\int_{s}^{s_1} p\,ds,$$

or, otherwise expressed,

$$\mathrm{W}=p(s-\sigma)+\int_{0}^{t} p\frac{d\sigma}{dt}\,dt+\int_{t}^{t_1} p\frac{ds}{dt}\,dt,$$

where $p$ is the function of the temperature which defines the pressure.

On substituting this expression for W in equation (d), we have

$$-r+\int_0^t c\,dt+\int_t^{t_1} h\,dt=\mathrm{U}+\mathrm{A}\left[p(s-\sigma)+\int_0^t p\frac{d\sigma}{dt}\,dt+\int_t^{t_1} p\frac{ds}{dt}\,dt\right]. \quad \text{(e)}$$

We will now differentiate this equation according to $t$, as we formerly did the equation (b), and remember, in doing so, that the quantity U is independent of the intermediate temperature $t$. We thus obtain the equation

$$-\frac{dr}{dt}+c-h=\mathrm{A}\left[(s-\sigma)\frac{dp}{dt}+p\frac{d(s-\sigma)}{dt}+p\frac{d\sigma}{dt}-p\frac{ds}{dt}\right]$$

$$=\mathrm{A}(s-\sigma)\frac{dp}{dt},$$

whence we deduce

$$\frac{dr}{dt}=c-h-\mathrm{A}(s-\sigma)\frac{dp}{dt}. \quad \ldots\ldots \quad \text{(f)}$$

Replacing therein the expression $\mathrm{A}(s-\sigma)\frac{dp}{dt}$ by $-\frac{r}{a+t}$, in accordance with the equation (1) of the preceding Note, we obtain the equation there marked (2), namely,

$$\frac{dr}{dt}=c-h+\frac{r}{a+t}. \quad \ldots\ldots\ldots \quad \text{(g)}$$

On comparing the formation of the equation (f) or (g) with that of the equation (c), it will be seen that the principal difference between the two cases corresponding thereto arises from the circumstance that in the latter the exterior work is independent of the intermediate temperature at which freezing occurs, whereas in the former it is dependent thereon. In the equations (f) and (g), therefore, there occurs a term expressive of the variability of the heat expended on exterior work, whilst in the equation (c) this term is absent. Moreover a small difference also arises from the fact that the quantities $c'$ and $h'$ have not exactly the same values as $c$ and $h$. In another place I shall have occasion to return to the consideration of this difference, and an opportunity will then present itself of determining its numerical value.

In the last paragraph of the preceding Note allusion was made to Person's remark, that ice near the temperature 0° is softer than at lower temperatures, and that this circumstance must exert an appreciable influence on the latent heat. If the cohesion of the ice change, of course the interior work inseparable from the act of fusion or solidification, and with it the heat corresponding to this work, will likewise change. At the same time, however, it must be remembered that a certain amount of interior work is necessary in order to diminish the cohesion of the ice, and that the heat expended in this work must necessarily be contained in the specific heat of the ice. We must conclude, therefore, that when the differential coefficient $\frac{dr}{dt}\left(\text{or } \frac{dr'}{dt}\right)$ considerably decreases in the vicinity of 0°, that the quantity $h$ (or $h'$) which occurs, with a negative sign, on the right side of the foregoing equations increases just as considerably. The truth of the equations themselves cannot at all be impaired by this internal deportment, for these equations were established on perfectly general principles, without predicating anything whatever relative to the internal deportment of ice and water during changes of temperature.

It is scarcely necessary to mention, in conclusion, that the preceding developments, *which have been applied to water merely for the sake of an example,* are equally applicable to every other liquid. With respect to the circumstances where the difference $s-\sigma$ comes into consideration, a behaviour analogous to that of water, or opposite thereto, will present itself, according as the substance under examination occupies a greater or a less volume in the solid than it does in the liquid state.

# SECOND MEMOIR.

## ON THE DEPORTMENT OF VAPOUR DURING ITS EXPANSION UNDER DIFFERENT CIRCUMSTANCES[*].

NOT long ago, Mr. Rankine[†] and myself[‡] gave utterance almost contemporaneously to the proposition,—that when the saturated vapour of water, contained in a vessel impervious to heat, is subjected to compression, it does not remain saturated, but can part with a certain quantity of heat without being precipitated; and conversely, when, under the same circumstances, the vapour is suffered to expand, to preserve it from precipitation a certain amount of heat must be imparted from without.

In connexion with this proposition, Mr. W. Thomson, in a letter to Mr. Joule, refers to the fact "that the hand may be held with impunity in a current of steam issuing from the safety-valve of a high-pressure boiler"[§]. From this he concludes that the stream of vapour carries no water along with it, and holds that this conclusion must contradict the above proposition, if the existence of a source of heat from which the vapour shall receive a quantity sufficient to preserve it from precipitation cannot be established. This source he finds in the friction which takes place during the issue of the steam from the orifice.

Although Mr. Thomson himself observes, in the course of his letter, that, according to the mechanical theory of heat, different states of the vapour are induced by different methods of expansion, still in making the remark cited above he does not appear to have taken this circumstance into account. He, in fact, applies the proposition to a case, to which, according to its deve-

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[*] Published in Poggendorff's *Annalen*, Feb. 1851, vol. lxxxii. p. 263, and translated in the Philosophical Magazine, May 1851, S. 4. vol. i. p. 398.

[†] Transactions of the Royal Society of Edinburgh, vol. xx. part 1. p. 147; and Pogg. *Ann.* vol. lxxxi. p. 172 (abstract).

[‡] Pogg. *Ann.* vol. lxxix. pp. 368 and 500; *Monatsberichte der K. Preuss. Acad. der Wiss.* Feb. 1850 (abstract); and Phil. Mag. S. 4. vol. ii. pp. 1 and 102. [FIRST MEMOIR of this collection.]

[§] Phil. Mag. vol. xxxvii. p. 387; and Pogg. *Ann.* vol. lxxxi. p. 477.

lopment, it is altogether inapplicable. For vapour escaping from a boiler into the air the theory would give a totally different result, which latter may be likewise easily deduced.

From the innumerable modifications to which the expansion of the steam may be subjected, I will choose three which may be considered the most important, and in which the essential differences exhibit themselves with peculiar clearness.

We will consider the matter as subjected successively to the two following conditions :—first, that the vapour during its expansion has to overcome a resistance which corresponds to its entire expansive power; and secondly, that it escapes into the open air, in which case the pressure of the atmosphere alone is opposed to it. We will further consider the two cases embraced by the last condition; namely, that in which the vapour is separated from water and left to itself to expand, and that in which the vessel which contains the vapour contains water also, which by its evaporation always replaces the quantity of vapour which escapes.

*First*, then, suppose a unit of weight of vapour at its maximum density to be contained in a vessel separated from water*, and let the vapour expand itself by pushing back a piston, for instance. Let us suppose that the vapour in each stage of its expansion exerts against the piston the *entire* expansive force due to that stage. To effect this, it is only necessary that the piston should recede so slowly, that the vapour which follows it can always adjust its expansive force to that of the vapour in the remaining portion of the vessel. During the expansion so much heat is to be communicated to the vapour, or abstracted from it, as is necessary to its preservation in the saturated gaseous state. The question is, what quantity of heat is here necessary?

To this case the proposition expressed by Mr. Rankine and myself applies. The work performed by the vapour in this instance, and the quantity of heat consumed in its production, are so considerable, that, were this heat supplied from the vapour itself, the latter would be cooled to an extent that would render the retention of the gaseous condition impossible. It will therefore be necessary to *communicate* heat to it from without.

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* For the sake of brevity I will always speak of water, although the same reasoning holds, substantially, for all other liquids.

The quantity of heat to be communicated, which corresponds to an alteration of temperature $dt$, I have expressed in my former memoir by $hdt$, where $h$ is a negative quantity; so that the product $hdt$ for increasing temperatures is negative, and for decreasing temperatures is positive. The value of $h$ in the case of water I have expressed as a function of the temperature $t$ in equation (33)*, thus:

$$h=0{\cdot}305-\frac{606{\cdot}5-0{\cdot}695t-0{\cdot}00002t^2-0{\cdot}0000003t^3}{273+t}\dagger.$$

If, therefore, the quantity of heat necessary to be communicated to the unit-weight of vapour, when its temperature changes from $t_1$ to $t_2$, be called $Q_1$, we have

$$Q_1=\int_{t_1}^{t_2} hdt, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and from this we can readily calculate the value of $Q_1$ for each particular case. For example, let the tension of the vapour at the beginning be five or ten atmospheres, and let the expansion be carried on until the tension sinks to one atmosphere. According to Regnault's determination, we must put $t_1=152°{\cdot}2$ or $=180°{\cdot}3$, and $t_2=100°$; on doing so we obtain the values

$$Q_1=52{\cdot}1 \text{ or } =74{\cdot}9 \text{ units of heat.} \quad . \quad . \quad . \quad (I)$$

*Secondly*, let us again assume that a unit-weight of saturated vapour at the temperature $t_1$, above 100°, is enclosed in a vessel separated from water, and that an orifice is made in the vessel through which the vapour can issue into the atmosphere. Let us follow it at the other side of the orifice until a distance is attained where its expansive force is exactly equal to the atmospheric pressure, the vapour being supposed to remain unmixed with air, and inquire how much heat must be imparted to the entire mass of vapour during its passage, so that it may remain throughout gaseous and saturated.

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* [See p. 65.]

† [In a note appended to this equation I remarked that by means of a simplified empirical formula proposed by me for the latent heat $r$, and which very well represents the results of Regnault's observations, the equation for $h$ assumes the form

$$h=1{\cdot}013-\frac{800{\cdot}3}{273+t},$$

and thereby becomes more convenient for calculation.—1864.]

The *interior* work which the vapour has to execute during this expansion is exactly the same as in the first case; for here the state of the vapour at the commencement and at the end is the same as there. The *exterior* work, on the contrary, is much less; for while, in the first case, the resistance at the commencement was equal to the tension which corresponds to the temperature $t_1$, and decreased slowly to one atmosphere, in the present instance the resistance is only one atmosphere from beginning to end. The amount of heat converted into work is therefore in the present case less, and hence a much smaller quantity is required from without to preserve the vapour gaseous.

That this difference in regard to the quantity of heat consumed actually occurs, is already established with complete distinctness by the experiments of Joule with atmospheric air*. He found that by pumping air into a rigid vessel, the mode of compression here being analogous to the first of the above two cases, much more heat was developed than disappeared when the compressed air was permitted to stream into a space where the pressure of one atmosphere was exerted, the process here being analogous to our second case. These two quantities were nearly in the ratio of the quantities of work calculated according to the foregoing principles.

In order to carry out the calculation in our case, we must, in reality, besides the resistance of the atmosphere, take two other quantities into account; namely, the resistance due to the friction of the vapour as it issues, and the work which must be expended to communicate to the vapour the motion which it still possesses at the point where its tension is equal to the pressure of the atmosphere. To overcome the friction, a certain quantity of heat must be consumed; by the friction, however, heat will be again developed; and although a portion of this is conducted away by the surrounding mass, still the remaining portion communicates itself to the vapour. It is here, however, evident that the effect of friction does not, as Mr. Thomson supposes, exhibit itself in a *gain* of heat, but, on the contrary, in a *loss* of heat; the latter, however, not corresponding to the entire quantity of work expended in overcoming the friction, but only to a portion

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* "On the Changes of Temperature produced by the Rarefaction and Condensation of Air, by J. P. Joule," Phil. Mag. S. 3. vol. xxvi. p. 369.

thereof. We will neglect this, and also the loss arising from the second circumstance alluded to, which is undoubtedly inconsiderable*,—in this way the calculation is rendered very simple.

It is here necessary to subtract from the amount of heat $\int_{t_1}^{t_2} hdt$ found in the former case, the heat which corresponds to the difference of the quantities of exterior work produced in both cases. Let $p$ be the tension of the vapour for the temperature $t$, and $s$ the volume of the unit of weight belonging to this temperature. Further, let $p_1$ and $p_2$ be the values of $p$, and $s_1$ and $s_2$ the values of $s$ at the commencement and at the end of the operation, $p_2$ being, according to our assumption, the pressure of one atmosphere; the exterior work then is—

$$\text{in the first case} = \int_{s_1}^{s_2} pds,$$

$$\text{in the second case} = \int_{s_1}^{s_2} p_2 ds.$$

The corresponding amounts of heat are obtained by multiplying these quantities by the heat-equivalent of the unit of work, which equivalent I have formerly denoted by A. If $Q_2$

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* [The velocity of the current of vapour, and the *vis viva* corresponding thereto are different at different distances from the orifice. In the orifice itself the velocity is considerable; it is due of course to the difference between the pressure in the vessel, and that in the orifice. Beyond the orifice, in the space where the stream of vapour spreads out, the velocity diminishes again quickly. The cause of this diminution of velocity will be discussed in the appendix to this memoir. Without any such special examination, however, we may safely conclude that with the decrease of *vis viva* in the current is associated an increase in the *vis viva* of the molecules of the vapour; in other words, that the destruction of *vis viva* in the current is accompanied by the generation of heat. Now when, as in the present case, our object is, not to follow individually the various phenomena which present themselves during the several phases of the vapour's efflux, but merely to determine the total quantity of heat which must be imparted to the vapour in order that it may, without partial condensation, remain precisely at its maximum density, we may from the commencement leave out of consideration both the heat expended in the production of motion, and that which is generated by the decrease of the motion; for the two having opposite signs will in our calculations cancel each other. If, moreover, we assume that at the place where we finally examined the vapour the velocity of the current is so small as to justify our neglecting the *vis viva* corresponding thereto, then we need not in our calculations pay any attention whatever to the velocity of the current.—1864.]

express the quantity of heat sought, or that which is required by the unit of vapour as it issues, we must put

$$Q_2=\int_{t_1}^{t_2} hdt-A\int_{s_1}^{s_2} pds+A\int_{s_1}^{s_2} p_2 ds. \quad . \quad . \quad . \quad . \quad (2)$$

It is, however, evident that

$$\int_{s_1}^{s_2} p_2 ds=p_2(s_2-s_1),$$

and

$$\int_{s_1}^{s_2} pds=p_2(s_2-\sigma)-p_1(s_1-\sigma)-\int_{p_1}^{p_2}(s-\sigma)dp$$

$$=p_2(s_2-\sigma)-p_1(s_1-\sigma)-\int_{t_1}^{t_2}(s-\sigma)\frac{dp}{dt}dt,$$

where $\sigma$ is an arbitrary constant*, for which we will substitute the volume of a unit of weight of water, since the alteration of the latter with the change of temperature may be so much the more neglected, inasmuch as the entire volume of the water is scarcely deserving of notice. This expression introduced into (2) gives

$$Q_2=\int_{t_1}^{t_2}\left[h+A(s-\sigma)\frac{dp}{dt}\right]dt+Ap_1(s_1-\sigma)\left(1-\frac{p_2}{p_1}\right). \quad . \quad . \quad (3)$$

The sum $h+A(s-\sigma)\frac{dp}{dt}$ is, according to equation (III) of my former memoir†, $=\frac{dr}{dt}+c$; and this sum again, according to the determinations of Regnault, is nearly a constant quantity, viz. 0·305. Equation (3) thus passes into

$$Q_2=-0\cdot305(t_1-t_2)+Ap_1(s_1-\sigma)\left(1-\frac{p_2}{p_1}\right). \quad . \quad . \quad (4)$$

The only unknown quantity here is $Ap_1(s_1-\sigma)$, and this can be expressed as a function of the initial temperature by means of

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* [In fact, if in place of $ds$ we put the equivalent differential $d(s-\sigma)$, $\sigma$ being regarded as any constant quantity whatever, we shall have, as is well known, the equation

$$\int pd(s-\sigma)=p(s-\sigma)-\int(s-\sigma)dp,$$

and if we here conceive the integration to be effected between the determinate limits which correspond to the assumed extreme temperatures $t_1$ and $t_2$, we shall obtain the equation given in the text.—1864.]

† [See p. 34.]

equation (26) of my former memoir*; so that for every initial pressure and the corresponding initial temperature the value of $Q_2$ may be calculated. Supposing, for example, the pressure at the commencement, as in the former case, to be five or ten atmospheres, we obtain

$$Q_2 = 19{\cdot}5 \text{ or } = 17{\cdot}0 \text{ units of heat.} \quad . \quad . \quad . \quad \text{(II)}$$

As $Q_2$ is a positive quantity, it follows that in this case also heat must not be withdrawn, but on the contrary *communicated*, to preserve the vapour from partial precipitation; which, however, would take place not only at the orifice, but also within the vessel. The quantity of vapour thus precipitated would be smaller than in the former case, inasmuch as $Q_2$ is less than $Q_1$.

It may appear singular that the equation (II) gives for an initial pressure of five atmospheres a greater quantity of heat than for ten atmospheres. This is explained by the fact, that under a pressure of five atmospheres the volume of the vapour is already so small, and under ten atmospheres is reduced to so small an amount, that the increase of work thus rendered necessary during the issue of the vapour is more than compensated by the excess of the sensible heat in the one state over that in the other, the vapour being heated in one case to 180°·3, and in the other case to 152°·2.

The second case which we have just considered, can be applied with some degree of approximation to the case of vapour issuing, *without expansion* from the cylinder of a high-pressure engine after the completion of work; provided we assume that the vapour, as long as it remains in connexion with the boiler, is completely gaseous and at the same time completely saturated. In engines where the *expansive principle* is applied, the first case becomes applicable from the moment when the steam is shut off and the piston is driven by expansion alone. Strictly speaking, the case applies to those engines only in which the expansion continues

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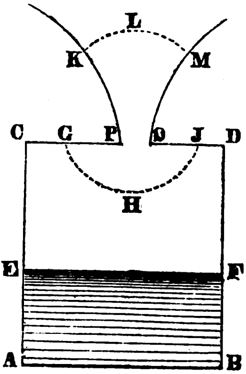
* [See p. 59. In place of the equation (26), which constitutes an empirical formula adapted for numerical calculation, the principal equation (Va) p. 51, may, of course, be employed. The latter gives at once the equation

$$A(s-\sigma) = \frac{r}{(a+t)\frac{dp}{dt}},$$

in which the quantities on the right are all known from observation.—1864.]

until the pressure within is equal to that of the atmosphere; and even here the correspondence would not be perfectly exact, inasmuch as the heat developed by the friction of the piston must certainly be considerable*.

We will finally apply ourselves to the consideration of the *third* case, that is to say, to the case to which the remark of Mr. Thomson refers. Let the vessel ABCD (see the accompanying figure) be supposed to be filled with water to EF, and from here upwards to be filled with vapour. Let PQ be the orifice, connected with which is a neck PQKM, which widens slowly, and renders the expansion of the vapour more regular. This is not essential, but is merely assumed to render the conception of the matter easier. By the application of a proper source of heat, let the water be preserved at the constant temperature $t$, so that the vapour which escapes shall be continually replaced by newly developed vapour, the state of things as regards the issue of the vapour being thus preserved stationary.



Let GHJ represent a surface in which the vapour which passes has, everywhere, the expansive force $p_1$, the temperature $t_1$, and the volume $S_1$, which exist within the vessel, and with which the new vapour is developed†. Let KLM, on the other hand, represent a surface in which the vapour which passes has, everywhere, the expansive force $p_2$, equal to one atmosphere, the vapour

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* In connexion with the proposition which applies to the first case, I cited in my former memoir the experiment made by Pambour with the steam proceeding from a high-pressure engine after the completion of work. I deemed it sufficient to notice the fact, that Pambour did not find a higher temperature than that which corresponded to the pressure observed at the same time, although according to the common theory he must have done so. To require from such observations that they shall exhibit the exact quantity of water mixed with the vapour which the theory gives, would, for the reasons given above, and on account of many other simultaneous causes of disturbance, be unjustifiable.

† [In the figure given in the first editions of this memoir the surface GHJ is drawn too near the orifice. Notice was given of this in the *corrigenda* of the volume of Poggendorff's *Annalen*, wherein the memoir appeared.—1864.]

being supposed to be unmixed with air. During the passage of the vapour from GHJ to KLM let heat be continually withdrawn or communicated, so that the vapour may remain completely gaseous and quite saturated, and hence at the surface KLM have the temperature $t_2=100°$ exactly, and the corresponding volume $s_2$. The question is, what quantity of heat $Q_3$ must be imparted to, or withdrawn from, the issuing vapour so that this condition shall be fulfilled.

The *interior* work performed by the vapour during its issue in the present instance is exactly the same as in the other cases. With regard to the *exterior* work, however, an entirely new circumstance enters into the consideration, which renders this case essentially different from the former ones.

We must here, in fact, consider the quantity of work produced at *both* the surfaces GHJ and KLM. Through the surface GHJ the vapour is driven with the volume $s_1$ and the pressure $p_1$, it therefore produces the work

$$p_1 \cdot s_1.$$

This work proceeds from the vapour within the vessel, and moreover only from that portion of it which, during the time of issue, is developed anew. To obtain room for itself, this presses the neighbouring stratum forwards, this the next, and so on. The intervening layers thus serve merely to transmit the force from the surface of the water to the orifice. The quantity of heat consumed in the production of this work is contained in the latent heat of the developed steam, and need not in the present consideration be further taken into account.

If now in the surface KLM exactly the same work be produced as in GHJ, then in the interval between both surfaces no proper work is produced, inasmuch as in this case there would be merely a transmission of work from one surface to the other. If, on the contrary, the work accomplished at the surface KLM be different from that produced at GHJ, the difference must be referred to the said interval. But through KLM the unit of weight of steam with the volume $s_2$ and the pressure $p_2$ is driven, and hence produces the work

$$p_2 \cdot s_2.$$

The work performed in the intervening space is then

$$p_2 \cdot s_2 - p_1 \cdot s_1,$$

which is a negative quantity. This shows, that, during the passage from surface to surface, a portion of the exterior work already completed is actually lost again*.

The quantity $p_2 . s_2 - p_1 s_1$ must be treated as the quantity $\int_{s_1}^{s_2} p_2 ds$ in the second case; in this way we obtain the following equation, which corresponds to equation (2):

$$Q_3 = \int_{t_1}^{t_2} h dt - A \int_{s_1}^{s_2} p ds + A(p_2 . s_2 - p_1 . s_1). \quad . \quad . \quad (5)$$

Subjecting this equation to the same process as that applied in the deduction of equation (4) from equation (2), and neglecting the terms which contain the factor $\sigma$, we obtain

$$Q_3 = -0{\cdot}305\,(t_1 - t_2)\dagger. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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* [The deportment of the vapour in the space between the two surfaces GHJ and KLM is by no means simple, inasmuch as the velocity of the stream from the first surface to the orifice PQ is greatly accelerated, whilst that from the orifice to the second surface is, approximately, quite as strongly retarded. As already remarked in a previous note, however, it is not necessary, in determining the total quantity of heat which must be communicated to the vapour, to take into consideration the peculiarities of this deportment; for it may be predicated with certainty that heat will be expended during the increase of the *vis viva* of the stream, and generated during its decrease. It will suffice, therefore, to know what takes place at the two limiting surfaces chosen for consideration, and the *vis viva* in these surfaces being small enough to be neglected, we need only take cognizance of the mechanical work which is performed on the passage of the vapour by the pressure which there exists, the latter being estimated in the direction of the stream.—1864.]

† [As already remarked when transforming the equation (2), the following equation holds:

$$\int_{s_1}^{s_2} p ds = p_2(s_2 - \sigma) - p_1(s_1 - \sigma) - \int_{t_1}^{t_2} (s - \sigma) \frac{dp}{dt} dt,$$

and in virtue of it the equation (5) takes the form

$$Q_3 = \int_{t_1}^{t_2} \left[ h + A(s - \sigma) \frac{dp}{dt} \right] dt - A\sigma(p_1 - p_2).$$

On substituting herein the expression $\frac{dr}{dt} + c$ for its equal $h + A(s - \sigma)\frac{dp}{dt}$, and neglecting the term which contains the factor $\sigma$, we have

$$Q_3 = \int_{t_1}^{t_2} \left( \frac{dr}{dt} + c \right) dt.$$

This equation, when specially applied to water by putting, with Regnault,

$$\frac{dr}{dt} + c = 0{\cdot}305,$$

leads to the equation (6).—1864.]

Calculating from this the numerical value of $Q_3$ for an initial pressure of five or ten atmospheres, we obtain

$$Q_3 = -15{\cdot}9 \text{ or } = -24{\cdot}5 \text{ units of heat, respectively} . \quad \text{(III)}$$

The value of $Q_3$ being negative, it follows that in this case heat is not to be communicated, but, on the contrary, must be *withdrawn,* the quantity being the same as that found by applying the common theory of heat. If this withdrawal up to the place under consideration be not sufficiently effected, then the vapour at this place will have a temperature which exceeds 100°; and hence, if water be not *mechanically* carried along with the vapour, the latter must be completely dry.

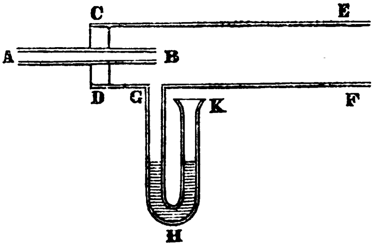
It is thus shown that the friction is not necessary to the explanation of the fact adduced by Mr. Thomson; the effect of this friction, as already mentioned, being exactly opposite to what he supposes it to be. The loss of heat arising from this cause is not reckoned above. In such cases as the issuing of steam from the safety-valve of a high-pressure engine, this loss is by no means capable of effecting the consumption of the quantity of heat found by equation (6).

## APPENDIX TO SECOND MEMOIR [1864].

### ON THE VARIATIONS OF PRESSURE IN A SPREADING STREAM OF GAS.

In the preceding memoir it was stated that the velocity of the stream diminishes considerably, from the orifice PQ to the surface KLM, in the gradually widening neck of the vessel drawn on p. 97. The force which causes this diminution must be sought for in the difference between the pressure which prevails near the orifice, and that which exists at the surface KLM.

Such a difference of pressure invariably occurs when a stream of gas spreads out; its existence may be detected readily by means of a well-known little instrument. Let AB in the adjoining figure be a narrow tube fitted, by means of a cork, into a wider tube CDEF; so that



a stream of air, driven through the narrow tube from A to B, can spread itself out in the wider tube, before it reaches the free atmosphere. Just below the mouth of the small tube a siphon-shaped tube G H K is fitted to the wide tube, and partially filled with a liquid. On blowing through the narrow tube AB, the liquid in the branch H G of the siphon-shaped tube is seen to rise; thereby showing that during the blast the pressure in the wide tube near the mouth of the small one is less than that of the surrounding atmosphere. Hence the pressure at B in the stream of air which flows in the wide tube from B to E F is smaller than at the mouth of the latter, where the atmospheric pressure exists; it is this difference of pressure which retards the current and causes so great a diminution in its velocity that the same quantity of air which in a given time passes through the small section at B, is able throughout that time to fill the wider section E F.

The origin of this difference of pressure may be thus explained:—The stream of air in the neighbourhood of the orifice B, where it has not yet spread itself so far as to occupy, in a uniform manner, the whole section of the wide tube, seeks to carry with it the still air at its side, and in consequence of this effort a portion of the circumjacent air is removed at the commencement of the current, and a rarefaction thereby ensues which continues as long as the current lasts.

A deportment precisely similar to the one observed in the small apparatus just described, must also present itself in the gradually widening neck P Q K M of the vessel previously alluded to. Here also, in the neighbourhood of the narrow orifice P Q, the pressure must be less than at the broader part of the neck, and the stream of vapour must be retarded in its passage from the narrow, to the broader parts. When the gradually widening neck is withdrawn, which separates from the exterior air the stream of vapour during its expansion and consequent retardation, that is to say, when the vapour passes directly, with its full velocity of efflux, into the atmosphere, a slight difference arises from the circumstance that the stream of vapour continually sets in motion a certain quantity of the circumjacent air, the air carried with it being continually replaced by new air streaming in from the surrounding space. On the whole, however, the phenomena under these circumstances must be similar to those previously considered.

In the letter written by Mr. W. Thomson to Mr. Joule, and cited in the preceding memoir, Mr. Thomson commences with comparing the case where steam issues from the safety-valve of a boiler, with that where vapour, contained in a vessel without liquid, expands by overcoming a resistance corresponding to its entire expansive force. To prevent partial condensation in the latter case, a certain quantity of heat must be imparted to the vapour, and Mr. Thomson holds the opinion that it is "by the friction of the steam as it rushes through the orifice" that this quantity of heat, necessary to prevent partial condensation during the efflux of the steam, is produced. I understood by the expression above quoted, the friction of the vapour in the orifice itself, that is to say against the fixed walls thereof as the vapour rushes past them, and it is to Mr. Thomson's views thus interpreted that reference is made in the preceding memoir. On comparison with the words used, my interpretation of the expression will be found to be a very natural one, and Mr. Thomson himself, in his reply*, nowhere states that I have misinterpreted that expression. In this reply, however, he has chosen another form of expression, when alluding to his former explanation, and that without either stating his reasons for so doing, or even drawing attention to the difference. He there says, in fact, that in his former explanation he stated that the quantity of heat in question was generated "by the fluid friction in the neighbourhood of the aperture." If from the beginning Mr. Thomson had used the latter form of expression, which I cannot consider as identical with the previous one, the difference of opinion between us would have been to some extent, if not wholly, avoided. It has, in fact, been already stated that the difference of pressure, which retards the stream of vapour or other expanding gas (with which retardation a development of heat is associated), arises from the circumstance that the stream of gas seeks to carry with it the surrounding gaseous particles, and hence it is clear that the phenomenon must be referred, ultimately, to the action of the particles of gas upon one another; to this action, although it is not of a very simple kind, the term

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* Phil. Mag. S. 4. vol. i. p. 474.

*friction* may be applied. It was not my intention to dispute, in the least degree, the influence of *this* friction, occurring in the stream of gas beyond the orifice; I merely objected to the too great part which, as it appeared to me, was ascribed to the friction against the walls of the orifice.

It is now, indeed, of little importance whether the difference of meaning which gave rise to the preceding memoir was an essential one, or whether, and to what extent, it arose merely from the use of an inappropriate form of expression. The memoir itself will scarcely be affected thereby, and quite apart from the way in which it originated, I trust that the developments it contains, and particularly the precise distinction which is therein drawn between the three cases treated, and the consideration, in the last case, of the work done in the surface G H J (not alluded to by Mr. Thomson), will not be without scientific interest.

# THIRD MEMOIR.

## ON THE THEORETIC CONNEXION OF TWO EMPIRICAL LAWS RELATING TO THE TENSION AND THE LATENT HEAT OF DIFFERENT VAPOURS[*].

A SUPERFICIAL contemplation of the tension series, experimentally developed for the vapours of different liquids, suffices to show that a certain uniformity exists therein; and hence the various efforts which have been made to ascertain a definite law by means of which the series which holds good for one liquid, water for instance, might be applied to other liquids.

A very simple law of this nature was expressed by Dalton. Calling those temperatures which belong to equal tensions *corresponding* temperatures, the law ran thus:—In the case of any two liquids *the differences between the corresponding temperatures are all equal.*

This law agrees pretty well with experience in the case of those liquids whose boiling-points are not far apart; for those, however, which possess very different degrees of volatility, it is inexact. This is shown by a comparison of the vapour of mercury with that of water, according to the observations of Avogrado[†]. Still more decidedly does the divergence exhibit itself in the investigations of Faraday[‡] on the condensation of gases.

In the "Additional Remarks" to his memoir, Mr. Faraday, after having disproved the applicability of the law of Dalton to gases, expresses himself as follows:—"As far as observations upon the following substances, namely, water, sulphurous acid,

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[*] Published in Poggendorff's *Annalen*, February 1851, vol. lxxxii. p. 274; and translated in the Philosophical Magazine, December 1851, S. 4. vol. ii. p. 483.

[†] Abstracts in *Ann. de Chim. et de Phys.* xlix. p. 369; and Pogg. *Ann.* vol. xxvii. p. 60. Complete in *Mém. de l'Acad. de Turin*, vol. xxxvi.

[‡] Phil. Trans. of the Roy. Soc. of London for 1845, p. 155; and Pogg. *Ann.* vol. lxxii a. p. 193.

cyanogen, ammonia, arseniuretted hydrogen, sulphuretted hydrogen, muriatic acid, carbonic acid, olefiant gas, &c., justify any conclusion respecting a general law, it would appear that the more volatile a body is, the more rapidly does the force of its vapour increase by further addition of heat, commencing at a given point of pressure for all;" and further on, "there seems every reason therefore to expect that the increasing elasticity is directly as the volatility of the substance, and that by further and more correct observation of the forces a general law may be deduced, by the aid of which and only a single observation of the force of any vapour in contact with its liquid, its elasticity at any other temperature may be obtained"*.

What Faraday here expresses with evident reserve and caution,

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* [By the more recent appearance of the second volume of Regnault's Experimental Researches, in which extensive tension series are given for a considerable number of substances, an opportunity is afforded of testing more accurately than it was possible to do according to previous data, the mutual relations of the several tension series. In order to elucidate what has been said in the text, I will here tabulate some of the numbers, given by Regnault's observations, which are most suitable for comparison. The first horizontal line contains the boiling-points of the several substances, that is to say, those corresponding temperatures to which belongs a vapour-tension of one atmosphere. The second line likewise contains corresponding temperatures solely, namely, those to which a vapour-tension of five atmospheres belongs. The lowest line, finally, contains the differences between the numbers in the two first lines.

| | Sulphurous Acid. | Ether. | Sulphide of Carbon. | Alcohol. | Water. | Mercury. | Sulphur. |
|---|---|---|---|---|---|---|---|
| Boiling-points .. | −10° | 35° | 46° | 78° | 100° | 357° | 448° |
| Temperatures for a tension of five atmospheres .. | 33 | 89 | 106 | 125 | 152 | 458 | 568 |
| Differences...... | 43 | 54 | 60 | 47 | 52 | 101 | 120 |

According to Dalton's law, the differences in the last horizontal line should be equal to one another; this, however, is manifestly not the case, the differences being, in general, greater the higher the boiling-point of the liquid. The latter progression, it is true, is not so regular that each difference is greater than the preceding one; but on the whole, and particularly so far as liquids are concerned whose boiling-points lie far asunder, it is unmistakeable. —1864.]

we find again in the form of an equation in a later memoir by M. Groshans*. The equation (3) of the said memoir contains, implicitly, the following law:—*If all temperatures be counted from* $-273°$ C. (that is, from that temperature which is expressed by the inverse value of the coefficient of expansion for atmospheric air), *then for any two liquids the corresponding temperatures are proportional.*

Although this carries with it a great degree of probability, at least as an *approximate* law, and is undoubtedly proved by the experimental researches of Avogrado and Faraday to be preferable to the law of Dalton, still the manner in which M. Groshans deduces his equations leaves much to be desired. He bases the deduction upon two equations which can only be regarded as approximately correct, inasmuch as they contain the expression of the law of Mariotte and Gay-Lussac for vapours at their maximum density. For the further development, however, he makes use of the following proposition:—If in the case of any two vapours the temperatures are so chosen that the tensions of both are equal, then, if the density of each vapour at the temperature in question be measured by its density at the boiling-point, these densities are equal. This proposition is introduced by the author in the memoir alluded to without any proof whatever. In a later memoir†, however, he says that he was led to the above conclusion by observing that in the case of seven different bodies composed of $p\,C+q\,H+r\,O$ the density of the vapour at the boiling-point compared with the density of steam at 100° could be expressed by the formula

$$D=\frac{p+q+r}{3};$$

and immediately afterwards‡ he states, that "there are several bodies to which the formula

$$D=\frac{p+q+r}{3}$$

is inapplicable." From this it appears that the foundation on which the proposition rests cannot be regarded as established. It seems to me, that although the law mentioned above has ob-

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[*] Pogg. *Ann.* vol. lxxviii. p. 112.

[†] Pogg. *Ann.* vol. lxxix. p. 290.

[‡] *Ibid.* p. 292.

tained from M. Groshans a more definite form than in Faraday's expression, its probable validity is in no way augmented thereby.

In this state of uncertainty every new point of view from which a more extended insight as to the deportment of liquids during evaporation may be obtained is deserving of attention; and hence it will not perhaps be without interest, to establish such a connexion between the above law as regards the *tension* and another law regarding the *latent heat*,—the latter being also empirically established in a manner totally independent of the former—that the one shall appear to be a necessary consequence of the other.

I refer to the law, *that the latent heat of a unit of volume of vapour developed at the boiling-point is the same for all liquids.* Although this has not been completely corroborated by the experiments hitherto made, and even if it were perfectly true, could not be so corroborated, our knowedge of the volumes of vapours at their maximum density being too scanty, still, an approximation is observed which it is impossible to regard as accidental. We will therefore for the present assume the law to be correct, and thus make use of it for further deductions.

In the first place, it is clear that if the law be true for the boiling-points of all liquids, it must also be true for every other system of corresponding temperatures; for the boiling-points depend merely upon the accidental pressure of the atmosphere, and hence the law can be immediately extended thus: *the latent heat calculated for the unit of volume of vapour is, for all liquids, the same function of the tension.* Let $r$ be the latent heat of a unit of weight of vapour at the temperature $t$, the volume of the unit of weight for the same temperature being $s$, the latent heat of a unit of volume will then be expressed by the fraction $\frac{r}{s}$; let $p$ be the corresponding tension; the law will then be expressed by the equation

$$\frac{r}{s}=f(p), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{I})$$

in which $f$ is the symbol of a function which is the same for all liquids.

Let this function be substituted for $\frac{r}{s}$ in the equation (V$a$) of my memoir "On the Moving Force of Heat"*, by neglecting therein the volume $\sigma$ of a unit of weight of liquid as compared with that of vapour, we thus obtain

$$f(p)=A(a+t)\frac{dp}{dt},$$

where A and $a$ are two constants, the latter denoting the number 273, so that $a+t$ is the temperature of the vapour reckoned from $-273°$. If, for the sake of brevity, we call this quantity T, we have

$$\frac{dT}{T}=\frac{A\,dp}{f(p)};$$

and from this we obtain by integration

$$c\,.\,T=F(p),$$

in which F is the symbol of another function, which is likewise the same for all liquids, and $c$ is an arbitrary constant which must be determined for each liquid†. Let us suppose this equation solved for $p$, it will assume the form

$$p=\phi(c.T), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

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* [See p. 51. The equation (V$a$) here cited is

$$r=A\,(a+t)\,(s-\sigma)\frac{dp}{dt},$$

whence

$$\frac{r}{s-\sigma}=A(a+t)\frac{dp}{dt},$$

in which, with great approximation, we may put $\frac{r}{s}$ for $\frac{r}{s-\sigma}$.—1864.]

† [By integration, in fact, we have in the first place

$$\log T=\int_{p_1}^{p}\frac{A\,.\,dp}{f(p)}+k,$$

where $k$ is an arbitrary constant, and $p_1$ represents, for all liquids, one and the same arbitrary initial tension; for instance, a tension of one atmosphere. From this equation it follows that

$$T=e^{\int_{p_1}^{p}\frac{A\,.\,dp}{f(p)}}\cdot e^{k},$$

or

$$e^{-k}.T=e^{\int_{p_1}^{p}\frac{A\,.\,dp}{f(p)}}.$$

Introducing here the abbreviations

$$F\,(p)=e^{\int_{p_1}^{p}\frac{A\,dp}{f(p)}},$$

$$c=e^{-k},$$

the equation in the text is at once obtained.—1864.]

where $\phi$ is the symbol of a third function, which is the same for all liquids.

This equation is evidently the mathematical expression of the law of tension mentioned above; for to apply the function which in the case of any one liquid determines the tension from the temperature, to any other liquid, it is only necessary to multiply the temperature by a different constant, which constant is easily found when the tension for a single temperature is known.

It is thus shown, that, in so far as the validity of equation (V*a*) is granted, the two laws expressed by the equations (I) and (II) are so connected with each other that when *one* of them is true, the *other* must necessarily be true also.

But in case both laws are only approximations to the truth, as to me appears most probable, the equation (V*a*), which by introducing T instead of *t* becomes

$$\frac{r}{s-\sigma}=\mathrm{A}.\mathrm{T}.\frac{dp}{d\mathrm{T}},$$

enables us at least to conclude, from the manner and degree of divergence between two vapours with regard to their latent heat, what divergence there is between their tension series, and *vice versâ**. Thus, for instance, in comparing water with other liquids, it is observed that, relatively to its boiling-point, the tension of the vapour of the former increases more quickly with the temperature than the tension of other vapours. There is a complete coincidence between this fact and that observed by Andrews†, that the vapour of water possesses a greater latent heat than an equal volume of the vapour of any other liquid which

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* [For if the fraction $\frac{r}{s-\sigma}$ relative to the boiling-point, and almost identical with $\frac{r}{s}$, has a greater value for a certain liquid than it has for others, we must conclude that, for the former, the product $\mathrm{T}\,\frac{dp}{d\mathrm{T}}$ is also greater, and hence that the vapour-tension near the value of one atmosphere increases more quickly with increasing temperature than one would anticipate from the height of the liquid's boiling-point. In a similar manner, from the circumstance that an exceptionally quick increase of the vapour-tension of a liquid takes place, we should conclude that the latent heat, calculated according to the volume of the vapour, has an unusually large value.—1864.]

† Quarterly Journal of the Chem. Soc. of London, No. 1. p. 27.

Andrews examined, alcohol excepted. From this we perceive that it is by no means advantageous for the application of the above two laws to choose, as is generally done, water as the liquid of comparison; but that, on the contrary, the comparison of water with liquids of lower boiling-points is peculiarly calculated to support the law of Dalton*.

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* [Since, in the case of water, the fraction $\frac{r}{s}$ is greater than for most other liquids, the tension of aqueous vapour must, according to the foregoing note, increase more quickly in the neighbourhood of the boiling-point, and, as a consequence of this, the difference between two corresponding temperatures must be smaller than the height of the boiling-point would lead us to expect; so that in this respect water approaches the liquids having lower boiling-points. The same remark must apply still more forcibly to alcohol, for which liquid the fraction $\frac{r}{s}$ is still greater. This is verified, in fact, by the small Table given in a note on p. 105; for on comparing the differences between the systems of corresponding temperatures there selected for consideration, it will be found that these differences are smaller for water and alcohol than for sulphide of carbon and ether, although the latter substances have lower boiling-points than the former.—1864.]

# FOURTH MEMOIR.

## ON A MODIFIED FORM OF THE SECOND FUNDAMENTAL THEOREM IN THE MECHANICAL THEORY OF HEAT[*].

In my memoir "On the Moving Force of Heat, &c."[†], I have shown that the theorem of the equivalence of heat and work, and Carnot's theorem, are not mutually exclusive, but that, by a small modification of the latter, which does not affect its principal part, they can be brought into accordance. With the exception of this indispensable change, I allowed the theorem of Carnot to retain its original form, my chief object then being, by the application of the two theorems to special cases, to arrive at conclusions which, according as they involved known or unknown properties of bodies, might suitably serve as proofs of the truth of the theorems, or as examples of their fecundity.

This form, however, although it may suffice for the deduction of the equations which depend upon the theorem, is incomplete, because we cannot recognize therein, with sufficient clearness, the real nature of the theorem, and its connexion with the first fundamental theorem. The modified form in the following pages will, I think, better fulfil this demand, and in its applications will be found very convenient.

Before proceeding to the examination of the second theorem, I may be allowed a few remarks on the first theorem, so far as this is necessary for the supervision of the whole. It is true that I might assume this as known from my former memoirs or from those of other authors, but to refer back would be inconvenient; and besides this, the exposition I shall here give is preferable to my former one, because it is at once more general and more concise.

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[*] Published in Poggendoff's *Annalen*, December 1854, vol. xciii. p. 481; translated in the *Journal de Mathématiques*, vol. xx. Paris, 1855, and in the Philosophical Magazine, August 1856, S. 4. vol. xii. p. 81.

[†] [First Memoir of this Collection.]

### *Theorem of the equivalence of Heat and Work.*

Whenever a moving force generated by heat acts against another force, and motion in the one direction or the other ensues, positive work is performed by the one force at the same time that negative work is done by the other. As this work has only to be considered as a simple quantity in calculation, it is perfectly arbitrary, in determining its sign, which of the two forces is chosen as the indicator. Accordingly in researches which have a special reference to the moving force of heat, it is customary to determine the sign by counting as positive the work done by heat in overcoming any other force, and as negative the work done by such other force. In this manner the theorem of the equivalence of heat and work, which forms only a particular case of the general relation between *vis viva* and mechanical work, can be briefly enunciated thus :—

*Mechanical work may be transformed into heat, and conversely heat into work, the magnitude of the one being always proportional to that of the other.*

The forces which here enter into consideration may be divided into two classes : those which the atoms of a body exert upon each other, and which depend, of course, upon the nature of the body, and those which arise from the foreign influences to which the body may be exposed. According to these two classes of forces which have to be overcome (of which the latter are subjected to essentially different laws), I have divided the work done by heat into *interior* and *exterior* work.

With respect to the interior work, it is easy to see that when a body, departing from its initial condition, suffers a series of modifications and ultimately returns to its original state, the quantities of interior work thereby produced must exactly cancel one another. For if any positive or negative quantity of interior work had remained, it must have produced an opposite exterior quantity of work or a change in the existing quantity of heat; and as the same process could be repeated any number of times, it would be possible, according to the sign, either to produce work or heat continually from nothing, or else to lose work or heat continually, without obtaining any equivalent; both of which cases are universally allowed to be impossible. But if at every return of the body to its initial condition the quantity of interior work is zero, it follows, further, that the interior work corresponding to any given change in the condition of the body is completely determined by the initial and final conditions of the latter, and is independent of the path pursued in passing from one condition to the other. Conceive a body to pass successively in different ways from the first to the second condition, but always to return in the same manner to its initial state. It is evident that the quantities of interior work produced along the different paths must all cancel the common quantity produced during the return, and consequently must be equal to each other.

It is otherwise with the exterior work. With the same initial and final conditions, this can vary just as much as the exterior influences to which the body may be exposed can differ.

Let us now consider at once the interior and exterior work produced during any given change of condition. If opposite in sign they may partially cancel each other, and what remains must then be proportional to the simultaneous change which has occurred in the quantity of existing heat. In calculation, however, it amounts to the same thing if we assume an alteration in the quantity of heat equivalent to each of the two kinds of work. Let Q, therefore, be the quantity of heat which must be imparted to a body during its passage, in a given manner, from one condition to another, any heat withdrawn from the body being counted as an imparted negative quantity of heat. Then Q may be divided into three parts, of which the first is employed in increasing the heat actually existing in the body, the second in producing the interior, and the third in producing the exterior work. What was before stated of the second part also applies to the first—it is independent of the path pursued in the passage of the body from one state to another: hence both parts together may be represented by one function U, which we know to be completely determined by the initial and final states of the body. The third part, however, the equivalent of exterior work, can, like this work itself, only be determined when the precise manner in which the changes of condition took place is known. If W be the quantity of exterior work, and A the equivalent of heat for the unit of work, the value of the third part will be A . W, and the first fundamental theorem will be expressed by the equation

$$Q = U + A . W. \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

When the several changes are of such a nature that through them the body returns to its original condition, or when, as we shall in future express it, these changes form a *cyclical* process, we have

$$U=0,$$

and the foregoing equation becomes

$$Q=A.W. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

In order to give special forms to equation (I), in which it shall express definite properties of bodies, we must make special assumptions with respect to the foreign influences to which the body is exposed. For instance, we will assume that the only active exterior force, or at least the only one requiring consideration in the determination of work, is an exterior pressure which (as is always the case with liquid and gaseous bodies, when other foreign forces are absent, and might at least be the case with solid bodies) is everywhere normal to the surface, and equally intense at every point thereof. It will be seen that under this condition it is not necessary, in determining the exterior work, to consider the variations in form experienced by the body, and its expansion or contraction in different directions, but only the total change in its volume. We will further assume that the pressure always changes very gradually, so that at any moment it shall differ so little from the opposite expansive force of the body, that both may be counted as equal. Thus the pressure constitutes a property of the body itself, which can be determined from its other contemporaneous properties.

In general, under the above circumstances, we may consider the pressure as well as the whole condition of the body, so far as it is essential to us, as determined so soon as its temperature $t$ and volume $v$ are given. We shall make these two magnitudes, therefore, our independent variables, and shall consider the pressure $p$ as well as the quantity U in the equation (I) as functions of these. If, now, $t$ and $v$ receive the increments $dt$ and $dv$, the corresponding quantity of exterior work done can be easily ascertained. If any increase of temperature is not accompanied by a change of volume, no exterior work is produced; on the other hand, if, with respect to the differentials, we neglect terms higher than the first in order, then the work done during an increment of volume $dv$ will be $pdv$. Hence the work done during a simultaneous increase of $t$ and $v$ is

$$dW = pdv,$$

and when we apply this to the equation (I), we obtain

$$dQ = dU + A \, . \, pdv. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

On account of the term $A \, . \, pdv$, this equation can only be integrated when we have a relation given, by means of which $t$ may be expressed as a function of $v$, and therefore $p$ as a function of $v$ alone*. It is this relation which, as above required, defines the manner in which the changes of condition take place.

The unknown function U may be eliminated from this equation. When written in the form

$$\frac{dQ}{dt}dt + \frac{dQ}{dv}dv = \frac{dU}{dt}dt + \left(\frac{dU}{dv} + A \, . \, p\right)dv\dagger,$$

we easily see that it is divisible into the two equations

$$\frac{dQ}{dt} = \frac{dU}{dt},$$

and

$$\frac{dQ}{dv} = \frac{dU}{dv} + A \, . \, p.$$

Let the first of these be differentiated according to $v$ and the second according to $t$. In doing so we may apply to U the well-known theorem, that when a function of two independent varia-

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* [In fact since $dU$ is itself a complete differential, the magnitude $A \, . \, pdv$ must also be one, in order that the whole of the expression on the right may be so; but this can only be the case when $p$ is expressible as a function of $v$ alone.—1864.]

† [In this and the following memoirs the notation for partial differential coefficients is somewhat different from that employed in the first memoir; the brackets, which were there used for the sake of clearness, are here omitted, since, as stated in the Introduction, no misunderstanding can be thereby produced. The same simplified notation is also retained in the present reprint, in order to preserve unchanged the form of the memoirs. It would certainly have been more convenient to the reader had I, on collecting into one volume the memoirs written at various epochs, adopted one and the same notation throughout; nevertheless every mathematician is so accustomed to see first one and then the other notation employed, that the transition will probably be scarcely noticed; at all events, it will not render the memoirs themselves less intelligible, or seriously impair the facility with which one may be compared with another.—1864.]

bles is successively differentiated according to both, the order in which this is done does not affect the result. This theorem, however, does not apply to the magnitude Q, so that for it we must use symbols which will show the order of differentiation. This is done in the following equations :—

$$\frac{d}{dv}\left(\frac{dQ}{dt}\right)=\frac{d^2U}{dtdv},$$

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right)=\frac{d^2U}{dtdv}+A\,.\,\frac{dp}{dt}.$$

By subtraction, we have

$$\frac{d}{dt}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dt}\right)=A\,.\,\frac{dp}{dt}, \quad . \quad . \quad . \quad . \quad (3)$$

an equation which no longer contains U.

The equations (2) and (3) can be still further specialized by applying them to particular classes of bodies. In my former memoir I have shown these special applications in two of the most important cases, viz. permanent gases and vapours at a maximum density. On this account I will not here pursue the subject further, but pass on to the consideration of the second fundamental theorem in the mechanical theory of heat.

### *Theorem of the equivalence of transformations.*

Carnot's theorem, when brought into agreement with the first fundamental theorem, expresses a relation between two kinds of transformations, the transformation of heat into work, and the passage of heat from a warmer to a colder body, which may be regarded as the transformation of heat at a higher, into heat at a lower temperature. The theorem, as hitherto used, may be enunciated in some such manner as the following :—*In all cases where a quantity of heat is converted into work, and where the body effecting this transformation ultimately returns to its original condition, another quantity of heat must necessarily be transferred from a warmer to a colder body; and the magnitude of the last quantity of heat, in relation to the first, depends only upon the temperatures of the bodies between which heat passes, and not upon the nature of the body effecting the transformation.*

In deducing this theorem, however, a process is contemplated which is of too simple a character; for only two bodies losing or receiving heat are employed, and it is tacitly assumed that one of the two bodies between which the transmission of heat takes place is the source of the heat which is converted into work. Now by previously assuming, in this manner, a particular temperature for the heat converted into work, the influence which a change of this temperature has upon the relation between the two quantities of heat remains concealed, and therefore the theorem in the above form is incomplete.

It is true this influence may be determined without great difficulty by combining the theorem in the above limited form with the first fundamental theorem, and thus completing the former by the introduction of the results thus arrived at. But by this indirect method the whole subject would lose much of its clearness and facility of supervision, and on this account it appears to me preferable to deduce the general form of the theorem immediately from the same principle which I have already employed in my former memoir, in order to demonstrate the modified theorem of Carnot.

This principle, upon which the whole of the following development rests, is as follows:—*Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time**. Everything we know concerning

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* [The principle may be more briefly expressed thus: *Heat cannot by itself pass from a colder to a warmer body*; the words "by itself," (*von selbst*) however, here require explanation. Their meaning will, it is true, be rendered sufficiently clear by the expositions contained in the present memoir, nevertheless it appears desirable to add a few words here in order to leave no doubt as to the signification and comprehensiveness of the principle.

In the first place, the principle implies that in the immediate interchange of heat between two bodies by conduction and radiation, the warmer body never receives more heat from the colder one than it imparts to it. The principle holds, however, not only for processes of this kind, but for all others by which a transmission of heat can be brought about between two bodies of different temperatures, amongst which processes must be particularly noticed those wherein the interchange of heat is produced by means of one or more bodies which, on changing their condition, either receive heat from a body, or impart heat to other bodies.

On considering the results of such processes more closely, we find that in one and the same process heat may be carried from a colder to a warmer body and another quantity of heat transferred from a warmer to a colder body without any other permanent change occurring. In this case we have not a the interchange of heat between two bodies of different temperatures confirms this; for heat everywhere manifests a tendency to equalize existing differences of temperature, and therefore to pass in a contrary direction, *i. e.* from warmer to colder bodies. Without further explanation, therefore, the truth of the principle will be granted.

For the present we will again use the well-known process first conceived by Carnot and graphically represented by Clapeyron, with this difference, however, that, besides the two bodies between which the transmission of heat takes place, we shall assume a third, at any temperature, which shall furnish the heat converted into work. An example being the only thing now required, we shall choose as the changing body one whose changes are governed by the simplest possible laws, *e. g.* a permanent gas*. Let, therefore, a quantity of permanent gas having the temperature $t$ and volume $v$ be given. In the adjoining figure we shall suppose the volume represented by the abscissa $o\,h$, and the pressure exerted by the gas at this volume, and at the tem-

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simple transmission of heat from a colder to a warmer body, or an *ascending* transmission of heat, as it may be called, but two connected transmissions of opposite characters, one ascending and the other descending, which compensate each other. It may, moreover, happen that instead of a descending transmission of heat accompanying, in the one and the same process, the ascending transmission, another permanent change may occur which has the peculiarity of not being reversible without either becoming replaced by a new permanent change of a similar kind, or producing a descending transmission of heat. In this case the ascending transmission of heat may be said to be accompanied, not immediately, but mediately, by a descending one, and the permanent change which replaces the latter may be regarded as a compensation for the ascending transmission.

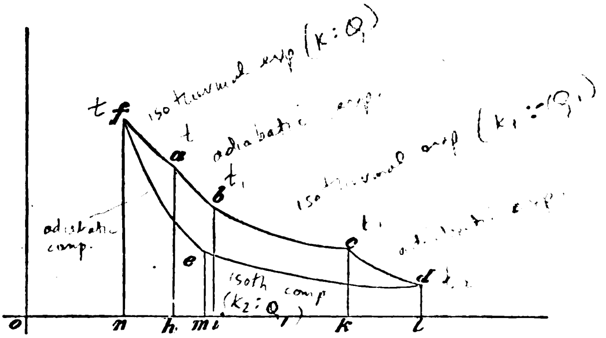
Now it is to these *compensations* that our principle refers; and with the aid of this conception the principle may be also expressed thus: *an uncompensated transmission of heat from a colder to a warmer body can never occur.* The term "uncompensated" here expresses the same idea as that which was intended to be conveyed by the words "by itself" in the previous enunciation of the principle, and by the expression "without some other change, connected therewith, occurring at the same time" in the original text.—1864.]

* [It will readily be understood that everything here said, by way of example, concerning a gas applies, essentially, to every other body whose condition is determined by its temperature and volume. Of course the shapes of the curves, representing the decrease of pressure corresponding to an augmentation of volume, differ for different bodies; in other words, the aspect of the figure will depend upon the choice of the body.—1864.]

perature $t$, by the ordinate $h\,a$. This gas we subject, successively, to the following operations :—

1. The temperature $t$ of the gas is changed to $t_1$, which, for the sake of an example, may be less than $t$. To do this, the gas may be enclosed within a surface impenetrable to heat, and allowed to expand without either receiving or losing heat. The diminution of pressure, consequent upon the simultaneous increase of volume and decrease of temperature, is represented by the curve $a\,b$; so that, when the temperature of the gas has reached $t_1$, its volume and pressure have become $o\,i$ and $i\,b$ respectively.

Fig. 7.



2. The gas is next placed in communication with a body $K_1$, of the temperature $t_1$, and allowed to expand still more, in such a manner, however, that all the heat lost by expansion is again supplied by the body. With respect to this body, we shall assume that, owing to its magnitude or to some other cause, its temperature does not become appreciably lower by this expenditure of heat, and therefore that it may be considered constant. Consequently, during expansion the gas will also preserve a constant temperature, and the diminution of the pressure will be represented by a portion of an equilateral hyperbola $b\,c$. The quantity of heat furnished by $K_1$ shall be $Q_1$.

3. The gas is now separated from the body $K_1$ and allowed to expand still further, but without receiving or losing heat, until its temperature has diminished from $t_1$ to $t_2$. The consequent diminution of pressure is represented by the curve $c\,d$, which is of the same nature as $a\,b$.

4. The gas is now put in communication with a body $K_2$,

having the constant temperature $t_2$, and compressed; all the heat thus produced in it being imparted to $K_2$. This compression is continued until $K_2$ has received the same quantity of heat $Q_1$ as was before furnished by $K_1$. The pressure will increase according to the equilateral hyperbola *d e*.

5. The gas is then separated from the body $K_2$ and compressed, without being permitted to receive or lose heat, until its temperature rises from $t_2$ to its original value $t$, the pressure increasing according to the curve *e f*. The volume *o n* to which the gas is thus reduced is smaller than its original volume *o h*, for the pressure which had to be overcome in the compression *d e*, and therefore the work to be spent, were less than the corresponding magnitudes during the expansion *b c*; so that, in order to restore the same quantity of heat $Q_1$, the compression must be continued further than would have been necessary merely to annul the expansions.

6. The gas is at length placed in communication with a body K, of the constant temperature $t$, and allowed to expand to its original volume *o h*, the body K replacing the heat thus lost, the amount of which may be Q. When the gas reaches the volume *o h* with the temperature $t$, it must exert its original pressure; and the equilateral hyperbola, which represents the last diminution of pressure, will precisely meet the point *a*.

These six changes together constitute a *cyclical process*, the gas ultimately returning to its original condition. Of the three bodies K, $K_1$ and $K_2$, which throughout the whole process are considered merely as sources or reservoirs of heat, the two first have lost the quantities of heat Q and $Q_1$, and the third has received the quantity $Q_1$, or, as we may express it, $Q_1$ has been transferred from $K_1$ to $K_2$, and Q has disappeared. The last quantity of heat must, according to the first theorem, have been converted into exterior work. The pressure of the gas during expansion being greater than during compression, and therefore the positive amount of work greater than the negative, there has been a gain of exterior work, which is evidently represented by the area of the closed figure *a b c d e f*. If we call this amount of work W, then, according to equation (1),

$$Q = A \, . \, W*.$$

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* [The cyclical process here described differs from the one described at

The whole of the above-described cyclical process may be reversed or executed in an opposite manner by connecting the gas with the same bodies and, under the same circumstances as before, executing the reverse operations, *i. e.* commencing with the compression *af*, after which would follow the expansions *fe* and *ed*, and lastly the compressions *dc*, *cb*, and *ba*. The bodies K and $K_1$ will now evidently *receive* the quantities of heat Q and $Q_1$, and $K_2$ will *lose* the quantity $Q_1$. At the same time the negative work is now greater than the positive, so that the area of the closed figure now represents a *loss* of work. The result of the reverse process, therefore, is that the quantity of heat $Q_1$ has been transferred from $K_2$ to $K_1$, and the quantity of heat Q, generated from work, given to the body K.

In order to learn the mutual dependence of the two simultaneous transformations above described, we shall first assume that the temperatures of the three reservoirs of heat remain the same, but that the cyclical processes through which the transformations are effected are different. This will be the case when, instead of a gas, some other body is submitted to similar transformations, or when the cyclical processes are of any other kind, subject only to the conditions that the three bodies K, $K_1$ and $K_2$ are the only ones which receive or impart heat, and of the two latter the one receives as much as the other loses. These several processes can be either reversible, as in the foregoing case, or not, and the law which governs the transformations will vary accordingly. Nevertheless the modification which the law for non-reversible processes suffers may be easily applied afterwards, so that at present we will confine ourselves to the consideration of *reversible* cyclical processes.

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page 23 of the First Memoir, and there graphically represented in fig. 1, only by the circumstance that three, instead of two bodies, serving as reservoirs of heat, now present themselves. If we assume the temperature $t$ of the body K to be equal to the temperature $t_1$ of the body $K_1$, we may dispense with the body K altogether, and instead thereof employ the body $K_1$; the result of this would be that the body $K_1$ would give up, on the whole, the quantity $Q+Q_1$ of heat, and the body $K_2$ would receive the quantity $Q_1$. It would then be said that of the total quantity of heat given up by the body $K_1$, the portion Q is transformed into work, and the other part $Q_1$ is transferred to the body $K_2$; but this occurred in the previously described process, so that the latter must be regarded as a special case of the one here described.—1864.]

With respect to all these it may be proved from the foregoing principle, that the quantity of heat $Q_1$, transferred from $K_1$ to $K_2$, has always the same relation to $Q$, the quantity of heat transformed into work. For if there were two such processes wherein, $Q$ being the same, $Q_1$ was different, then the two processes could be executed successively, the one in which $Q_1$ was smaller in a direct, the other in an opposite manner. Then the quantity of heat $Q$, which by the first process was converted into work, would be again transformed into heat by the second process and restored to the body $K$, and in other respects everything would ultimately return to its original condition; with this sole exception, however, that more heat would have passed from $K_2$ to $K_1$ than in the opposite direction. On the whole, therefore, a transmission of heat from a colder body $K_2$ to a warmer $K_1$ has occurred, which in contradiction to the principle before mentioned, has not been compensated in any manner.

Of the two transformations in such a reversible process either can replace the other, if the latter is taken in an opposite direction; so that if a transformation of the one kind has occurred, this can be again reversed, and a transformation of the other kind may be substituted without any other permanent change being requisite thereto. For example, let the quantity of heat $Q$, produced in any manner whatever from work, be received by the body $K$; then by the foregoing cyclical process it can be again withdrawn from $K$ and transformed back into work, but at the same time the quantity of heat $Q_1$ will pass from $K_1$ to $K_2$; or if the quantity of heat $Q_1$ had previously been transferred from $K_1$ to $K_2$, this can be again restored to $K_1$ by the reversed cyclical process whereby the transformation of work into the quantity of heat $Q$ of the temperature of the body $K$ will take place.

We see, therefore, that these two transformations may be regarded as phenomena of the same nature, and we may call two tranformations which can thus mutually replace one another *equivalent*. We have now to find the law according to which the transformations must be expressed as mathematical magnitudes, in order that the equivalence of two transformations may be evident from the equality of their values. The mathematical value of a transformation thus determined may be called its *equivalence-value* (Aequivalenzwerth).

With respect to the direction in which each transformation is to be considered positive, it may be chosen arbitrarily in the one, but it will then be fixed in the other, for it is clear that the transformation which is equivalent to a positive transformation must itself be positive. In future we shall consider *the conversion of work into heat and, therefore, the passage of heat from a higher to a lower temperature as positive transformations**.

With respect to the magnitude of the equivalence-value, it is first of all clear that the value of a transformation from work into heat must be proportional to the quantity of heat produced; and besides this it can only depend upon the temperature. Hence the equivalence-value of the transformation of work into the quantity of heat Q, of the temperature $t$, may be represented generally by

$$Q \,.\, f(t),$$

wherein $f(t)$ is a function of the temperature, which is the same for all cases. When Q is negative in this formula, it will indicate that the quantity of heat Q is transformed, not from work into heat, but from heat into work. In a similar manner the value of the passage of the quantity of heat Q, from the temperature $t_1$ to the temperature $t_2$, must be proportional to the quantity Q, and besides this, can only depend upon the two temperatures. In general, therefore, it may be expressed by

$$Q \,.\, F(t_1, t_2),$$

wherein $F(t_1, t_2)$ is a function of both temperatures, which is the same for all cases, and of which we at present only know that, without changing its numerical value, it must change its sign when the two temperatures are interchanged; so that

$$F(t_2, t_1) = -F(t_1, t_2). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to institute a relation between these two expressions, we have the condition, that in every reversible cyclical process of the above kind, the two transformations which are involved must be equal in magnitude, but opposite in sign; so that their algebraical sum must be zero. For instance, in the process for

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* [The reason why this choice of the positive and negative senses is preferable to the opposite one, will become apparent after the theorems relative to the transformations have been enunciated.—1864.]

a gas, so fully described above, the quantity of heat Q, at the temperature $t$, was converted into work; this gives $-Q\,.\,f(t)$ as its equivalence-value, and that of the quantity of heat $Q_1$, transferred from the temperature $t_1$ to $t_2$, will be $Q_1\,.\,F(t_1, t_2)$, so that we have the equation

$$-Q\,.\,f(t)+Q_1\,.\,F(t_1, t_2)=0. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Let us now conceive a similar process executed in an opposite manner, so that the bodies $K_1$ and $K_2$, and the quantity of heat $Q_1$ passing between them, remain the same as before; but that instead of the body K of the temperature $t$, another body K′ of the temperature $t'$ be employed; and let us call the quantity of heat produced by work in this case Q′,—then, analogous to the last, we shall have the equation

$$Q'.f(t')+Q_1\,.\,F(t_2, t_1)=0. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Adding these two equations, and applying (4), we have

$$-Q\,.f(t)+Q'\,.f(t')=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If now we regard these two cyclical processes together as one cyclical process, which is of course allowable, then in the latter the transmissions of heat between $K_1$ and $K_2$ will no longer enter into consideration, for they precisely cancel one another, and there remain only the quantity of heat Q taken from K and transformed into work, and the quantity Q′ generated by work and given to K′. These two transformations of the *same* kind, however, may be so divided and combined as again to appear as transformations of *different* kinds. If we hold simply to the fact that a body K has lost the quantity of heat Q, and another body K′ has received the quantity Q′, we may without hesitation consider the part common to both quantities as transferred from K to K′, and regard only the other part, the excess of one quantity over the other, as a transformation from work into heat, or *vice versâ*. For example, let the temperature $t'$ be greater than $t$, so that the above transmission, being a transmission from the colder to the warmer body, will be negative. Then the other transformation must be positive, that is, a transformation from work into heat, whence it follows that the quantity of heat Q′ imparted to K′ must be greater than the quantity Q lost by K. If we divide Q′ into the two parts

$$Q \text{ and } Q'-Q,$$

the first will be the quantity of heat transferred from K to K′, and the second the quantity generated from work.

According to this view the double process appears as a process of the same kind as the two simple ones of which it consists; for the circumstance that the generated heat is not imparted to a third body, but to one of the two between which the transmission of heat takes place, makes no essential difference, because the temperature of the generated heat is arbitrary, and may therefore have the same value as the temperature of one of the two bodies; in which case a third body would be superfluous. Consequently, for the two quantities of heat Q and Q′−Q, an equation of the same form as (6) must hold, *i. e.*

$$(Q'-Q).f(t')+Q.F(t,t')=0.$$

Eliminating the magnitude Q′ by means of (7), and dividing by Q, this equation becomes

$$F(t,t')=f(t')-f(t), \quad . \quad . \quad . \quad . \quad . \quad (8)$$

so that the temperatures $t$ and $t'$ being arbitrary, the function of two temperatures which applies to the second kind of transformation is reduced, in a general manner, to the function of one temperature which applies to the first kind.

For brevity, we will introduce a simpler symbol for the last function, or rather for its reciprocal, inasmuch as the latter will afterwards be shown to be the more convenient of the two. Let us therefore make

$$f(t)=\frac{1}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

so that T is now the unknown function of the temperature involved in the equivalence-values. Further, $T_1$, $T_2$, &c. shall represent particular values of this function, corresponding to the temperatures $t_1$, $t_2$, &c.

According to this, the second fundamental theorem in the mechanical theory of heat, which in this form might appropriately be called the *theorem of the equivalence of transformations*, may be thus enunciated:

*If two transformations which, without necessitating any other permanent change, can mutually replace one another, be called* *equivalent, then the generation of the quantity of heat* Q *of the temperature* t *from work, has the equivalence-value*

$$\frac{Q}{T},$$

*and the passage of the quantity of heat* Q *from the temperature* $t_1$ *to the temperature* $t_2$, *has the equivalence-value*

$$Q\left(\frac{1}{T_2}-\frac{1}{T_1}\right),$$

*wherein* T *is a function of the temperature, independent of the nature of the process by which the transformation is effected.*

If to the last expression we give the form

$$\frac{Q}{T_2}-\frac{Q}{T_1},$$

it is evident that the passage of the quantity of heat Q, from the temperature $t_1$ to the temperature $t_2$, has the same equivalence-value as a double transformation of the first kind, that is to say, the transformation of the quantity Q from heat at the temperature $t_1$ into work, and from work into heat at the temperature $t_2$. A discussion of the question how far this external agreement is based upon the nature of the process itself would be out of place here*; but at all events, in the mathematical determination of the equivalence-value, every transmission of heat, no matter how effected, can be considered as such a combination of two opposite transformations of the first kind.

By means of this rule, it will be easy to find a mathematical expression for the total value of all the transformations of both kinds, which are included in any cyclical process, however complicated. For instead of examining what part of a given quantity of heat received by a reservoir of heat, during the cyclical process, has arisen from work, and whence the other part has come, every such quantity received may be brought into calculation as if it had been generated by work, and every quantity lost by a reservoir of heat, as if it had been converted into work. Let us assume that the several bodies $K_1$, $K_2$, $K_3$, &c., serving as reservoirs of heat at the temperatures $t_1$, $t_2$, $t_3$, &c., have received during the process the quantities of heat $Q_1$, $Q_2$, $Q_3$, &c., whereby the loss of a quantity of heat will be counted

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[* This subject is discussed in one of the subsequent memoirs.—1864.]

as the gain of a negative quantity of heat; then the total value N of all the transformations will be

$$N=\frac{Q_1}{T_1}+\frac{Q_2}{T_2}+\frac{Q_3}{T_3}+\&c.\,.=\Sigma\frac{Q}{T}. \quad . \quad . \quad . \quad (10)$$

It is here assumed that the temperatures of the bodies $K_1$, $K_2$, $K_3$, &c. are constant, or at least so nearly constant, that their variations may be neglected. When one of the bodies, however, either by the reception of the quantity of heat Q itself, or through some other cause, changes its temperature during the process so considerably that the variation demands consideration, then for each element of heat $dQ$ we must employ that temperature which the body possessed at the time it received it, whereby an integration will be necessary. For the sake of generality, let us assume that this is the case with all the bodies; then the foregoing equation will assume the form

$$N=\int\frac{dQ}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

wherein the integral extends over all the quantities of heat received by the several bodies.

If the process is *reversible*, then, however complicated it may be, we can prove, as in the simple process before considered, *that the transformations which occur must exactly cancel each other, so that their algebraical sum is zero.*

For were this not the case, then we might conceive all the transformations divided into two parts, of which the first gives the algebraical sum zero, and the second consists entirely of transformations having the same sign. By means of a finite or infinite number of simple cyclical processes, the transformations of the first part must admit of being cancelled*, so that the transformations of the second part would alone remain

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* [By a simple cyclical process is here to be understood one in which, as above described, a quantity of heat is transformed into, or arises from work, whilst a second quantity is transferred from one body to another. Now it may be readily shown that every two transformations whose algebraical sum is zero may be cancelled by means of one or two simple cyclical processes.

In the first place, let the two given transformations be of different kinds. For instance, let the quantity of heat Q at the temperature $t$ be transformed into work, and the quantity $Q_1$ be transferred from a body $K_1$ of the temperawithout any other change. Were these transformations *negative*, i. e. transformations from heat into work, and passages of heat from lower to higher temperatures, then of the two kinds the first could be replaced by transformations of the

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ture $t_1$ to a body $K_2$ of the temperature $t_2$, whereby we will assume, since our intended exposition will be thereby facilitated, that Q and $Q_1$ denote the *absolute* values of the quantities of heat, so that the positive or negative character of each transformation must be denoted explicitly by a prefixed + or − sign. Suppose, moreover, that the magnitudes of the two quantities of heat are related to one another in the manner expressed by the equation

$$-\frac{Q}{T}+Q_1\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=0.$$

Conceive the cyclical process above described to be performed in a contrary manner, so that the quantity of heat Q at the temperature $t$ arises from work, and another quantity of heat is transferred from the body $K_2$ to the body $K_1$. This latter quantity must then be precisely the quantity $Q_1$ which enters into the above equation, and thus the given transformations are cancelled.

In the next place, let a transformation from work to heat, and another from heat to work be given; for instance, let the quantity of heat Q, at the temperature $t$, be generated by work, and the quantity $Q'$, at the temperature $t'$, be converted into work, and suppose the two quantities to be so related to one another that

$$\frac{Q}{T}-\frac{Q'}{T'}=0.$$

Conceive the above-described cyclical process to be first performed, whereby the quantity of heat Q at the temperature $t$ is converted into work, and another quantity $Q_1$ transferred from a body $K_1$ to another body $K_2$. Afterwards conceive a second cyclical process of the opposite kind to be performed, in which the last-named quantity of heat $Q_1$ is transported back from $K_2$ to $K_1$, and, besides this, a quantity of heat of the temperature $t'$ is generated from work. This conversion of work into heat must then, apart from its sign, be equivalent to the preceding conversion of heat into work, since both are equivalent to one and the same transmission of heat. The heat at the temperature $t'$, which has arisen from work, must consequently be just as great as the quantity $Q'$ involved in the last equation, and the given transformations are thus cancelled.

In the last place, let two transmissions of heat be given; for instance, let the quantity of heat $Q_1$ be transferred from a body $K_1$, of the temperature $t_1$, to a body $K_2$ of the temperature $t_2$, and let another quantity $Q'_1$ be conveyed from a body $K'_2$, of the temperature $t'_2$, to a body $K'_1$, of the temperature $t'_1$, and suppose these two quantities to stand to each other in the relation

$$Q_1\left(\frac{1}{T_2}-\frac{1}{T_1}\right)+Q'_1\left(\frac{1}{T'_1}-\frac{1}{T'_2}\right)=0.$$

Conceive now two cyclical processes to be performed, in one of which the quantity of heat $Q_1$ is carried from $K_2$ to $K_1$, and thereby the quantity Q at the temperature $t$ generated by work, whilst in the second the same quanlatter kind*, and ultimately transmissions of heat from a lower to a higher temperature would alone remain, which would be compensated by nothing, and therefore contrary to the above principle. Further, were those transformations *positive,* it would only be necessary to reverse the operations in order to render them negative, and thus we should again obtain the foregoing impossible case. Hence we conclude that the second part of the transformations can have no existence.

Consequently the equation

$$\int\frac{dQ}{T}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

is the analytical expression, for all *reversible cyclical processes,* of the second fundamental theorem in the mechanical theory of heat.

The application of this equation can be considerably extended by giving to the magnitude $t$ involved in it a somewhat different signification. For this purpose, let us consider a cyclical process consisting of a series of changes of condition made by a

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tity of heat Q is reconverted into work, and thereby another quantity transferred from $K'_1$ to $K'_2$. This other quantity must then be precisely that which is denoted by $Q_1'$, and the two given transformations are thus cancelled.

If now, instead of two, any number of transformations were given, having an algebraical sum equal to zero, we could always separate and combine them so as to obtain, solely, groups consisting each of two transformations whose algebraical sum is equal to zero; and the two transformations of each such group could then, as has just been shown, be cancelled by means of one or two simple cyclical processes. If continuous changes of temperature should present themselves in the given original process, so that the quantities of heat given up and received would have to be divided into infinitesimal elements, the number of the groups which would have to be formed, and consequently also the number of simple cyclical processes, would be infinite; as far as the principle is concerned, however, this makes no difference.—1864.]

* [For if the given transformation consist in the conversion into work of the quantity of heat Q at the temperature $t$, we have, as already explained in the text in reference to the opposite case, merely to conceive the above-described cyclical process performed in a contrary manner, whereby the quantity of heat Q at the temperature $t$ will be generated by work; and at the same time another quantity $Q_1$ will be transferred from a body $K_2$, of the temperature $t_2$, to a body $K_1$ of the higher temperature $t_1$. The given transformation from heat to work will thus be cancelled, and replaced by the transmission of heat from $K_1$ to $K_2$.—1864.]

body which ultimately returns to its original state, and for simplicity, let us assume that all parts of the body have the same temperature; then in order that the process may be reversible, the changing body when imparting or receiving heat can only be placed in communication with such bodies as have the same temperature as itself, for only in this case can the heat pass in an opposite direction. Strictly speaking, this condition can never be fulfilled if a motion of heat at all occurs; but we may assume it to be so nearly fulfilled, that the small differences of temperature still existing may be neglected in the calculation. In this case it is of course of no importance whether $t$, in the equation (II), represents the temperature of the reservoir of heat just employed, or the momentary temperature of the changing body, inasmuch as both are equal. The latter signification being once adopted, however, it is easy to see that any other temperatures may be attributed to the reservoirs of heat without producing thereby any change in the expression $\int\frac{dQ}{T}$ which shall be prejudicial to the validity of the foregoing equation. As with this signification of $t$ the several reservoirs of heat need no longer enter into consideration, it is customary to refer the quantities of heat, not to them, but to the changing body itself, by stating what quantities of heat this body successively receives or imparts during its modifications. If hereby a quantity of heat received be again counted as positive, and a quantity imparted as negative, all quantities of heat will of course be affected with a sign opposite to that which was given to them with reference to the reservoirs of heat, for every quantity of heat *received* by the changing body is *imparted* to it by some reservoir of heat; nevertheless, this circumstance can have no influence upon the equation which expresses that the value of the whole integral is zero. From what has just been said, it follows, therefore, that when for every quantity of heat $dQ$ which the body receives or, if negative, imparts during its changes, the temperature of the body at the moment be taken into calculation, the equation (II) may be applied without further considering whence the heat comes or whither it goes, provided the process be in other respects reversible.

To the equation (II) thus interpreted we can now give a more special form, as was formerly done to equation (I), in which form it shall express a particular property of the body. We shall thus obtain an equation essentially the same as the well-known one deduced by Clapeyron from the theorem of Carnot*. With respect to the nature of the changes, we shall assume the same conditions as before led to the deduction of the equations (2) and (3) from (I), and which also suffice for the fulfilment of equation (II)†. Hence, the condition of the body being defined by its temperature $t$ and volume $v$, we have

$$dQ = \frac{dQ}{dt}dt + \frac{dQ}{dv}dv.$$

Inasmuch as by (II) $\int \frac{dQ}{T}$ must always equal zero, whenever $t$ and $v$ assume their initial values, the expression under the integral sign, which by the foregoing equation becomes

$$\frac{1}{T} \cdot \frac{dQ}{dt}dt + \frac{1}{T} \cdot \frac{dQ}{dv}dv,$$

must be a complete differential, if $t$ and $v$ are independent variables; and the two terms of the expression must consequently satisfy the following condition,

$$\frac{d}{dt}\left(\frac{1}{T} \cdot \frac{dQ}{dv}\right) = \frac{d}{dv}\left(\frac{1}{T} \cdot \frac{dQ}{dt}\right).$$

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* *Journ. de l'Ecole Polytechnique*, tome xiv.

† [These conditions were that the sole exterior force in operation is a pressure acting everywhere with the same intensity upon, and perpendicularly to the surface, and that this pressure always differs so little from the expansive force of the body that the two may be regarded as equal to one another in all calculations. Hence it follows that the changeable body may be again compressed under the same pressure as that under which it expands, and consequently that its changes of volume have occurred in a reversible manner. A certain temperature $t$ was likewise ascribed to the entire changeable body—an assumption which implies that all parts of the latter have one and the same temperature, or at all events, that the differences of temperature which present themselves are small enough to be neglected. Hence it follows that within the body no transmissions of heat occur from warmer to colder places, which are of sufficient importance to be taken into calculation. All the changes, therefore, of which the body is susceptible may be regarded as *reversible*, and for the truth of the equation (II) nothing more than this is requisite.—1864.]

From this we obtain

$$\frac{1}{\mathrm{T}}\cdot\frac{d}{dt}\left(\frac{d\mathrm{Q}}{dv}\right)-\frac{d\mathrm{Q}}{dv}\cdot\frac{\frac{d\mathrm{T}}{dt}}{\mathrm{T}^2}=\frac{1}{\mathrm{T}}\cdot\frac{d}{dv}\left(\frac{d\mathrm{Q}}{dt}\right)$$

or

$$\frac{d\mathrm{Q}}{dv}\cdot\frac{d\mathrm{T}}{dt}=\mathrm{T}\cdot\left[\frac{d}{dt}\left(\frac{d\mathrm{Q}}{dv}\right)-\frac{d}{dv}\left(\frac{d\mathrm{Q}}{dt}\right)\right]. \quad . \quad . \quad . \quad (12)$$

Substituting, from equation (3), the value of the expression within the [ ], we obtain the desired equation,

$$\frac{d\mathrm{Q}}{dv}\cdot\frac{d\mathrm{T}}{dt}=\mathrm{A}\,.\,\mathrm{T}\frac{dp}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which, on account of the relation

$$\frac{dp}{dt}=\frac{dp}{d\mathrm{T}}\cdot\frac{d\mathrm{T}}{dt},$$

may be written thus :

$$\frac{d\mathrm{Q}}{dv}=\mathrm{A}\,.\,\mathrm{T}\frac{dp}{d\mathrm{T}}*. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13a)$$

If we compare this result with the before-mentioned equation established by Clapeyron, we shall at once see the relation which exists between the function T, here introduced, and that used by Clapeyron, denoted by C, and known as Carnot's function, which I have also used in former memoirs. This relation may be expressed thus :

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* [I may here remark that the equation (12) may be transformed in the same way as the equation (13) has already been transformed. For putting therein

$$\frac{d\mathrm{Q}}{dt}=\frac{d\mathrm{Q}}{d\mathrm{T}}\cdot\frac{d\mathrm{T}}{dt},$$

$$\frac{d}{dt}\left(\frac{d\mathrm{Q}}{dv}\right)=\frac{d}{d\mathrm{T}}\left(\frac{d\mathrm{Q}}{dv}\right)\cdot\frac{d\mathrm{T}}{dt},$$

and dividing throughout by $\frac{d\mathrm{T}}{dt}$, we have

$$\frac{d\mathrm{Q}}{dv}=\mathrm{T}\left[\frac{d}{d\mathrm{T}}\left(\frac{d\mathrm{Q}}{dv}\right)-\frac{d}{dv}\left(\frac{d\mathrm{Q}}{d\mathrm{T}}\right)\right];$$

or, otherwise written,

$$\frac{d}{d\mathrm{T}}\left(\frac{d\mathrm{Q}}{dv}\right)-\frac{d}{dv}\left(\frac{d\mathrm{Q}}{d\mathrm{T}}\right)=\frac{1}{\mathrm{T}}\cdot\frac{d\mathrm{Q}}{dv}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

Hereby the meaning of the equation (II) is expressed, even more simply than in (12), in the form of a partial differential equation of the second order. —1864.]

$$\frac{\frac{dT}{dt}}{T}=\frac{A}{C}\text{*}. \qquad (14)$$

We proceed now to the consideration of *non-reversible* cyclical processes.

In the proof of the previous theorem, that in any reversible cyclical process, however complicated, the algebraical sum of all the transformations must be zero, it was first shown that the sum could not be *negative*, and afterwards that it could not be *positive*, for if so it would only be necessary to reverse the process in order to obtain a negative sum. The first part of this proof remains unchanged even when the process is not reversible; the second part, however, cannot be applied in such a case. Hence we obtain the following theorem, which applies generally to all cyclical processes, those that are reversible forming the limit:—

*The algebraical sum of all transformations occurring in a cyclical process can only be positive.*

A transformation which thus remains at the conclusion of a cyclical process without another opposite one, and which according to this theorem can only be positive, we shall, for brevity, call an *uncompensated* transformation.

The different kinds of operations giving rise to uncompensated transformations are, as far as external appearances are concerned, rather numerous, even though they may not differ very essentially. One of the most frequently occurring examples is that of the transmission of heat by mere conduction, when two bodies of different temperatures are brought into immediate contact; other cases are the production of heat by friction, and by an electric current when overcoming the resistance due to imperfect conductibility, together with all cases where a force, in doing mechanical work, has not to overcome an equal resistance, and therefore produces a perceptible external motion, with more or

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* [The equation established by Clapeyron, when written in the form given to it in the notes to the equations (IV) and (V) of the First Memoir (pp. 47, 48), is

$$\frac{dQ}{dv}=C\frac{dp}{dt},$$

and on comparing this expression for $\frac{dQ}{dv}$ with the one which results from the equation (13), we obtain the equation (14).—1864.]

less velocity, the *vis viva* of which afterwards passes into heat. An instance of the last kind may be seen when a vessel filled with air is suddenly connected with an empty one ; a portion of air is then propelled with great velocity into the empty vessel and again comes to rest there. It is well known that in this case just as much heat is present in the whole mass of air after expansion as before, even if differences have arisen in the several parts, and therefore there is no heat permanently converted into work. On the other hand, however, the air cannot again be compressed into its former volume without a simultaneous conversion of work into heat.

The principle according to which the equivalence-values of the uncompensated transformations thus produced are to be determined, is evident from what has gone before, and I will not here enter further into the treatment of particular cases.

In conclusion, we must direct our attention to the function T, which hitherto has been left quite undetermined; we shall not be able to determine it entirely without hypothesis, but by means of a very probable hypothesis it will be possible so to do. I refer to an accessory assumption already made in my former memoir, to the effect that *a permanent gas, when it expands at a constant temperature, absorbs only so much heat as is consumed by the exterior work thereby performed.* This assumption has been verified by the later experiments of Regnault, and in all probability is accurate for all gases to the same degree as Mariotte and Gay-Lussac's law, so that for an *ideal* gas, for which the latter law is perfectly accurate, the above assumption will also be perfectly accurate.

The exterior work done by a gas during an expansion $dv$, provided it has to overcome a pressure equivalent to its total expansive force $p$, is equal to $pdv$, and the quantity of heat absorbed thereby is expressed by $\frac{dQ}{dv}dv$. Hence we have the equation

$$\frac{dQ}{dv}=A\,.\,p,$$

and by substituting this value of $\frac{dQ}{dv}$ in the equation (13), the latter becomes

$$\frac{\frac{d\mathrm{T}}{dt}}{\mathrm{T}}=\frac{\frac{dp}{dt}}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

But, according to Mariotte and Gay-Lussac's law,

$$p=\frac{a+t}{v} \,.\, \text{const.},$$

where $a$ is the inverse value of the coefficient of expansion of the permanent gases, and nearly equal to 273, if the temperature be given in Centigrade degrees above the freezing-point. Eliminating $p$ from (15) by means of this equation, we have

$$\frac{d\mathrm{T}}{\mathrm{T}}=\frac{dt}{a+t}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

whence, by integration,

$$\mathrm{T}=(a+t) \,.\, \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

It is of no importance what value we give to this constant, because by changing it we change all equivalence-values proportionally, so that the equivalences before existing will not be disturbed thereby. Let us take the simplest value, therefore, which is unity, and we obtain

$$\mathrm{T}=a+t. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

According to this, T is nothing more than the temperature counted from $a^\circ$, or about 273° C. below the freezing-point; and, considering the point thus determined as the absolute zero of temperature, T is simply the *absolute temperature*. For this reason I introduced, at the commencement, the symbol T for the reciprocal value of the function $f(t)$. By this means all changes which would otherwise have had to be introduced in the form of equations, after the determination of the function, are rendered unnecessary; and now, according as we feel disposed to grant the sufficient probability of the foregoing assumption or not, we may consider T as the absolute temperature, or as a yet undetermined function of the temperature. I am inclined to believe, however, that the first may be done without hesitation.

# FIFTH MEMOIR.

## ON THE APPLICATION OF THE MECHANICAL THEORY OF HEAT TO THE STEAM-ENGINE*.

1. As our present modified views respecting the nature and deportment of heat, which constitute the mechanical theory of heat, had their origin in the well-known fact that heat may be employed for producing mechanical work, we may naturally anticipate that the theory so originated will in its turn help to place this application of heat in a clearer light. At all events the more general views thus obtained must enable us to pronounce safely upon the efficiency of the several machines for thus applying heat, as to whether they already perfectly fulfil their purpose, or whether and to what extent they are capable of being perfected.

Besides these reasons, which apply to all thermo-dynamic machines, there are others, applicable more particularly to the most important of them, the steam-engine, which appear to render a new investigation of the latter, conducted according to the principles of the mechanical theory of heat, desirable. It is precisely with respect to vapour at a maximum density that this new theory has led us to laws which differ essentially from those formerly accepted as true, or at least introduced into former calculations.

2. I may here be allowed to refer to a fact proved by Rankine and myself, that when a quantity of vapour, at its maximum density and enclosed by a surface impenetrable to heat, expands and thereby displaces a moveable part of the enclosing surface, *e. g.* a piston, with its full force of expansion, a part of the vapour must undergo condensation; whereas in most works on the steam-engine, amongst others in the excellent work of De

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* Published in Poggendorff's *Annalen*, March and April 1856, vol. xcvii. pp. 441 and 513; translated in the Philosophical Magazine, S. 4. vol. xii. pp. 241, 338 and 426; and in Silliman's Journal, S. 2. vol. xxii. pp. 180 and 364, vol. xxiii. p. 25.

Pambour*, Watt's theorem, that under these circumstances the vapour remains precisely at its maximum density, is assumed as a fundamental one.

Further, in the absence of more accurate knowledge, it was formerly assumed, in determining the volumes of the unit of weight of saturated vapour at different temperatures, that vapour even at its maximum density still obeys Mariotte's and Gay-Lussac's laws. In opposition to this, I have already shown in my first memoir† on this subject, that the volumes in question can be calculated from the principles of the mechanical theory of heat under the assumption, *that a permanent gas when it expands at a constant temperature only absorbs so much heat as is consumed in the external work thereby performed*, and that these calculations lead to values which, at least at high temperatures, differ considerably from Mariotte's and Gay-Lussac's laws.

Even the physicists who had occupied themselves more especially with the mechanical theory of heat, did not at that time coincide with this view of the deportment of vapour. William Thomson in particular opposed it. In a memoir‡ presented to the Royal Society of Edinburgh a year later, in March 1851, he only regarded this result as a proof of the improbability of the above assumption which I had employed.

Since then, however, he and J. P. Joule have together undertaken to test experimentally the accuracy of this assumption§. By a series of well-contrived experiments, executed on a large scale, they have in fact shown that, with respect to the *permanent* gases, atmospheric air and hydrogen, the assumption is so nearly true, that in most calculations the deviations from exactitude may be disregarded. With carbonic acid, the non-permanent gas they investigated, the deviations were greater. This is in perfect accordance with the remark I made on first making the assumption, which was that the latter would probably be found to be accurate for each gas in the same measure as Mariotte's and Gay-Lussac's laws were applicable thereto. In consequence of

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* *Théorie des Machines à Vapeur*, par le Comte F. M. G. de Pambour. Paris, 1844.

† [First Memoir of this collection.]

‡ Transactions of the Royal Society of Edinburgh, vol. xx. part 2, p. 261.

§ Phil. Trans. vol. cxliii. part 3, p. 357; and vol. cxliv. part 2, p 321.

these experiments, Thomson now calculates the volumes of saturated vapours in the same manner as myself. There is reason to believe, therefore, that the accuracy of this method of calculation will be gradually more and more recognized by other physicists.

3. These two examples will suffice to show that the principles upon which our former theory of steam-engines was founded have suffered such essential modifications through the mechanical theory of heat, as to render a new investigation of the subject necessary.

In the present memoir I have attempted to develope the principles of the calculation of the work of the steam-engine in accordance with the mechanical theory of heat. I have, however, limited myself to the steam-engines now in use, without at present entering into a consideration of the more recent and certainly very interesting attempts to employ vapour in a superheated state.

In recording the results of my investigation, I shall only assume, on the part of the reader, an acquaintance with my last memoir, "On a modified Form of the Second Fundamental Theorem in the Mechanical Theory of Heat"*. This will of course necessitate the deduction, in a somewhat different manner, of results which are no longer new, but have already been found by myself or others; I believe, however, that this repetition, by leading to greater unity and facility of comprehension, will not be found superfluous. At the proper places I shall, to the best of my ability, cite the papers wherein these results first appeared.

4. The expression "*a machine is driven by heat,*" is not of course strictly accurate. By it we must understand, that, in consequence of the changes produced by heat upon some kind of matter in the machine, the parts of the latter are set in motion. We shall refer to this matter as that *which manifests the action of heat.*

If a continuously-acting machine is in uniform action, all accompanying changes occur periodically, so that the condition which at a given time prevails in the machine and all its parts returns at equal intervals. Hence the matter which manifests

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* [Fourth Memoir of this collection.]

the action of the applied heat must at such regularly-recurring periods be present in the machine in equal quantity, and in the same state. This condition can be fulfilled in two different ways.

First. One and the same quantity of matter may always remain in the machine, when the changes of condition which this matter suffers during the action of the machine will be such, that at the end of each period it will regain its original condition and recommence the same cycle of changes.

Secondly. The machine may always expel the matter which served to produce the effect during a period, and in its place receive from an external source just as much matter of the same kind.

5. The last method is the one usually employed in most machines. This is the case, for instance, in machines with heated air as at present constructed; for after every stroke, the air which moved the piston in the driving cylinder is expelled into the atmosphere, and in its place an equal quantity of air from the same source is received into the feeding cylinder. Similarly in steam-engines without condensers, steam is driven from the cylinder into the atmosphere, and in its place fresh water is pumped from a reservoir into the boiler.

Further, a similar method is at least partially adopted even in steam-engines provided with a condenser as usually constructed. In them the water condensed from the steam is only partially pumped back into the boiler, for being mixed with the cooling water, a part of the latter also reaches the boiler. The remaining part of the condensed water, together with the remaining part of the cooling water, has to be got rid of.

The first method has lately been employed in steam-engines propelled by two vapours, *e. g.* those of water and æther. In these machines the steam is condensed solely by contact with metallic tubes filled with liquid æther, and the water thus produced is then completely pumped back into the boiler. In the same manner the vapour of the æther is condensed in metal tubes, which are merely surrounded by cold water, and subsequently it is pumped back into the first space intended for the vaporization of the æther. In order to maintain a uniform action, therefore, only so much fresh water and æther is necessary as will replace the leakage consequent upon imperfect construction.

6. In a machine of this kind, where the same matter is continually re-employed, the several changes which this matter suffers during a period must, as above stated, form a closed cycle, or, according to the nomenclature in my former memoir, a *cyclical process*.

On the contrary, machines in which a periodical reception and expulsion of matter occurs are not necessarily subject to this condition, though they may also fulfil it by expelling the matter in the same condition in which it was received. This is the case in steam-engines with condensers, where the water is ultimately expelled from the condenser in the liquid state, and at the same temperature as it had when introduced from the condenser into the boiler*.

In other machines, the condition, when expelled, is different from what it was when received. For example, heated-air machines, even when provided with regenerators, expel the air at a higher temperature than it formerly had; and steam-engines without condensers receive water in the liquid, and expel it in the gaseous form. Strictly, therefore, the complete cyclical process is not fulfilled in these cases; nevertheless we may always conceive a second machine appended to the given one which shall receive the matter from the first, reduce it in some manner to its original condition, and then expel it. Both machines may then be regarded as constituting one and the same machine, which will fulfil the above condition. In many cases this addition may be made without introducing greater complexity into the investigation. For example, a steam-engine with a condenser at a temperature of 100° C. may be substituted for a machine without a condenser, provided we assume the latter to be fed with water at 100° C.

Hence, if we assume that machines which do not fulfil the above condition are theoretically completed in the above manner, we may apply the theorems concerning cyclical processes to all thermo-dynamic machines, and thereby arrive at conclusions

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* The cooling water, which enters the condenser at a low, and leaves it at a high temperature, is not here taken into consideration, inasmuch as it does not form a part of the matter manifesting the effect of the applied heat, but merely constitutes a negative source of heat.

which are quite independent of the nature of the processes executed by the several machines.

7. In my former memoir I have represented the two fundamental theorems which hold good in every cyclical process by the following equations :—

$$Q=A.W, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

$$\int\frac{dQ}{T}=-N, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

wherein the letters have the same signification as before, viz.—

A is the thermal equivalent of the unit of work.

W represents the external work performed during the cyclical process.

Q signifies the heat imparted to the changeable body during a cyclical process, and $dQ$ an element of the same, whereby any heat withdrawn from the body is to be considered as an imparted negative quantity of heat. The integral in the second equation is extended over the whole quantity Q.

T is a function of the temperature which the changing matter has at the moment when it receives the element of heat $dQ$; or should the temperature of different parts of the body be different, a function of the temperature of the part which receives $dQ$. With respect to the form of the function T, I have shown in my former memoir that it is probably the temperature itself reckoned from a point which may be determined from the reciprocal value of the coefficient of expansion of an ideal gas, and which must be in the neighbourhood of $-273°$ C.; so that if $t$ represents the temperature above the freezing-point,

$$T=273+t. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the present memoir T will always have this signification, and for brevity will be called the *absolute temperature*. It may be here remarked, however, that the conclusions do not essentially depend upon this signification, but remain true even when T is considered as an undetermined function of the temperature.

Lastly, N denotes the equivalence-value of all the uncompensated transformations* involved in a cyclical process.

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* One species of uncompensated transformations requires further remark. The sources from which the changing matter derives heat must have higher temperatures than itself; and, on the other hand, those from which it derives

8. If the process is such that it can be reversed in the same manner, then N=0. If, however, one or more changes of con-

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negative quantities of heat, or which deprive it of heat, must have lower temperatures than itself. Therefore whenever heat is interchanged between the changing body and any source whatever, heat passes immediately from the body at a higher to the one at a lower temperature, and thus an uncompensated transformation occurs which is greater the greater the difference between the temperatures. In determining such uncompensated transformations, not only must the changes in the condition of the variable matter be taken into consideration, but also the temperatures of the sources of heat which are employed; and these uncompensated transformations will be included in N or not, according to the signification which is attached to the temperature occurring in equation (II). If thereby the temperature of the *source of heat* belonging to $dQ$ is understood, the above changes will be included in N. If, however, agreeably to the above definition, and to our intention throughout this memoir, the temperature of the changing matter is understood, then the above transformations are excluded from N. One more remark must be added concerning the minus sign prefixed to N, which did not appear in the same equation in my former memoir. This difference arises from the different application of the terms negative and positive with respect to quantities of heat. Before, a quantity of heat received by the changeable body was considered as negative because it was lost by the source of heat; now, however, it is considered as positive. Hereby every element of heat embraced by the integral, and consequently the integral itself, changes its sign; and hence, to preserve the correctness of the equation, the sign on the other side must be changed.

[The reason why, in different investigations, I have changed the significations of positive and negative quantities of heat, is that the points of view from which the processes in question are regarded, differ according to the nature of the investigations. In purely theoretical investigations on the transformations between heat and work, and on the other transformations connected therewith, it is convenient to consider heat generated by work as positive, and heat converted into work as negative. Now the heat generated by work during any cyclical process must be imparted to some body serving as a reservoir or as a source of heat, and the heat converted into work must be withdrawn from one of these bodies. Quantities of heat will receive appropriate signs in theoretical investigation, therefore, when the heat gained by a reservoir is calculated as positive, and that which it loses as negative. There are investigations, however, in which it is not necessary to take into special consideration the reservoirs or sources which receive the heat that is generated, or furnish the heat that is consumed by work, the condition of the variable body being the chief object of research. In such cases it is customary to regard the heat received by the changing body as positive, and the heat which it loses as negative; to deviate from this custom, for the sake of consistency, would be attended with many inconveniences. Researches on the interior processes in a steam-engine are of the latter kind, and accordingly I have deemed it advisable to adopt the customary choice of signs.—1864.]

dition occur in a cyclical process which are not reversible, then uncompensated transformations necessarily arise, and the magnitude N has consequently a determinable and necessarily positive value.

Amongst the operations to which the last remark is applicable, is one which in the following will be often mentioned. When a quantity of gas or vapour expands, and thereby overcomes a pressure equivalent to its total expansive force, it may be again compressed into its former volume by employing the same power, when all the phenomena which accompanied the expansion will take place in an inverse manner. This is not the case, however, when the gas or vapour does not, during its expansion, encounter all the resistance it is capable of overcoming; when, for instance, it issues from a vessel in which the pressure is greater than in the one into which it enters. In this case a compression, under circumstances similar to those accompanying expansion, is impossible.

By equation (II) we can determine the sum of all the uncompensated transformations in a cyclical process. As, however, a cyclical process may consist of several changes of condition in the given matter, of which some have occurred in a reversible, and others in an irreversible manner, it is often interesting to know how much of the whole sum of uncompensated transformations has resulted from changes of each kind. For this purpose let us conceive the matter, after the changes of condition which has to be examined in this manner, reduced to its original condition by any reversible operation. We shall thereby obtain a small cyclical process, to which the equation (II) will be just as applicable as to the whole. Consequently, if we know the quantities of heat which the matter has received during the process, and the temperatures which correspond thereto, the negative integral $-\int\frac{dQ}{T}$ will give the uncompensated transformation involved therein. But as the uncompensated transformation involved in the given change of condition could not have been increased by the above reduction, which was executed in a reversible manner, it will be fully represented by the above expression*.

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* [Let us suppose the changeable body to be a quantity of gas, and that one of the changes which this gas has suffered consists of an expansion, with-

Having thus investigated all the parts of the whole cyclical process which are not reversible, and found the values $N_1$, $N_2$, &c., which must all be positive, their sum will give the magni-

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out change of temperature, from the volume $v_1$ to the volume $v_2$. As already stated in the text, this expansion may occur in several ways. The gas may so expand that at every moment the pressure which it has to overcome corresponds to its expansive force at that moment; or it may be allowed to expand without overcoming any resistance whatever, by suddenly placing an empty vessel in connexion with the one in which it occupied the volume $v_1$; or lastly, it may, during its expansion, have to overcome a resistance less than that which corresponds to its own expansive force. If we wish to know the magnitude of the uncompensated transformation involved in this change of volume, we have merely to conceive the gas to be again compressed, at a constant temperature, from the volume $v_2$ to the volume $v_1$, and to determine the quantities of heat received and withdrawn during the cyclical process thus completed.

If during its expansion the gas has the full resistance to overcome, it must receive just as much heat as it afterwards gives off during compression, so that we obtain for the cyclical process the equation

$$-\int\frac{dQ}{T}=0.$$

If the gas has no resistance to overcome during expansion, and if we moreover assume it to be a *perfect* gas, it need not receive any heat during expansion. During compression, however, it must give off a quantity of heat equal to that which is generated by the exterior work necessary for compression. For each element of the change of volume this will be represented by $A.pdv$, where $p$ denotes the pressure, and the positive or negative sense is already expressed in the formula itself, since a quantity of heat to be received is positive, and one to be given off is negative. We must put then

$$-\int\frac{dQ}{T}=-\int_{v_2}^{v_1}\frac{A.pdv}{T}.$$

Now, according to the law of M. and G.,

$$p=\frac{RT}{v},$$

where R is an already known constant, so that

$$-\int\frac{dQ}{T}=-AR\int_{v_2}^{v_1}\frac{dv}{v}=AR\log\frac{v_2}{v_1}.$$

This, therefore, is the value of the uncompensated transformation when a perfect gas has expanded from the volume $v_1$ to the volume $v_2$ without having had to overcome any exterior resistance.

If, lastly, the gas, on expanding, has to overcome some, but not the full resistance, it will on so doing receive some heat, but not so much as it will give off on compression. We should now obtain, for the uncompensated transformation corresponding to the expansion, a value between zero and the one last calculated.—1864.]

tude N corresponding to the whole cyclical process, without its being necessary to take into consideration those parts which are known to be reversible.

9. If we now apply the equations (I) and (II) to the cyclical process which occurs during a period in a thermo-dynamic machine, it will be at once evident that, the whole quantity of heat communicated during this period to the matter in the machine being given, the corresponding amount of work can be immediately determined from the first equation without its being necessary to know the nature of the operations constituting the cyclical process.

In an equally general manner the work may be determined from other data by a combination of both equations.

We will assume that the quantities of heat successively imparted to the changing material, as well as the temperatures at the times of reception, are given, and that only one temperature, $T_0$, remains at which a certain as yet unknown quantity of heat was imparted or, if negative, abstracted. The sum of all the known quantities of heat shall be represented by $Q_1$, and the unknown quantity of heat by $Q_0$.

We will divide the integral in equation (II) into two parts, of which the one shall extend over the known quantity of heat $Q_1$, and the other over the unknown quantity $Q_0$. In the latter part, T having a constant value $T_0$, the integration may be immediately effected, and as result we have

$$\frac{Q_0}{T_0}.$$

The equation (II) thus becomes

$$\int_0^{Q_1}\frac{dQ}{T}+\frac{Q_0}{T_0}=-N,$$

whence results

$$Q_0=-T_0\cdot\int_0^{Q_1}\frac{dQ}{T}-T_0\cdot N.$$

Further, seeing that in our case

$$Q=Q_1+Q_0.$$

we have from equation (I),

$$W=\frac{1}{A}(Q_1+Q_0).$$

Substituting the above-found value of $Q_0$ in this equation, it becomes

$$W=\frac{1}{A}\left(Q_1-T_0\int_0^{Q_1}\frac{dQ}{T}-T_0 . N\right). \quad . \quad . \quad . \quad (2)$$

If, as a special case, the whole cyclical process is reversible, then

$$N=0,$$

and the above equation becomes

$$W=\frac{1}{A}\left(Q_1-T_0 . \int_0^{Q_1}\frac{dQ}{T}\right). \quad . \quad . \quad . \quad . \quad (3)$$

This expression differs from the preceding one only in the absence of the term $-\frac{T_0}{A}N$. Now as N can only be positive, this term must necessarily be negative; and thus we see that, under the above conditions with respect to the communication of heat, the greatest possible amount of work is obtained when the whole process is reversible; and that every circumstance which renders one of the operations in the cyclical process not reversible, diminishes the amount of work,—a conclusion which results easily from a direct consideration of the subject.

The equation (2) leads to the value of the amount of work in a manner opposite to that usually followed. The amounts of work done in the several operations are not separately determined and then added together, but, instead of this, the maximum of work is first found, and the losses occasioned by the several imperfections of the process are subsequently deducted from it.

If, with respect to the communication of heat, we introduce a still more limited condition, and assume that the whole quantity of heat $Q_1$ is also imparted to the body at a constant temperature $T_1$, then the integration which embraces this quantity of heat may also be executed, and gives

$$\frac{Q_1}{T_1},$$

whereby the equation (3) for the maximum of work assumes the form

$$W=\frac{Q_1}{A} . \frac{T_1-T_0}{T_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In this special form the equation has already been deduced by William Thomson and Rankine from a combination of Carnot's theorem, as modified by me, and the theorem of the equivalence of heat and work*.

10. Before we proceed, from these considerations which apply to all thermo-dynamic engines, to treat of the steam-engine, we must first premise something concerning the deportment of vapours at a maximum density.

In a memoir of mine, published as early as 1850, "On the Moving Force of Heat," &c.†, I have already established the equations which show the application of the two fundamental theorems of the mechanical theory of heat to vapours at a maximum density, and I have there employed these equations in deducing several consequences. But as in my last memoir, "On a modified Form of the Second Fundamental Theorem of the Mechanical Theory of Heat‡," I proposed a somewhat different mode of treating the whole subject, it appears preferable to me to assume the last memoir only as known. I shall therefore deduce those equations once more, in a different manner, by means of the results established in my last memoir.

It was there assumed, in order to apply the general equations which were first established to a somewhat more special case, that the only foreign force, acting upon the changing material, which required consideration in determining the external work, was an external pressure equally intense at all points of the surface, and directed everywhere at right angles to the same; and further, that this pressure always changed so slowly, and consequently at each moment differed so little from the opposite expansive force of the body, that in calculation the two might be considered equal. Let then $p$ be the pressure, $v$ the volume, and T the absolute temperature of the body. We introduce the last instead of $t$, the temperature counted from the freezing-point, because thereby the formulæ assume a simpler form. The equations already established in this case are

$$\frac{d}{dT}\left(\frac{dQ}{dv}\right)-\frac{d}{dv}\left(\frac{dQ}{dT}\right)=A\,.\,\frac{dp}{dT}, \quad . \quad . \quad . \quad \text{(III)}$$

$$\frac{dQ}{dv}=A\,.\,T\,\frac{dp}{dT}§. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IV)}$$

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* Phil. Mag. July 1851.

† [First Memoir of this Collection.]

‡ [Fourth Memoir of this Collection.]

§ [Instead of this equation (IV), which is identical with (13$a$) of the Fourth

These equations shall next be applied to the still more special case of vapours at their maximum density.

11. Let M be the mass of the matter whose vapour is to be considered, and which is placed in a perfectly closed expansible vessel. Let the part $m$ be in a vaporous, and the rest, $M-m$, in a liquid state. This mixed mass shall be the changing body to which the foregoing equations are to be referred.

The condition of the mass, as far as it here enters into consideration, is perfectly determined as soon as its temperature T and its volume $v$, *i. e.* the volume of the vessel, are given. For, according to hypothesis, the vapour is always in contact with the liquid, and therefore remains at its maximum density; so that its condition, as well as that of the liquid, depends only upon the temperature T. It only remains to be seen, therefore, whether the magnitude of each of the parts in different conditions is perfectly determined, from the condition that both parts together exactly fill the space enclosed by the vessel. Let $s$ represent the volume of the unit of weight of vapour at its maximum density where the temperature is T, and $\sigma$ that of the unit of weight of liquid, then

$$\begin{aligned} v &= m s + (M-m)\sigma \\ &= m(s-\sigma) + M\sigma. \end{aligned}$$

The magnitude $s$ never occurs hereafter except in the combination $s-\sigma$, so that we will introduce another letter for this difference, and make

$$u = s - \sigma, \quad \ldots\ldots\ldots \quad (5)$$

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Memoir (p. 132), the equation (12) of that memoir may be written, which latter at once assumes the form (12 *a*), there given in a note, on regarding T as the absolute temperature, and introducing it into the differential coefficients instead of the temperature estimated from the freezing-point. For the sake of reference I will here write all three equations, and that in the following order:

$$\frac{d}{dT}\left(\frac{dQ}{dv}\right) - \frac{d}{dv}\left(\frac{dQ}{dT}\right) = A \cdot \frac{dp}{dT}, \quad \ldots\ldots\ldots \quad (a)$$

$$\frac{d}{dT}\left(\frac{dQ}{dv}\right) - \frac{d}{dv}\left(\frac{dQ}{dT}\right) = \frac{1}{T} \cdot \frac{dQ}{dv}, \quad \ldots\ldots\ldots \quad (b)$$

$$\frac{dQ}{dv} = A \cdot T \frac{dp}{dT}. \quad \ldots\ldots\ldots \quad (c)$$

Of these equations (a) expresses the first fundamental theorem, and (b) the second fundamental theorem employed in its modified form. The equation (c) is obtained by combining both these theorems.—1864.]

in consequence of which the foregoing equation becomes

$$v = mu + M\sigma, \qquad (6)$$

and we have

$$m = \frac{v - M\sigma}{u}. \qquad (7)$$

By this equation $m$ is expressed as a function of T and $v$, because $u$ and $\sigma$ are functions of T.

12. In order to be able to apply equations (III) and (IV) to our case, we must next determine the magnitudes $\frac{dQ}{dv}$ and $\frac{dQ}{dT}$.

If the volume of the vessel increases by $dv$, then the quantity of heat which must be imparted to the mass in order to maintain a constant temperature will be generally expressed by

$$\frac{dQ}{dv}dv.$$

But this quantity of heat is expended solely in the vaporization which takes place during the expansion; so that if $r$ represents the heat required to vaporize the unit of mass, the above quantity of heat may also be represented by

$$r\frac{dm}{dv}dv,$$

and we have

$$\frac{dQ}{dv} = r\frac{dm}{dv}.$$

But according to (7),

$$\frac{dm}{dv} = \frac{1}{u};$$

hence

$$\frac{dQ}{dv} = \frac{r}{u}. \qquad (8)$$

Let us next assume that, whilst the volume of the vessel remains constant, the temperature of the mass increases by $dT$; then the general expression for the requisite quantity of heat will be

$$\frac{dQ}{dT}dT.$$

This quantity of heat consists of three parts:—

(1) The liquid part $M - m$ of the whole mass suffers an increment of temperature $dT$, for which, $c$ being the specific heat of

the liquid, the quantity of heat

$$(M-m)c\,dT$$

is necessary.

(2) The vaporous part $m$ will also undergo an increment of temperature $dT$, but it will be thereby compressed so as still to remain at its maximum density for the increased temperature $T+dT$. For an increment of temperature $dT$, we will represent by $h\,.\,dT$ the quantity of heat which must be imparted to the unit of mass of vapour during its contraction, in order that at every density it may have precisely that temperature for which this density is a maximum. The value and even the sign of the magnitude $h$ is at present unknown. The quantity of heat necessary in our case will therefore be

$$mh\,dT.$$

(3) During the elevation of temperature, a small quantity of liquid, represented generally by

$$\frac{dm}{dT}dT,$$

becomes vaporized, for which the quantity of heat

$$r\frac{dm}{dT}dT$$

is necessary. Herein, according to equation (7),

$$\begin{aligned}\frac{dm}{dT}&=-\frac{v-M\sigma}{u^2}\cdot\frac{du}{dT}-\frac{M}{u}\cdot\frac{d\sigma}{dT}\\&=-\frac{m}{u}\cdot\frac{du}{dT}-\frac{M}{u}\cdot\frac{d\sigma}{dT};\end{aligned}$$

so that by substitution the last expression becomes

$$-r\left(\frac{m}{u}\cdot\frac{du}{dT}+\frac{M}{u}\cdot\frac{d\sigma}{dT}\right)dT.$$

Equating the sum of these three quantities of heat and the former expression $\frac{dQ}{dT}dT$, we obtain the equation

$$\frac{dQ}{dT}=M\left(c-\frac{r}{u}\cdot\frac{d\sigma}{dT}\right)+m\left(h-c-\frac{r}{u}\cdot\frac{du}{dT}\right).\quad .\quad .\quad (9)$$

13. As indicated by equation (III), the above expression for $\frac{dQ}{dv}$ must be differentiated according to T, and the expression for

$\frac{dQ}{dT}$ according to $v$. The magnitude M is constant, the magnitudes $u, \sigma, r, c$ and $h$ are all functions of T alone, and only the magnitude $m$ is a function of T and $v$, so that

$$\frac{d}{dT}\left(\frac{dQ}{dv}\right)=\frac{1}{u}\cdot\frac{dr}{dT}-\frac{r}{u^2}\cdot\frac{du}{dT}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\frac{d}{dv}\left(\frac{dQ}{dT}\right)=\left(h-c-\frac{r}{u}\cdot\frac{du}{dT}\right)\frac{dm}{dv};$$

or, substituting for $\frac{dm}{dv}$ its value $\frac{1}{u}$,

$$\frac{d}{dv}\left(\frac{dQ}{dT}\right)=\frac{h-c}{u}-\frac{r}{u^2}\cdot\frac{du}{dT}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

By substituting the expressions given in (10), (11), and (8) in (III) and (IV), we obtain the required equations, which represent the two principal theorems of the mechanical theory of heat as applied to vapours at their maximum density. These are

$$\frac{dr}{dT}+c-h=A\,.\,u\frac{dp}{dT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (V)$$

$$r=A\,.\,Tu\frac{dp}{dT}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (VI)$$

and from a combination of both we have

$$\frac{dr}{dT}+c-h=\frac{r}{T}*. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

14. By means of these equations we will now treat a case, which in the following will so frequently occur, as to render it desirable at once to establish the results which have reference thereto.

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* [These equations, written in the following order,

$$\frac{dr}{dT}+c-h=A\,.\,u\frac{dp}{dT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$\frac{dr}{dT}+c-h=\frac{r}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

$$r=A\,.\,Tu\frac{dp}{dT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

correspond to the three equations (a), (b), (c) of the last note (p. 148). The first, containing the quantity $h$, is therefore a consequence of the first fundamental theorem, and the second follows from the modified form of the second fundamental theorem; the third equation, which does not contain $h$, arises from a combination of both these fundamental theorems.—1864.]

Let us suppose that the vessel before considered, containing the liquid and vaporous parts of the mass, changes its volume *without heat being imparted to, or withdrawn from, the mass.* Then, simultaneously with the volume, the temperature and magnitude of the vaporous part of the mass will change; and besides this—seeing that during the change of volume the pressure of the enclosed vapour is active, which pressure during expansion overcomes, and during contraction is overcome by an external force—a positive or negative amount of external work will be done by the heat which produces the pressure.

*Under these circumstances, the magnitude of the vaporous part* m, *the volume* v, *and the work* W *shall be determined as functions of the temperature* T.

15. It has already been shown that, in order that the volume and temperature may suffer any infinitely small increments $dv$ and $d\mathrm{T}$, a quantity of heat expressed by the sum

$$r\frac{dm}{dv}\,dv+\left[(\mathrm{M}-m)c+mh+r\frac{dm}{d\mathrm{T}}\right]d\mathrm{T}$$

must be imparted to the mass. In consequence of the present condition, according to which heat is neither imparted to, nor abstracted from the mass, this sum must be set equal to zero. Accordingly, writing $dm$ in place of

$$\frac{dm}{dv}\,dv+\frac{dm}{d\mathrm{T}}\,d\mathrm{T},$$

we obtain the equation

$$rdm+m(h-c)d\mathrm{T}+\mathrm{M}cd\mathrm{T}=0. \quad . \quad . \quad . \quad . \quad (13)$$

But by (12),

$$h-c=\frac{dr}{d\mathrm{T}}-\frac{r}{\mathrm{T}};$$

so that by again writing $dr$ in the place of $\frac{dr}{d\mathrm{T}}d\mathrm{T}$, $r$ being a function of T alone, we have

$$rdm+mdr-\frac{mr}{\mathrm{T}}\,d\mathrm{T}+\mathrm{M}cd\mathrm{T}=0,$$

or

$$d(mr)-\frac{mr}{\mathrm{T}}\,d\mathrm{T}+\mathrm{M}cd\mathrm{T}=0^{*}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

---

* [It is manifest that the expressions in the left of the equations (13) and (14), which are respectively equal to zero when heat is neither imparted to

This equation, divided by T, becomes

$$\frac{d(mr)}{T}-\frac{mr}{T^2}dT+Mc\frac{dT}{T}=0,$$

or

$$d\left(\frac{mr}{T}\right)+Mc\frac{dT}{T}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

Inasmuch as the specific heat of a liquid changes only very slowly with its temperature, we will in future always consider the magnitude $c$ as constant. In this case the above equation can be immediately integrated, and gives

$$\frac{mr}{T}+Mc\log T=\text{const.};$$

or if $T_1$, $r_1$, and $m_1$ be the initial values of T, $r$, and $m$,

$$\frac{mr}{T}=\frac{m_1r_1}{T_1}-Mc\log\frac{T}{T_1}*. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (VII)$$

If $r$ may be considered as a known function of the temperature, as through Regnault's experiments it may be in the case of steam, then by means of this equation $m$ is also expressed as a function of the temperature.

In order to give some idea of the deportment of this function, I have, for one particular case, collected together a few calculated values in the following Table. For instance, it is assumed that

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the mass nor abstracted from it, must in general be equated to $dQ$. For every change of volume and temperature, therefore, whereby the quantity of the vaporous part likewise changes in a corresponding manner, we have the equations

$$dQ=rdm+m(h-c)dT+McdT$$
$$=d(mr)-\frac{mr}{T}dT+McdT,$$

the frequent applicability of which is obvious.—1864.]

* [If the constancy of $c$ be not assumed, the integral of the equation (15) will be

$$\frac{mr}{T}=\frac{m_1r_1}{T_1}-M\int_{T_1}^{T}\frac{cdT}{T},$$

wherein the integration indicated in the last term may be effected as soon as $c$ is given as a function of the temperature. All those equations in the sequel, which contain an integral in whose development $c$ was regarded as a constant, are susceptible of a similar modification. I have not thought it necessary actually to write the equations in this form, since the modification in question is a self-evident one.—1864.]

at the commencement the vessel contains no water in a liquid state, but is exactly filled with vapour at a maximum density, so that $m_1 = M$; and that an expansion of the vessel now takes place. If the vessel has to be compressed, then the assumption that at the commencement it contained no liquid could not be made, because in such a case the vapour would not remain at a maximum density, but would become over-heated by the heat generated through compression. During expansion, however, not only does the vapour remain at a maximum density, but a part of it is actually condensed; and it is the diminution of $m$ consequent thereon which is exhibited in the Table. The initial temperature is supposed to be 150° C., and the values of $\frac{m}{M}$ are given which correspond to the periods when, by expansion, the temperature is reduced to 125°, 100°, &c. . . . . As before, in order to distinguish it from the absolute temperature T, the temperature counted from the freezing-point is represented by $t$.

| $t$. | 150° | 125° | 100° | 75° | 50° | 25° |
|---|---|---|---|---|---|---|
| $\frac{m}{M}$ | 1 | 0·956 | 0·911 | 0·866 | 0·821 | 0·776 |

16. In order to express the relation which exists between the volume $v$ and the temperature, we must employ the equation (6), according to which

$$v = mu + M\sigma.$$

The magnitude $\sigma$ herein involved, which represents the volume of a unit of weight of liquid, changes very little with the temperature; and these small changes may be the more safely neglected, because the whole value of $\sigma$ is very small in comparison to $u$; we shall consequently consider $\sigma$, as well as the product $M\sigma$, as constant. The product $mu$ therefore alone remains to be determined. For this purpose we have only to substitute the value of $r$, as given in equation (VI), in equation (VII), and we obtain

$$mu\frac{dp}{dT} = m_1 u_1 \left(\frac{dp}{dT}\right)_1 - \frac{Mc}{A}\log\frac{T}{T_1}. \quad . \quad . \quad . \qquad \text{(VIII)}$$

The differential coefficient $\frac{dp}{dT}$ which here appears, is to be considered as known, $p$ itself being given as a function of the temperature. Hence the product $mu$ is determined by this equation, and by the addition of $M\sigma$ the required value of $v$ will also result from it.

The same suppositions being made as before, the following Table shows a series of values of the fraction $\frac{v}{v_1}$ calculated from this equation. For the sake of comparison the values of $\frac{v}{v_1}$ are also appended which would be obtained if the two assumptions formerly made in the theory of the steam-engine were correct; that is to say, (1) that the vapour during expansion remains without partial condensation at a maximum density; (2) that it follows Mariotte's and Gay-Lussac's laws. According to these hypotheses, we should have

$$\frac{v}{v_1}=\frac{p_1}{p}\cdot\frac{T}{T_1}.$$

| *t.* | 150° | 125° | 100° | 75° | 50° | 25° |
|---|---|---|---|---|---|---|
| $\frac{v}{v_1}$ | 1 | 1·88 | 3·90 | 9·23 | 25·7 | 88·7 |
| $\frac{p_1}{p}\cdot\frac{T}{T_1}$ | 1 | 1·93 | 4·16 | 10·21 | 29·7 | 107·1 |

17. We have still to determine the work done during the change of volume. In order to do so, we have the general equation

$$W=\int_{v_1}^{v} pdv. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

But, considering $\sigma$ constant, we have from equation (6),

$$dv=d(mu);$$

therefore

$$pdv=pd(mu),$$

for which we may also write

$$pdv=d(mup)-mu\frac{dp}{dT}dT. \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

In the place of $mu\frac{dp}{dT}$ we might here substitute the expression given in (VIII), and then integrate; but the result is at once obtained in a rather more convenient form by the following substitution. According to (VI),

$$mu\frac{dp}{d\mathrm{T}}d\mathrm{T}=\frac{1}{\mathrm{A}}\cdot\frac{mr}{\mathrm{T}}d\mathrm{T};$$

and through the application of equation (14), this becomes

$$mu\frac{dp}{d\mathrm{T}}d\mathrm{T}=\frac{1}{\mathrm{A}}\left[d(mr)+\mathrm{M}cd\mathrm{T}\right].$$

By means of this (17) becomes

$$pdv=d(mup)-\frac{1}{\mathrm{A}}\left[d(mr)+\mathrm{M}cd\mathrm{T}\right]^{*};$$

and integrating this equation, we have

$$\mathrm{W}=mup-m_1u_1p_1+\frac{1}{\mathrm{A}}\left[m_1r_1-mr+\mathrm{M}c(\mathrm{T}_1-\mathrm{T})\right], \qquad \text{(IX)}$$

whence, the magnitudes *mr* and *mu* being already known from former equations, W may be calculated.

I have also made this calculation for the above special case, and given the values of $\frac{\mathrm{W}}{\mathrm{M}}$, *i. e.* of the work done during expansion by the unit of mass, in the following Table. A kilogramme is chosen as unit of mass, and a kilogramme-metre as unit of work. For $\frac{1}{\mathrm{A}}$, the value 423·55, as found by Joule, is employed†.

For the sake of comparison with the numbers in the Table, it may be well to state that when 1 kilogramme of water is evaporated at the temperature of 150°, and under the corresponding pressure, the quantity of work done by the vapour during its formation in overcoming the external counter-pressure has the value 18700.

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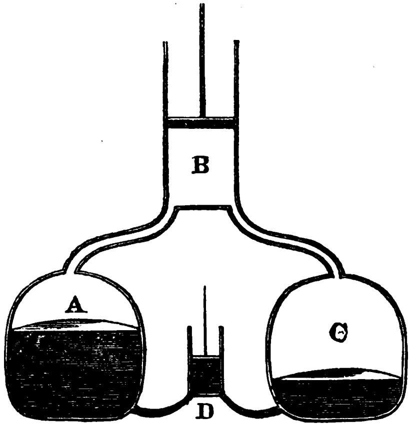
* [If instead of assuming $\sigma$ to be constant, it be thought desirable to obtain an accurate expression for *pdv*, it will be necessary merely to supply the expression in the text with the additional term $\mathrm{M}pd\sigma$.—1864.]

† $\frac{1}{\mathrm{A}}$ is the equivalent of work for the unit of heat; and the above number denotes, therefore, that the quantity of heat which can raise a kilogramme of water from 0° to 1° C., when converted into mechanical work, gives an amount equal to 423·55 kilogramme-metres.

| $t$. | 150° | 125° | 100° | 75° | 50° | 25° |
|---|---|---|---|---|---|---|
| $\frac{W}{M}$ | 0 | 11300 | 23200 | 35900 | 49300 | 63700* |

18. We proceed now to the consideration of the steam-engine itself.

Fig. 8.



In the adjoining fig. 8, which is intended merely to facilitate our oversight of the whole series of operations involved in the working of a common steam-engine, A represents the boiler whose contents are maintained by the source of heat at a constant temperature $T_1$. A part of the steam passes from the boiler to the cylinder B and raises the piston a certain height. The cylinder and boiler are next disconnected, and the vapour contained in the former raises the piston still higher by its own expansion. After this the cylinder is put in communication with the space C, which shall represent the condenser. We shall suppose the latter to be kept cold by external cooling, and not by injected water, which, as before remarked, causes no essential difference in the results, and yet simplifies our problem. The constant temperature of the condenser shall be $T_0$. During the connexion of the cylinder with the condenser the piston retraces the whole of its former path, and thus all the vapour which did not immediately pass by itself into the condenser is driven into it, and there becomes condensed. In order to complete the cycle of operations, it is now necessary to convey the liquid produced by condensation back again into the boiler. This is done by means of the small pump D, whose action is so regulated, that at every ascent of the piston just as much

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* [With respect to certain formulæ of approximation, which have been employed by Zeuner in order more easily to calculate the results given above and in the Second Memoir, see the *Appendix* to the present memoir.]

liquid is withdrawn from the condenser as entered it by the above condensation; and during the descent of the piston this same quantity of liquid is forced back into the boiler. As soon as this liquid is again raised in the boiler to the temperature $T_1$, everything is once more in its initial condition, and the same series of operations can commence again. Here, therefore, we have a complete cyclical process.

In ordinary steam-engines the steam enters the cylinder not only at one end, but alternately at both. But the only difference produced thereby is, that during an ascent and descent of the piston, two circular processes take place instead of one; and in this case even the determination of the work for one of the processes is sufficient, because from it the total amount of work done during any time can be deduced*.

19. In making this determination, we shall, as is indeed usual in such cases, consider the cylinder as impenetrable to heat, so that we may neglect the interchange of heat which takes place during a stroke between the walls of the cylinder and the vapour.

The mass in the cylinder can only consist of vapour *at a maximum density*, together with some admixed liquid. For it is evident from the foregoing that, during its expansion in the cylinder, after the latter is cut off from the boiler, the vapour cannot pass into the over-heated condition, but must, on the contrary, be partially condensed, provided no heat reaches it from an external source. In other operations hereafter to be mentioned, where this over-heated state might certainly occur, it will be prevented by the small amount of liquid which the vapour always carries with it into the cylinder, and with which it remains in contact.

The quantity of liquid thus mixed with the vapour is inconsiderable; and as it is for the most part distributed throughout the vapour in small drops, so that it can readily participate in any changes of temperature which the vapour may suffer during expansion, we shall incur no great inaccuracy if, in calculation, we consider the temperature at any moment as the same throughout the whole of the mass in the cylinder.

Further, in order to avoid complicating our formulas too much,

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* The space on one side of the piston is a little diminished by the piston-rod, but an allowance can easily be made for this small difference.

we will for the present determine the total amount of work done by the vapour pressure, without taking into consideration how much of this work is useful, and how much is again consumed by the machine itself in overcoming friction, and in working any pumps, which, besides the one in the figure, may be necessary to the efficiency of the machine. This part of the work may be afterwards determined and deducted, as will subsequently be shown.

With respect to the friction of the piston in the cylinder, however, we may remark, the work consumed in overcoming it cannot be considered as totally lost. For heat is generated by this friction, and consequently the interior of the cylinder kept warmer than it would otherwise be, and thus the force of the vapour increased.

Lastly, inasmuch as it is advisable first to study the actions of the most perfect machines before examining the influence of the several imperfections which practically are always unavoidable, we will add to these preliminary considerations two more suppositions, which shall afterwards be again relinquished. First, the canal from the boiler to the cylinder, and that from the cylinder to the condenser, or to the atmosphere, shall be so wide, or the speed of the machine shall be so slow, that the pressure in the part of the cylinder in connexion with the boiler shall be equal to that in the boiler itself, and similarly the pressure on the other side of the piston shall be equal to the pressure in the condenser or to the atmospheric pressure; and secondly, no vicious space shall be present.

20. Under these circumstances, the quantities of work done during a cyclical process can be written down, without further calculation, by help of the results above attained; and for their sum they give a simple expression.

Let M be the whole mass which passes from the boiler into the cylinder during the ascent of the piston, and of it let $m_1$ be the vaporous, and $M-m_1$ the liquid part. The space occupied by this mass is

$$m_1u_1+M\sigma;$$

where $u_1$ is the value of $u$ corresponding to $T_1$. The piston is raised therefore until this space is left free under it; and as this takes place under the action of the pressure $p_1$, corresponding to

$T_1$, the work performed during this first operation is

$$W_1 = m_1 u_1 p_1 + M\sigma p_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The expansion which now follows is continued until the temperature of the mass enclosed in the cylinder sinks from $T_1$ to a second given value $T_2$. The work thus done, which shall be $W_2$, is given immediately by equation (IX), if $T_2$ be taken therein as the final temperature, and for the other magnitudes involved in the equation the corresponding values be substituted, thus

$$W_2 = m_2 u_2 p_2 - m_1 u_1 p_1 + \frac{1}{A}\left[m_1 r_1 - m_2 r_2 + Mc(T_1 - T_2)\right]. \quad . \quad (19)$$

By the descent of the piston, which now commences, the mass, which at the close of the expansion occupied the volume

$$m_2 u_2 + M\sigma,$$

is driven from the cylinder into the condenser, and has to overcome the constant pressure $p_0$. The negative work hereby done by this pressure is

$$W_3 = -m_2 u_2 p_0 - M\sigma p_0. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Whilst the piston of the small pump now ascends, so as to leave the free space $M\sigma$ under it, the pressure $p_0$ in the condenser acts favourably and does the work,

$$W_4 = M\sigma p_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Lastly, during the descent of this piston, the pressure $p_1$ in the boiler must be overcome, and therefore it does the negative work,

$$W_5 = -M\sigma p_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

By adding these five magnitudes together we obtain the following expression for the work done by the vapour pressure, or, as we may say, by heat, during a cyclical process:

$$W' = \frac{1}{A}\left[m_1 r_1 - m_2 r_2 + Mc(T_1 - T_2)\right] + m_2 u_2 (p_2 - p_0). \qquad (X)$$

With respect to the magnitude $m_2$, which must be eliminated from this equation, it will be observed that, if for $u_2$ we substitute the value

$$\frac{r_2}{A.T_2\left(\frac{dp}{dT}\right)_2},$$

as given in (VI), it only occurs in the combination $m_2 r_2$, and for this product we have from equation (VII) the expression

$$m_2 r_2 = m_1 r_1 \frac{T_2}{T_1} - McT_2 \log \frac{T_2}{T_1}.$$

By employing this expression, therefore, we obtain an equation the right-hand side of which contains only known quantities; for the masses $m_1$ and M, and the temperatures $T_1$, $T_2$, and $T_0$ are assumed to be immediately given, and the magnitudes $r, p$, and $\frac{dp}{dT}$ are supposed to be known functions of the temperature.

21. If in the equation (X) we set $T_2 = T_1$, we find the amount of work, for the case that the machine works without expansion, to be

$$W' = m_1 u_1 (p_1 - p_0). \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

If, on the contrary, we suppose the expansion to be continued until the vapour sinks from the temperature of the boiler to that of the condenser,—which case cannot of course be strictly realized, but rather forms a limit which it is desirable to approach as much as possible,—we have only to set $T_2 = T_0$, when we obtain

$$W' = \frac{1}{A}[m_1 r_1 - m_0 r_0 + Mc(T_1 - T_0)]. \quad . \quad . \quad . \quad (24)$$

Eliminating $m_0 r_0$ by means of the equation before given, in which we must also set $T_2 = T_0$, we have

$$W' = \frac{1}{A}\left[m_1 r_1 \frac{T_1 - T_0}{T_1} + Mc\left(T_1 - T_0 + T_0 \log \frac{T_0}{T_1}\right)\right]^{*}. \quad (XI)$$

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[*] The above equations, representing the amount of work under the two simplifying conditions introduced at the close of Art. 19, were developed by me some time ago, and publicly communicated in my lectures at the Berlin University as early as the summer of 1854. Afterwards, on the appearance, in 1855, of the Philosophical Transactions for the year 1854, I found therein a memoir of Rankine's, "On the Geometrical Representation of the Expansive Action of Heat, and the Theory of Thermo-dynamic Engines," and was surprised to learn that at about the same date Rankine, quite independently, and in a different manner, arrived at equations which almost entirely agreed with mine, not only in their essential contents, but even in their forms; Rankine, however, did not take the circumstance into consideration, that, when entering the cylinder, a quantity of liquid is mixed with the vapour. By the earlier publication of this memoir I lost, of course, all claim to priority with respect to this part of my investigations; nevertheless the agreement was so far satisfactory as to furnish me with a guarantee for the accuracy of the method I had employed.

22. If to the foregoing equation we give the form

$$W' = m_1 r_1 \cdot \frac{T_1 - T_0}{AT_1} + Mc(T_1 - T_0) \cdot \frac{1}{A}\left(1 + \frac{T_0}{T_1 - T_0} \log \frac{T_0}{T_1}\right), \quad . \quad (25)$$

then the two products $Mc(T_1 - T_0)$ and $m_1 r_1$ which appear therein together represent the quantity of heat furnished by the source of heat during a cyclical process. For the first is the quantity of heat which is necessary to raise the temperature of the liquid mass M, coming from the condenser, from $T_0$ to $T_1$; and the latter is the quantity consumed in vaporizing the part $m_1$ at the temperature $T_1$. As $m_1$ is but little smaller than M, the last quantity of heat is far greater than the first.

In order more conveniently to compare the two factors with which these two quantities of heat are multiplied in equation (25), we will alter the form of the one which multiplies $Mc(T_1 - T_0)$. If, for brevity, we make

$$z = \frac{T_1 - T_0}{T_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

then

$$\frac{T_0}{T_1 - T_0} = \frac{1 - z}{z},$$

and

$$\frac{T_0}{T_1} = 1 - z;$$

so that we have

$$\begin{aligned} 1 + \frac{T_0}{T_1 - T_0} \log \frac{T_0}{T_1} &= 1 + \frac{1 - z}{z} \log (1 - z) \\ &= 1 - \frac{1 - z}{z}\left(\frac{z}{1} + \frac{z^2}{2} + \frac{z^3}{3} + \&c.\right) \\ &= \frac{z}{1.2} + \frac{z^2}{2.3} + \frac{z^3}{3.4} + \&c. \ldots \end{aligned}$$

Hence the equation (25) or (XI) becomes

$$W' = m_1 r_1 . \frac{z}{A} + Mc(T_1 - T_0) . \frac{z}{A}\left(\frac{1}{1.2} + \frac{z}{2.3} + \frac{z^2}{3.4} + \&c. \ldots\right). \quad (27)$$

It is easy to see that the value of the infinite series, which distinguishes the factor of the quantity of heat $Mc(T_1 - T_0)$ from that of the quantity of heat $m_1 r_1$, varies from ½ to 1, as $z$ increases from 0 to 1.

23. In the case last considered, where the vapour by expansion cools down to the temperature of the condenser, we can

easily obtain the expression for the work done in another manner, without considering the several operations which constitute the cyclical process.

For in this case every part of the cyclical process is reversible. We can imagine that the vaporization takes place in the condenser at the temperature $T_0$, and that the mass M, of which $m_0$ is vaporous and $M-m_0$ liquid, enters the cylinder and raises the piston; further, that by the descent of the piston the vapour is first compressed until its temperature is raised to $T_1$, and then that it is forced into the boiler; and lastly, that by means of the small pump the mass M is again conveyed in the liquid form from the boiler to the condenser, and allowed to cool there to the original temperature $T_0$. The matter here passes through the same conditions as before, but in an opposite order. All communications and abstractions of heat take place in opposite order, but in the same quantity and at the same temperature of the mass; all quantities of work have opposite signs, but the same numerical value.

Hence it follows that in this case no uncompensated transformation is involved in the cyclical process, and we must consequently set $N=0$ in equation (2), by which we obtain the following equation,—already given in (3), with the exception that $W'$ is here put in the place of W,—

$$W'=\frac{1}{A}\left(Q_1-T_0\int_0^{Q_1}\frac{dQ}{T}\right).$$

In our present case, $Q_1$ denotes the quantity of heat imparted to the mass M in the boiler, that is,

$$Q_1=m_1r_1+Mc(T_1-T_0).$$

In determining the integral $\int_0^{Q_1}\frac{dQ}{T}$, the two quantities of heat $Mc(T_1-T_0)$ and $m_1r_1$ contained in $Q_1$ must be separately considered. In order to execute the integration extending over the first quantity, we have but to give to the element of heat $dQ$ the form $McdT$, and this part of the integral is at once expressed by

$$Mc\int_{T_0}^{T_1}\frac{dT}{T}=Mc\log\frac{T_1}{T_0}.$$

During the communication of the latter quantity of heat, the temperature is constant and equal to $T_1$, and consequently the part of the integral referring to this quantity is simply

$$\frac{m_1 r}{T_1}.$$

By substituting these values, the foregoing expression for W′ becomes

$$\begin{aligned} W' &= \frac{1}{A}\left[m_1 r_1 + Mc(T_1 - T_0) - T_0\left(\frac{m_1 r_1}{T_1} + Mc \log \frac{T_1}{T_0}\right)\right] \\ &= \frac{1}{A}\left[m_1 r_1 \frac{T_1 - T_0}{T_1} + Mc\left(T_1 - T_0 + T_0 \log \frac{T_0}{T_1}\right)\right]; \end{aligned}$$

and this is the same expression as that contained in equation (XI), which was before obtained by the successive determination of the several quantities of work done during the cyclical process.

24. From this it follows that, *if the temperatures at which the matter manifesting the action of heat receives heat from the source of heat, or imparts heat to some external object, are considered as previously given,* then the steam-engine, under the conditions made in deducing the equation (XI), is a *perfect* machine; that is to say, for a certain amount of imparted heat it furnishes as much work as, according to the mechanical theory of heat, is possible at those temperatures.

It is otherwise, however, *when those temperatures, instead of being given, are also considered as a variable element, to be taken into consideration in judging the machine.*

One uncompensated transformation not included in N, which, with respect to the economy of heat, causes a great loss, arises from the fact that the liquid, during the processes of heating and evaporation, has far lower temperatures than the fire, and consequently the heat which is imparted to it must pass from a higher to a lower temperature. The amount of work which can be produced by the steam-engine from the quantity of heat $m_1 r_1 + Mc(T_1 - T_0) = Q_1$, is, as may be seen from equation (27), somewhat smaller than

$$\frac{Q_1}{A} \cdot \frac{T_1 - T_0}{T_1}.$$

If, on the contrary, we could impart the same quantity of heat $Q_1$ to a changeable body at the temperature of the fire, which may be T′, whilst the temperature during the abstraction of heat remained $T_0$, as before, then by equation (4) the greatest possible amount of work to be gained in such a case would be

$$\frac{Q_1}{A} \cdot \frac{T' - T_0}{T'}.$$

In order to compare the values of these expressions in a few examples, let the temperature $t_0$ of the condenser be fixed at 50° C., and for the boiler let us assume the temperatures 110°, 150°, and 180° C., of which the two first correspond approximately to the low- and the ordinary high-pressure machines respectively, and the last may be considered as the limit of the temperatures hitherto employed in steam-engines. In these cases the fraction dependent upon the temperatures has the following values:—

| $t_1$. | 110° | 150° | 180° |
|---|---|---|---|
| $\frac{T_1 - T_0}{T_1}$ | 0·157 | 0·236 | 0·287 |

whereas the corresponding value for the temperature of the fire $t'$, assuming the latter to be only 1000° C., is 0·746.

25. We may here easily discern, what has already been expressed by S. Carnot and several other authors, that in order to render machines driven by heat more efficient, attention must be particularly directed towards the enlargement of the interval of temperature between $T_1$ and $T_0$.

For instance, machines driven by heated air will only attain a decided advantage over steam-engines when a method is found of allowing them to work at a far higher temperature than steam-engines, in consequence of the danger of explosions, can bear. The same advantage, however, could be attained with over-heated vapour; for as soon as the vapour is separated from the liquid, it is just as safe to heat it further as to heat a permanent gas. Machines employing vapour in this condition may possess many of the advantages of the steam-engine besides those of air-machines, so that a practical improvement may sooner be expected from these than from air-machines.

In the machines above mentioned, where, besides water, a second more vaporizable substance was employed, the interval $T_1 - T_0$ is increased by lowering $T_0$. It has already been suggested that this interval might be increased in a similar manner on the upper side, by the addition of a third liquid less vaporizable than water. In such a case the fire would be immediately applied to the evaporation of the least vaporizable of the three substances, the condensation of this to the evaporation of the second, and the condensation of the second to the evaporation of the third. Theoretically, there is no doubt that such a combination would be advantageous; the practical difficulties, however, which would have to be overcome in realizing such a scheme cannot of course be predicted.

26. Besides the above-mentioned defect, arising out of the very nature of our ordinary steam-engines, these machines suffer from many other imperfections, which may be ascribed more immediately to defective construction.

One of these has already been considered in the foregoing development, and allowed for in equation (X), that is to say, the expansion cannot be continued nearly far enough to allow the vapour in the cylinder to reach the temperature of the condenser. If, for example, we assume the temperature of the boiler to be 150°, and that of the condenser to be 50°, then the Table in Art. 16 shows that, for the above purpose, the expansion must be prolonged to twenty-six times the original volume; whereas in practice, owing to many inconveniences attending great expansions, three or four, and at most ten times the original volume is attained.

Two other imperfections, however, are expressly excluded in the foregoing: these are, first, *that the pressure of the vapour in one part of the cylinder is smaller than in the boiler, and in the other part greater than in the condenser*; and secondly, *the presence of vicious space.*

We must consequently extend our former considerations so as to include these imperfections.

27. The influence exercised by the difference of pressure in the boiler and cylinder upon the work performed, has hitherto been most completely treated of by Pambour in his work on the *Théorie des Machines à Vapeur*. Before entering upon the subject myself, therefore, I may be allowed to state the most essential parts of his treatment, altering only the notation, and neglecting the magnitudes which have reference to friction. By

this means it will be easier, on the one hand, to judge how far this treatment is no longer in accordance with our more recent knowledge of heat, and, on the other, to add to it the new method of treatment which, in my opinion, must be substituted for the former one.

28. The two laws which, as was before mentioned, were formerly very generally applied to steam, form the basis of Pambour's theory. The first of these is Watt's law, according to which the sum of the latent and sensible heat is constant. From this law it was concluded that when a quantity of steam at its maximum density is enclosed within a surface impenetrable to heat, and the volume of the enclosing space is either increased or diminished, the steam will neither become over-heated nor partially condensed, but will remain precisely at its maximum density; and it was further assumed that this would take place quite independently of the manner in which the change of volume occurred, whether thereby the steam had, or had not, to overcome a pressure corresponding to its own expansive force. Pambour supposed that the steam in the cylinder of a steam-engine deported itself thus; and at the same time he did not assume that the particles of water, which in this case are mixed with the steam, could exert any appreciable influence.

Further, in order to establish a more accurate relation between the volume and the temperature, or the volume and the pressure of steam at a maximum density, Pambour applied, secondly, Mariotte's and Gay-Lussac's laws. If, with Gay-Lussac, we assume the volume of a kilogramme of steam at 100° C., and at its maximum density, to be 1·696 cubic metres, under a pressure of one atmosphere, which latter amounts to 10,333 kilogrammes on every square metre, then from the above law we obtain the equation

$$v = 1{\cdot}696 \cdot \frac{10333}{p} \cdot \frac{273+t}{273+100}, \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

where, with reference to the same units, $v$ and $p$ represent the volume and the pressure corresponding to any other temperature $t$. Herein it is only necessary to substitute in place of $p$ the values given in the tension series in order to have, according to the above assumption, the proper volume for each temperature.

29. In order, however, to be able conveniently to calculate the value of the integral

$$\int p dv,$$

which plays an important part in the formula for the work done by a steam-engine, it was necessary to find the simplest possible formula between $v$ and $p$ alone.

If, by means of the ordinary empirical formulæ for $p$, the temperature $t$ were eliminated from the above equation, the results would prove to be too complicated; hence Pambour preferred forming a special empirical formula for this purpose, to which, according to the proposal of Navier, he gave the following general form :—

$$v=\frac{B}{b+p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

wherein B and $b$ are constants. He then sought to determine these constants, so that the volumes calculated from this formula might agree as nearly as possible with those calculated from the foregoing one. As this could not be done with sufficient accuracy, however, for all the pressures which occur in steam-engines, he established two different formulæ for machines *with* and *without* condenser.

The first of these was

$$v=\frac{20000}{1200+p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29\,a)$$

which agrees best with the above formula (28) between ⅔ and 3½ atmospheres, but is also applicable for a somewhat wider interval, from about ½ to 5 atmospheres.

The second, for machines without condensers, is

$$v=\frac{21232}{3020+p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (29\,b)$$

which is most correct between 2 and 5 atmospheres, though the range of its applicability extends from about 1⅓ to 10 atmospheres.

30. The magnitudes which depend upon the dimensions of the steam-engine, and enter into the determination of the work, shall be here, somewhat differently from Pambour's method,

represented in the following manner. Let $v'$ be the whole space left free to the vapour during a stroke in the piston, the vicious space being also included. Let the vicious space form a fractional part $\epsilon$ of the whole space, so that this space itself will be represented by $\epsilon v'$, and that described by the surface of the piston by $(1-\epsilon)\,v'$. Further, let the part of the whole space left free to the vapour up to the moment of disconnecting the cylinder and boiler (also inclusive of vicious space) be represented by $ev'$. Consequently the space described by the surface of the piston during the entrance of the vapour will be expressed by $(e-\epsilon)v'$, and that described by it during expansion will be $(1-e)\,v'$.

In order to determine, in the next place, the amount of work done during the entrance of the vapour, the pressure acting in the cylinder during this time must be known. This is at any rate smaller than the pressure in the boiler, otherwise no influx of vapour could occur; but the magnitude of the difference cannot in general be stated; for it depends not only upon the construction of the engine, but also upon the engine-driver, how far he has opened the valve in the tube leading from the boiler, and with what velocity he drives the machine. These things being changed, the above difference may vary between wide limits. Further, the pressure in the cylinder need not be constant during the whole time of influx, because the velocity of the piston may vary, as well as the magnitude of the influx orifice left free by the valve or the slide.

With respect to the last circumstance, Pambour assumes that the mean pressure to be brought into calculation in determining the work may, with sufficient accuracy, be set equal to that which exists in the cylinder at the end of the influx, and at the moment of disconnexion from the boiler. Although I do not think it advisable to introduce such an assumption—which is only adopted for numerical calculation in the absence of more certain data—at once into the general formulæ, yet here, whilst explaining his theory, I must adopt his method.

Pambour determines the pressure existing in the cylinder at the moment of disconnexion by means of the relation, established by him, between volume and pressure; assuming at the same time that the quantity of steam which passes from the boiler into the cylinder in a unit of time, and therefore the quantity which passes during a stroke of the piston, is known from special observations. As before, we will represent by M the whole mass which enters the cylinder during a stroke, and by $m$ the vaporous part of the same. As this mass, of which Pambour only considers the vaporous part, fills the space $ev'$ at the moment of disconnexion, we have, according to (29), the equation

$$ev'=\frac{m\,.\,\mathrm{B}}{b+p_2},$$

where $p_2$ represents the pressure at the same moment. From this equation we deduce

$$p_2=\frac{m\,.\,\mathrm{B}}{ev'}-b. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (30)$$

Multiplying this magnitude by $(e-\epsilon)v'$, the space described by the surface of the piston up to the same moment, we obtain the following expression for the first part of the work :—

$$\mathrm{W}_1=m\,.\,\mathrm{B}\,.\,\frac{e-\epsilon}{e}-v'(e-\epsilon)b. \quad . \quad . \quad . \qquad (31)$$

The law according to which the pressure changes during the expansion which now follows, is also given by equation (29). If at any moment $v$ represents the variable volume, and $p$ the corresponding pressure, then

$$p=\frac{m\,.\,\mathrm{B}}{v}-b.$$

This expression must be substituted in the integral

$$\int pdv,$$

and the integration effected between the limits $v=ev'$ and $v=v'$; whence, as the second part of the work, we obtain

$$\mathrm{W}_2=m\mathrm{B}\,.\log\frac{1}{e}-v'(1-e)b. \quad . \quad . \quad . \qquad (32)$$

In order to determine the negative work done by the reacting pressure during the descent of the piston, this reaction must itself be known. Without at present inquiring into the relation which exists between the reaction and the pressure in the condenser, we will represent the mean reaction by $p_0$, so that the work done by it will be expressed by

$$W_3 = -v'(1-\epsilon)p_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

There yet remains the work necessary to convey the quantity M of liquid back again into the boiler. Pambour has not separately considered this work, but has included it in the friction of the machine. As I have included it in my formulæ, however, in order to have the cycle of operations complete, I will also here add it for the sake of easier comparison. As shown by equations (21) and (22), established in a former example, this work will on the whole be expressed by

$$W_4 = -M\sigma(p_1 - p_0), \quad . \quad . \quad . \quad . \quad . \quad (34)$$

where $p_1$ and $p_0$ respectively represent the pressures in the boiler and condenser. This expression, it is true, is not quite correct for our present case, because by $p_0$ we do not understand the pressure in the condenser itself, but in the parts of the cylinder in communication with the condenser. Nevertheless we will retain the expression in its present form, for owing to the smallness of $\sigma$, the whole expression has a value scarcely worth consideration; and the inaccuracy, being again small in comparison to the value of the expression itself, may with still greater impunity be disregarded.

By adding these four separate amounts of work together, we find the whole work done during the cyclical process to be

$$W' = mB\left(\frac{e-\epsilon}{e} + \log\frac{1}{e}\right) - v'(1-\epsilon)(b+p_0) - M\sigma(p_1 - p_0). \quad . \quad . \quad (35)$$

31. If, lastly, we wish to refer the work to the unit of weight of vapour instead of to a single stroke, during which the quantity $m$ of vapour acts, we have only to divide the foregoing value by $m$. We will put $l$ in place of the fraction $\frac{M}{m}$, which expresses the relation which the whole mass entering the cylinder bears to the vaporous part of the same, and whose value is consequently a little greater than unity; V in place of the fraction $\frac{v'}{m}$, or the whole space offered to the unit of weight of vapour in the cylinder; and W in place of the fraction $\frac{W'}{m}$, or the work correspond-

ing to the unit of weight of vapour. We thus obtain

$$W = B\left(\frac{e-\epsilon}{e} + \log\frac{1}{e}\right) - V(1-\epsilon)(b+p_0) - l\sigma(p_1-p_0). \quad . \qquad \text{(XII)}$$

Only one term of this equation depends upon V, and it contains V as factor. As this term is negative, it follows that the work which we can obtain from the unit of weight of vapour is, all other circumstances being the same, greatest when the volume offered to the vapour in the cylinder is smallest. The least value of this volume, which we may approach more and more although we may never quite reach, is that which is found by assuming that the machine goes so slowly, or that the influx canal is so wide, that the same pressure $p_1$ exists in the cylinder as in the boiler. This case therefore gives the maximum of work. If with equal influx of vapour the velocity of motion is greater, or with equal velocity of motion the influx of vapour is smaller, we obtain from the same quantity of vapour a less quantity of work.

32. Before we now proceed to consider connectedly the same series of processes according to the mechanical theory of heat, it will be best to submit one of the same, which requires especial investigation, to a separate treatment in order at once to establish the results which have reference thereto. I refer to the *entrance of vapour into the vicious space and into the cylinder, when it has there to overcome a smaller pressure than that with which it was forced out of the boiler.* In this investigation I can proceed according to the same principles as those which I have employed in a former memoir* when treating similar cases.

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* "Ueber das Verhalten des Dampfes bei der Ausdehnung unter verschiedenen Umständen" [Second Memoir of this Collection]. With reference to this memoir, and to a notice connected therewith, which appeared in the Philosophical Magazine, Helmholtz, in his report published in the *Fortschritte der Physik*, by the Physical Society of Berlin (years 1850 and 1851, p. 582), is of opinion that the principle is in many points incorrect. I have not, however, been able to understand the reasons he adduces in support of this opinion. Views are ascribed to me which I never held, and, on the other hand, theorems enunciated which I never disputed, and which, indeed, partially constitute the basis upon which my own researches in the mechanical theory of heat are founded; at the same time so great a generality is maintained throughout, that I found it impossible to recognize how far those

The vapour from the boiler first enters the vicious space, here compresses the vapour of small density which still remains from the former stroke, fills up the space thus becoming free, and then presses against the piston, which, in consequence of its assumed comparatively small charge, recedes so quickly that the vapour cannot follow it quickly enough to reach the same density in the cylinder as it had in the boiler.

If saturated vapour alone issued from the boiler, it must under such circumstances become over-heated in the cylinder, for the *vis viva* of the entering mass is here converted into heat; as the vapour, however, carries with it some finely divided drops of water, a part of the latter will be evaporated by the surplus heat, and thus the remaining vapour will be maintained in its saturated condition.

We must now consider the following problem:—*Given,* first, *the initial condition of the whole mass under consideration, viz. that which was previously in the vicious space, as well as that more recently arrived from the boiler*; secondly, *the magnitude of the work done by the pressure acting upon the piston during the entrance of the vapour*; and thirdly, *the pressure in the cylinder at the moment of cutting off the same from the boiler: to determine how much of the mass in the cylinder at this moment is vaporous.*

33. Let $\mu$ be the whole mass in the vicious space before the entrance of the fresh vapour, and, for the sake of generality, let us suppose that the part $\mu_0$ of it is vaporous and the rest liquid. For the present let $p_0$ and $T_0$ represent respectively the pressure of this vapour and its corresponding absolute temperature, without implying, however, that these are exactly the same values as those which refer to the condenser. As before, $p_1$ and $T_1$ shall be the pressure and temperature in the boiler, M the mass issuing from the boiler into the cylinder, and $m_1$ the vaporous

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views ought to follow from my words, and these theorems contradict my conclusions. I do not therefore feel myself called upon to defend my former researches against this censure. As the following development, however, rests precisely upon the same views which before served me, Helmholtz will probably again find the same inaccuracy of principle. In such a case I shall look forward to his objections, and request him merely to enter somewhat more specially into the subject.

part of the latter. As we have already remarked, the pressure upon the piston during the entrance of the vapour need not be constant. The *mean* pressure $p'_1$ may be defined as that by which the space described by the surface of the piston, during the entrance of the vapour, must be multiplied in order to obtain the same work as is actually done with the variable pressure. Further, let $p_2$ and $T_2$ be the pressure and corresponding temperature in the cylinder at the moment of cutting it off from the boiler; and lastly, $m_2$ the magnitude to be determined, that is to say, the vaporous part of the whole mass $M+\mu$ now in the cylinder.

To determine this magnitude, let us conceive the mass $M+\mu$ reduced in any manner to its original condition. For instance, thus: let the vaporous part $m_2$ be condensed in the cylinder by depressing the piston, whereby we shall suppose that the latter can also enter the vicious space. At the same time let heat be constantly withdrawn from the mass in such a manner that the temperature $T_2$ may remain constant. Then of the whole liquid mass, let the part M be forced back into the boiler, where it may assume its original temperature $T_1$. By this means the condition of the mass within the boiler is the same as it originally was, for of course it is of no importance whether precisely the *same* mass $m_1$, which was before vaporous, is again so now, or whether *another equally great* mass has taken its place*. With

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* [In fact at the end of the operation there is in the boiler just as much liquid water and just as much steam, both at the temperature $T_1$, as there was at the beginning; so that the original condition, so far as is necessary for our consideration, is reestablished; for we are concerned solely with the magnitudes of the vaporous and of the liquid portions of the whole mass, and have not to inquire which of the several molecules there present belong to the vaporous, and which to the liquid portion. If it were required that exactly the same molecules should constitute the vaporous portion at the end, as at the beginning of the operation, it would merely be necessary to assume, first, that the water forced back into the boiler is not only equal in quantity to that which originally quitted it, but that this water consists of the same molecules; and secondly, that of this water, after it has attained the temperature $T_1$, the formerly vaporous portion $m_1$ again vaporizes, an exactly equal quantity of that already present being precipitated. For this purpose, of course, no heat need be imparted to, or withdrawn from the total mass in the boiler; since the heat consumed in evaporation, and that generated by precipitation, would compensate each other.—1864.]

respect to the remaining part $\mu$, let it be at first cooled in the liquid state from $T_2$ to $T_0$, and at this temperature let the part $\mu_0$ become vaporous, to do which the piston must recede so that this vapour can again occupy its original volume.

34. In this manner the mass $M+\mu$ has gone through a complete cyclical process, to which we may apply the theorem, that the sum of all the quantities of heat received by the mass during a cyclical process must be equivalent to the whole amount of external work thereby performed.

The following quantities of heat have been successively consumed:—

(1) To raise the temperature of the mass M in the boiler from $T_2$ to $T_1$, and at the latter temperature to evaporate the part $m_1$,

$$m_1 r_1 + Mc(T_1 - T_2).$$

(2) To condense the part $m_2$ at the temperature $T_2$,

$$-m_2 r_2.$$

(3) To cool the part $\mu$ from $T_2$ to $T_0$,

$$-\mu c(T_2 - T_0).$$

(4) To evaporate the part $\mu_0$ at the temperature $T_0$,

$$\mu_0 r_0.$$

Hence the total quantity of heat is

$$Q = m_1 r_1 - m_2 r_2 + Mc(T_1 - T_2) + \mu_0 r_0 - \mu c(T_2 - T_0). \quad . \quad (36)$$

The quantities of work may be found as follows:—

(1) In order to find the space described by the surface of the piston during the entrance of the vapour, we know that at the end of that time the whole mass $M+\mu$ occupies the space

$$m_2 u_2 + (M+\mu)\sigma.$$

From this we must deduct the vicious space. As at the commencement, this was filled by the mass $\mu$, of which $\mu_0$ was vaporous, at the temperature $T_0$, its volume is

$$\mu_0 u_0 + \mu\sigma.$$

Deducting this from the foregoing magnitude, and multiplying the difference by the mean pressure $p'_1$, we have for the first amount of work,

$$(m_2 u_2 + M\sigma - \mu_0 u_0)p'_1.$$

(2) The work expended in condensing the mass $m_2$ is

$$-m_2u_2p_2.$$

(3) The work expended in forcing back the mass M into the boiler is

$$-M\sigma p_1.$$

(4) The work expended in evaporating the part $\mu_0$ is

$$\mu_0u_0p_0.$$

By adding these four magnitudes, we obtain for the whole work W the following expression :—

$$W=m_2u_2(p'_1-p_2)-M\sigma(p_1-p'_1)-\mu_0u_0(p_1'-p_0). \quad . \quad (37)$$

If in the equation (I), which was

$$Q=A \, . \, W,$$

we substitute the values of Q and W thus found, and then bring the terms involving $m_2$ to one side of the equation, we have

$$m_2[r_2+Au_2(p'_1-p_2)]=m_1r_1+Mc(T_1-T_2)+\mu_0r_0-\mu c(T_2-T_0)$$
$$+A\mu_0u_0(p'_1-p_0)+AM\sigma(p_1-p'_1). \quad . \quad . \quad . \quad . \quad . \quad (XIII)$$

By means of this equation the magnitude $m_2$ is expressed in terms of other magnitudes, all of which are supposed to be given.

35. If the mean pressure $p'_1$ were considerably greater than the final pressure $p_2$, it might happen that the value of $m_2$ would be less than $m_1+\mu_0$, which would denote that a part of the vapour originally present had become condensed. This would be the case, for instance, if we were to suppose that, during the time the vapour was entering the cylinder, the pressure there was nearly equal to that in the boiler, and that by the expansion of this vapour already in the cylinder, the pressure ultimately sunk to the smaller value $p_2$. On the contrary, if $p'_1$ were but a little greater, or indeed smaller than $p_2$, then for $m_2$ we should find a value greater than $m_1+\mu_0$. The latter ought to be considered as the rule in steam-engines, and amongst others it holds for the special case of $p'_1=p_2$ assumed by Pambour.

We have thus arrived at results which differ essentially from Pambour's views. Whilst he assumes that the two different kinds of expansion which successively take place in the steam-engine are governed by one and the same law, according to which the original quantity of vapour is neither increased nor diminished, but always remains exactly at its maximum density, we have found two different equations which point to different deportments. By the equation (XIII), fresh vapour must be produced by the first expansion during the entrance of the steam; and according to the equation (VII), a part of the then existing vapour must become condensed when the further expansion takes place, after disconnecting the cylinder and boiler, during which time the work done by the vapour corresponds to its full expansive force.

As these two opposite actions, consisting of an increase and a diminution of vapour, which must also exercise opposite influences on the work performed by the machine, partially cancel one another, the ultimate result may, under certain circumstances, be approximately the same as that to which Pambour's simpler assumption leads. We must not, however, on this account neglect to consider this difference when once established, especially if we wish to ascertain in what manner a change in the construction or driving of the steam-engine will affect the magnitude of its work.

36. According to what was said in Art. 8, we can easily determine the uncompensated transformation which occurs in the expansion by referring the integral contained in the equation

$$N=-\int\frac{dQ}{T}$$

to the several quantities of heat expressed in Art. 34.

The quantities of heat $m_1r_1$, $-m_2r_2$, and $\mu_0r_0$ are imparted at the constant temperatures $T_1$, $T_2$, and $T_0$, so that these parts of the integral are, respectively,

$$\frac{m_1r_1}{T_1},\quad -\frac{m_2r_2}{T_2},\text{ and }\frac{\mu_0r_0}{T_0}.$$

The parts of the integral arising from the quantities of heat $Mc(T_1-T_2)$ and—$\mu c(T_2-T_0)$, are found, by the method adopted in Art. 23, to be

$$Mc\log\frac{T_1}{T_2}\text{ and }-\mu c\log\frac{T_2}{T_0}.$$

By putting the sum of these magnitudes in place of the above integral, we obtain for the uncompensated transformation the value

$$N = -\frac{m_1 r_1}{T_1} + \frac{m_2 r_2}{T_2} - Mc \log\frac{T_1}{T_2} - \frac{\mu_0 r_0}{T_0} + \mu c \log\frac{T_2}{T_0}. \quad . \quad (38)$$

37. We can now return to the complete cyclical process which occurs in an acting steam-engine, and consider the several parts thereof in the same manner as before.

The mass M, of which the part $m_1$ is vaporous and the rest liquid, issues from the boiler, where the pressure is supposed to be $p_1$, into the cylinder. As before, the mean pressure acting in the cylinder during this time shall be $p'_1$, and the final pressure $p_2$.

The vapour now expands until its pressure sinks from $p_2$ to a given value $p_3$, and consequently its temperature from $T_2$ to $T_3$.

After this the cylinder is put in communication with the condenser, where the pressure is $p_0$, and the piston returns through the whole of the space it has just described. When the motion is somewhat quick, the reaction which it now experiences will be somewhat greater than $p_0$; to distinguish it from the latter value, we will represent the mean reaction by $p'_0$.

Similarly, the pressure of the vapour which remains in the vicious space after the piston's motion is completed will not necessarily be equal either to $p_0$ or to $p'_0$, and must consequently be represented by another symbol $p''_0$. It may be greater or less than $p'_0$, according as the communication with the condenser is cut off somewhat before, or somewhat after the conclusion of the piston's motion; for in the first case the vapour would be a little further compressed, whereas in the latter case it would have time to expand a little more by partially passing into the condenser.

Lastly, the mass M is conveyed back from the condenser into the boiler, when, as before, the pressure $p_0$ acts favourably, and the pressure $p_1$ has to be overcome.

38. The expressions for the amounts of work done in these processes will be quite similar to those in the simpler case before considered, except that a few simple changes in the indices of the letters will have to be made, and the magnitudes which refer to the vicious space will have to be added. In this manner we obtain the following equations.

During the time vapour is passing into the cylinder, we have, according to Art. 34,

$$W_1 = (m_2 u_2 + M\sigma - \mu_0 u''_0) p'_1, \quad . \quad . \quad . \quad . \quad (39)$$

where $u''_0$ is simply substituted for $u_0$.

By putting $M + \mu$ in place of M, we have, from equation (IX), during the expansion from the pressure $p_2$ to the pressure $p_3$,

$$W_2 = m_3 u_3 p_3 - m_2 u_2 p_2 + \frac{1}{A}[m_2 r_2 - m_3 r_3 + (M + \mu) c (T_2 - T_3)]. \quad (40)$$

During the return of the piston, when its surface is traversing the whole space occupied by the mass $M + \mu$ at the pressure $p_3$, diminished by the vicious space $\mu_0 u''_0 + \mu\sigma$, we have

$$W_3 = -(m_3 u_3 + M\sigma - \mu_0 u''_0) p'_0. \quad . \quad . \quad . \quad (41)$$

Lastly, during the conveyance of the mass M back into the boiler, we have

$$W_4 = -M\sigma(p_1 - p_0). \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Consequently the whole work done is

$$\left.\begin{array}{l} W' = \frac{1}{A}[m_2 r_2 - m_3 r_3 + (M + \mu) c (T_2 - T_3)] + m_2 u_2 (p'_1 - p_2) \\ + m_3 u_3 (p_8 - p'_0) - M\sigma(p_1 - p'_1 + p'_0 - p_0) - \mu_0 u''_0 (p'_1 - p'_0) \end{array}\right\}. \quad (43)$$

The masses $m_2$ and $m_3$ which are here involved, are given by the equations (XIII) and (VII), provided in the former we put $p''_0$ in the place of $p_0$, and change the magnitudes $T_0$, $r_0$, and $u_0$ in a similar manner, and in the latter we substitute $M + \mu$ for M. Nevertheless, although it is possible to eliminate $m_2$ and $m_3$ by means of these equations, I will here merely replace $m_2$ by its value; it being more convenient in calculation to consider the equation which thus results in connexion with the equations (XIII) and (VII) before obtained. The following, therefore, is the most general form of the system of equations which serve to determine the work done by the steam-engine:—

$$\left.\begin{array}{l} W' = \frac{1}{A}[m_1 r_1 - m_3 r_3 + Mc(T_1 - T_3) + \mu_0 r''_0 - \mu c (T_3 - T''_0)] \\ \qquad + m_3 u_3 (p_3 - p'_0) + \mu_0 u''_0 (p'_0 - p''_0) - M\sigma(p'_0 - p_0), \\ m_2[r_2 + Au_2(p'_1 - p_2)] = m_1 r_1 + Mc(T_1 - T_2) + \mu_0 r''_0 \\ - \mu c (T_2 - T''_0) + A\mu_0 u''_0 (p'_1 - p''_0) + AM\sigma(p_1 - p'_1), \\ \frac{m_3 r_3}{T_3} = \frac{m_2 r_2}{T_2} + (M + \mu) c \log \frac{T_2}{T_3}. \end{array}\right\} \text{(XIV)}$$

39. Before endeavouring to render these equations more convenient for application, it may not be without interest to show how, for an imperfect steam-engine, the same expressions may be arrived at by a method before alluded to, and opposite to the one just applied. In order to avoid prolixity in this digression, however, we will consider two only of the imperfections provided for in the above equations, viz. the presence of vicious space, and the existence of a smaller pressure in the cylinder than in the boiler during the time that the vapour is passing into the former. On the other hand, we shall assume the expansion to be complete, therefore $T_3 = T_0$, and the magnitudes $T_0$, $T'_0$, and $T''_0$ to be equal.

In this determination we shall have to employ the equation (2), to which we will give the following form:—

$$W' = \frac{1}{A}\left(Q_1 - T_0\int_0^{Q_1}\frac{dQ}{T}\right) - \frac{T_0}{A}N.$$

The first term on the right-hand side of this equation denotes the work which could be obtained from the employed quantity of heat $Q_1$, which in our case is represented by $m_1r_1 + Mc(T_1 - T_0)$, did not the two imperfections exist. This term has been already calculated in Art. 23, and found to be

$$\frac{1}{A}\left[m_1r_1 + Mc(T_1 - T_0) - T_0\left(\frac{m_1r_1}{T_1} + Mc\log\frac{T_1}{T_0}\right)\right].$$

The second term denotes the loss of work caused by those two imperfections. The magnitude N contained therein has been calculated in Art. 36, and is represented by the expression in equation (38).

Substituting these two expressions in the foregoing equation, we have

$$W' = \frac{1}{A}\left[m_1r_1 - \frac{T_0}{T_2}m_2r_2 + Mc(T_1 - T_0) - (M+\mu)cT_0\log\frac{T_2}{T_0} + \mu_0r_0\right]. \quad (44)$$

That this equation actually agrees with the equations (XIV), may be easily seen by using the third equation in (XIV) in order to eliminate $m_3$ from the first, and then setting $T_3 = T_0 = T'_0 = T''_0$.

In the same manner we might make allowance for the loss of work occasioned by incomplete expansion. To do so it would only be necessary to calculate the uncompensated transformation which occurs during the passage of the vapour from the cylinder to the condenser, and to include it in N. By this calculation, which need not here be executed, we obtain precisely the expression for the work which is given in (XIV).

40. In order next to be able to use the equations (XIV) in a numerical calculation, it will be necessary first to determine the magnitudes $p'_1$, $p'_0$, and $p''_0$ more precisely.

With respect to the manner in which the pressure in the cylinder varies during the entrance of the steam, no general law can be instituted, because the entrance canal is opened and closed in such a variety of ways in different machines. Hence no definite general value can be found for the relation between the mean pressure $p'_1$, and the final pressure $p_2$, as long as the latter is strictly interpreted. Nevertheless this will be possible if the signification of $p_2$ be slightly changed.

The cylinder and boiler cannot of course be instantaneously disconnected; more or less time is always required to move the necessary valves or slides, and during this interval the vapour in the cylinder expands a little, because the orifice being diminished, less steam enters than that which corresponds to the velocity of the piston. In general, therefore, we may assume that at the end of this time the pressure is already somewhat smaller than the mean pressure $p'_1$.

But if, in calculation, instead of restricting ourselves to the *end* of the time necessary for closing the entrance canal, we allow ourselves a little freedom in fixing the time of disconnexion, we shall be able to obtain other values for $p_2$. We can imagine the point of time so chosen, that if, previously thereto, the whole mass M had entered, the pressure at that moment would have been precisely equal to the mean pressure calculated up to the same time. By substituting this instantaneous disconnexion in place of the actual gradual one, we incur but an insignificant error, as far as the amount of work is concerned. We may therefore, with this modification, adopt Pambour's assumption, that $p'_1 = p_2$, reserving, however, for special consideration in each particular case the proper determination, according to the existing circumstances, of the moment of disconnexion.

41. With respect to the reaction $p'_0$ at the return of the piston, it is evident that, other circumstances being the same, the difference $p'_0 - p_0$ will be smaller the smaller $p_0$ is. In machines with a condenser, therefore, it will be smaller than in machines without a condenser, where $p_0$ is equal to one atmosphere. In locomotives, the most important machines without condensers, there is usually a particular circumstance tending to magnify this difference. The steam, instead of being allowed to pass off into the atmosphere through a tube as short and wide as possible, is conducted into the chimney and there made to issue through a somewhat contracted blowpipe in order to create an artificial draft.

In this case an exact determination of the difference is essential to the accuracy of the result. In doing so, regard must be had to the fact, that in one and the same machine the difference is not constant, but dependent upon the velocity with which it works; and the law which governs this dependence must be ascertained. Into these considerations, and into the investigations which have already been made upon the subject, I will not here enter, however, because they do not concern the present application of the mechanical theory of heat.

In machines where the vapour from the cylinder is not thus employed, and particularly in machines with a condenser, $p'_0$ differs so little from $p_0$, and therefore can change so little with the working velocity, that it is sufficient for most investigations to assume a mean value for $p'_0$.

Seeing, further, that the magnitude $p_0$ occurs only in one term of the equations (XIV), which term involves the factor $\sigma$, it can have but a very small influence on the amount of work; so that without hesitation we may put, in place of $p_0$, the most probable value of $p'_0$.

As already mentioned, the pressure $p''_0$ in the vicious space may vary very much, according as the cylinder is cut off from the condenser before or after the end of the piston's motion. But here, again, this pressure, and the magnitudes dependent thereon, occur only in terms of the equations (XIV), which involve the small factors $\mu$ and $\mu_0$; so that we may dispense with an accurate determination of this pressure, and rest satisfied with an approximate evaluation. In cases where no particular circumstances are present to cause $p''_0$ to differ essentially from $p'_0$, their difference, like the difference between $p'_0$ and $p_0$, may be neglected, and the most probable value of the mean reaction in the cylinder may be assumed as the common value of all the magnitudes. This value may be represented simply by $p_0$.

By introducing these simplifications, the equations (XIV) become

$$\left.\begin{aligned} W' &= \frac{1}{A}[m_1r_1 - m_3r_3 + Mc(T_1 - T_3) + \mu_0 r_0 - \mu c(T_3 - T_0)] \\ &\qquad + m_3u_3(p_3 - p_0), \\ m_2r_2 &= m_1r_1 + Mc(T_1 - T_2) + \mu_0 r_0 - \mu c(T_3 - T_0) + A\mu_0 u_0(p_2 - p_0) \\ &\qquad + AM\sigma(p_1 - p_2), \\ \frac{m_3r_3}{T_3} &= \frac{m_2r_2}{T_2} + (M + \mu)c\log\frac{T_2}{T_3}. \end{aligned}\right\} \text{(XV)}$$

42. In these equations it is assumed that the four pressures, $p_1$, $p_2$, $p_3$, and $p_0$, or what amounts to the same, the four temperatures $T_1$, $T_2$, $T_3$, and $T_0$ are given, as well as the masses $M$, $m_1$, $\mu$ and $\mu_0$, of which the first two must be known from direct observation, and the last two may be approximately determined from the magnitude of the vicious space. In practice, however, this condition is only partially fulfilled, so that in calculation we must have recourse to other data.

Of the four pressures, only two, $p_1$ and $p_0$, can be assumed as known. The first is given immediately by the manometer on the boiler, and the second may at least be approximately deduced from the indications of the manometer attached to the condenser. The two others, $p_2$ and $p_3$, are not given; but in their place we know the dimensions of the cylinder, and at what position of the piston the cylinder is cut off from the boiler. From these we may deduce the volumes occupied by the steam at the moment of disconnexion and at the end of the expansion, and these two volumes will then serve as data in place of the pressures $p_2$ and $p_3$.

We must now bring the equations into such a form that the calculation may be made by means of these data.

43. Let $v'$, as in the explanation of Pambour's theory, again be the whole space, including vicious space, set free during one

stroke in the cylinder; $ev'$ the space set free up to the time of disconnexion from the boiler; and $\epsilon v'$ the vicious space. Then, according to what was before said, we have the following equations:—

$$\begin{aligned} m_2u_2+(\mathrm{M}+\mu)\sigma &= ev', \\ m_3u_3+(\mathrm{M}+\mu)\sigma &= v', \\ \mu_0u_0+\mu\sigma &= \epsilon v'. \end{aligned}$$

The magnitudes $\mu$ and $\sigma$ are both so small that we may at once neglect their product, so that the above become

$$\left.\begin{aligned} m_2u_2 &= ev'-\mathrm{M}\sigma, \\ m_3u_3 &= v'-\mathrm{M}\sigma, \\ \mu_0 &= \frac{\epsilon v'}{u_0}. \end{aligned}\right\} \quad . \quad . \quad . \quad (45)$$

Further, according to equation (VI),

$$r=\mathrm{AT}ug,$$

where, on account of its subsequent frequent occurrence, a single letter $g$ is introduced in place of the differential coefficient $\frac{dp}{d\mathrm{T}}$. Accordingly, in the above system of equations we may express $r_2$ and $r_3$ in terms of $u_2$ and $u_3$; and then, as the masses $m_2$ and $m_3$ will only occur in the products $m_2u_2$ and $m_3u_3$, we may substitute the values of the latter as given in the first two of equations (45).

Similarly, by means of the last of these equations, we may eliminate the mass $\mu_0$; and as to the other mass $\mu$, although it may be a little greater than $\mu_0$, yet the terms which contain it as a factor are altogether so unimportant, that we may without hesitation give it the same value as we have found for $\mu_0$; in other words, for the numerical calculation we may give up the assumption, made for the sake of generality, that the mass in the vicious space is partially liquid and partially vaporous, and suppose that the mass in question consists entirely of vapour.

The substitutions here mentioned may be made in the general equations (XIV), as well as in the simplified equations (XV). As they present no difficulties, however, we will here limit ourselves to the last, in order to obtain the equations in a form convenient for numerical calculation.

After this change the equations become

$$\left.\begin{aligned} &W' = \frac{m_1 r_1 + Mc(T_1 - T_3)}{A} - (v' - M\sigma)(T_3 g_3 - p_3 + p_0) + \epsilon v' \frac{r_0 - c(T_3 - T_0)}{A u_0}, \\ &\quad (ev' - M\sigma) T_2 g_2 = \frac{m_1 r_1 + Mc(T_1 - T_2)}{A} + \epsilon v' \left( \frac{r_0 - c(T_2 - T_0)}{A u_0} + p_2 - p_0 \right) \\ &\qquad + M\sigma(p_1 - p_2), \\ &\quad (v' - M\sigma) g_3 = (ev' - M\sigma) g_2 + \left( M + \frac{\epsilon v'}{u_0} \right) \frac{c}{A} \log \frac{T_2}{T_3}. \end{aligned}\right\} \text{(XVI)}$$

44. In order to refer these equations, which now express the work done in a stroke or by the quantity $m_1$ of vapour, to the unit of weight of vapour, we have to proceed in the same manner as when the equations (35) were changed into (XII); that is to say, we divide each of the three equations by $m_1$, and set

$$\frac{M}{m_1} = l, \quad \frac{v'}{m_1} = V, \text{ and } \frac{W'}{m_1} = W.$$

Hereby the equations become

$$\left.\begin{aligned} &W = \frac{r_1 + lc(T_1 - T_3)}{A} - (V - l\sigma)(T_3 g_3 - p_3 + p_0) + \epsilon V \frac{r_0 - c(T_3 - T_0)}{A u_0}, \\ &(eV - l\sigma) T_2 g_2 = \frac{r_1 + lc(T_1 - T_2)}{A} + \epsilon V \left( \frac{r_0 - c(T_2 - T_0)}{A u_0} + p_2 - p_0 \right) + l\sigma(p_1 - p_2), \\ &(V - l\sigma) g_3 = (eV - l\sigma) g_2 + \left( l + \frac{\epsilon V}{u_0} \right) \frac{c}{A} \log \frac{T_2}{T_3}. \end{aligned}\right\} \text{(XVII)}$$

45. These equations may be applied in the following manner to the calculation of the work. From the intensity of evaporation, supposed to be known, and from the velocity with which the machine is at the same time driven, we determine the volume V which corresponds to the unit of weight of vapour. By means of this value we calculate the temperature $T_2$ from the second equation, afterwards the temperature $T_3$ from the third, and lastly, we employ the temperature $T_3$ to determine the work from the first equation.

In doing so, however, we encounter a peculiar difficulty. In order to calculate $T_2$ and $T_3$ from the two last equations, they ought in reality to be solved according to these temperatures. But they contain these temperatures not only explicitly, but implicitly, $p$ and $g$ being functions of the same. If, in order to eliminate these magnitudes, we were to replace $p$ by one of the ordinary empirical formulæ which express the pressure of a vapour as a function of its temperature, and $g$ by the differential coefficient of $p$, the equations would become too complicated for further treatment. We might, it is true, like Pambour did, help ourselves by instituting new empirical formulæ more convenient for our purpose, which, if not true for all temperatures, would be correct enough between certain limits. Instead of here making any such attempt, however, I will draw attention to another method, by which, although the calculation is somewhat tedious, the several parts thereof are capable of easy execution.

46. When the tension series for the vapour of any liquid is known with sufficient accuracy, the values of the magnitudes $g$ and T$g$ for the several temperatures can be calculated from it, and arranged in tables in the same manner as is usually done with the values of $p$.

In the case of steam, hitherto almost solely used in machines, and for the interval of temperature extending from 40° to 200° C., between which the application takes place, I have, with the help of Regnault's tension series, made such a calculation.

Strictly, I ought to have differentiated according to $t$ the formulæ which Regnault used in calculating the several values of $p$ below and above 100° C., and then to have calculated $g$ by means of the new formulæ thus obtained. But as it appeared to me that those formula did not fulfil their purpose perfectly enough to justify so large an amount of labour, and as the calculation and institution of another suitable formula would have been still more tedious, I contented myself with using the numbers already calculated for the pressure in order approximately to determine the differential coefficient of the pressure. For example, $p_{146}$ and $p_{148}$ being the pressures for the temperatures 146° and 148°, I have assumed that the magnitude

$$\frac{p_{148}-p_{146}}{2}$$

represents with sufficient accuracy the value of the differential coefficient for the mean temperature 147°.

In doing this, I have, for temperatures above 100°, used the numbers given by Regnault himself*. With respect to the values below 100°, Moritz† has lately drawn attention to the fact that the formula employed by Regnault between 0° and 100° was, especially in the vicinity of 100°, somewhat incorrect in consequence of his having used logarithms of seven places in calculating the constants. In consequence of this, Moritz has calculated those constants with logarithms of ten places, basing his calculations on the same observed values; and he has published the values of $p$ (as far as they differ from Regnault's, which only occurs above 40°) thus deduced from the corrected formulæ. I have used these values.

As soon as $g$ is calculated for the several temperatures, the calculation of $T.g$ also is attended with no further difficulty, because T is determined from the simple equation

$$T=273+t.$$

I have given the values of $g$ and $T.g$ thus found in a Table at the end of this memoir. For the sake of completeness, I have also added the corresponding values of $p$; those above 100° being calculated by Regnault, and those below by Moritz. To each of these three series of numbers are attached the differences between every two successive numbers; so that from the Table the values of the three magnitudes can be found for every temperature; and conversely, for any given value of one of the three magnitudes the corresponding temperature can be seen.

After what was before said of the calculation of $g$, it need scarcely be mentioned that the numbers of this Table are not to be considered as quite exact; they are only communicated in the absence of better ones. As, however, the calculations with reference to steam-engines are always based upon rather uncertain data, the numbers can without hesitation be used for this purpose, there being no fear that the uncertainty of the result will be much increased thereby‡.

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* *Mém. de l'Acad. des Sciences*, vol. xxi. p. 625.

† *Bulletin de la Classe Physico-mathématique de l'Acad. de St. Pétersbourg*, vol. xxi. p. 41.

‡ [Since the differential coefficient $\frac{dp}{dt}$ frequently presents itself in calcu-

As to the method of application, however, another remark is still necessary. In the equations (XVII), it is assumed that the pressure $p$ and its differential coefficient $g$ are expressed in kilogrammes to a square metre; whereas in the Table the same unit of pressure, a millimetre of mercury, is retained as that referred to in Regnault's tension series. In order, notwithstanding this, to be able to apply the Table, it is only necessary to divide every

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lations connected with vapour, it is of interest to know how far the convenient method of determining it, employed by me, is trustworthy. I will therefore here collect a few numbers for the sake of comparison.

In calculating the values of the vapour-tensions for temperatures above 100°, contained in his Tables, Regnault employed the formula

$$\text{Log}\,p=a-b\alpha^x-c\beta^x,$$

wherein Log refers to common or Briggs's logarithms, $x$ denotes the temperature calculated from $-20°$, so that $x=t+20$, and the five constants are given by the equations

$$\begin{aligned} a&=6{\cdot}2640348,\\ \text{Log}\,b&=0{\cdot}1397743,\\ \text{Log}\,c&=0{\cdot}6924351,\\ \text{Log}\,\alpha&=\bar{1}{\cdot}994049292,\\ \text{Log}\,\beta&=\bar{1}{\cdot}998343862. \end{aligned}$$

On deducing an equation for $\frac{dp}{dt}$ from this formula for $p$, we have

$$\frac{1}{p}\cdot\frac{dp}{dt}=\text{A}\alpha^t+\text{B}\beta^t,$$

wherein $\alpha$ and $\beta$ have the same values as before, and the new constants A and B are given by the equations

$$\begin{aligned} \text{Log A}&=\bar{2}{\cdot}5197602,\\ \text{Log B}&=\bar{2}{\cdot}6028403. \end{aligned}$$

On calculating from the above equation the value of the differential coefficient $\frac{dp}{dt}$ mentioned, by way of example, in the text and having reference to the temperature 147°, we find

$$\left(\frac{dp}{dt}\right)_{147}=90{\cdot}115.$$

By the above approximate method of determination we have, according to Regnault's Tables, the tensions

$$\begin{aligned} p_{148}&=3392{\cdot}98,\\ p_{146}&=3212{\cdot}74, \end{aligned}$$

and thence

$$\frac{p_{148}-p_{146}}{2}=\frac{180{\cdot}24}{2}=90{\cdot}12.$$

This approximate value, as is at once seen, agrees so well with the more accuterm in those equations, which does not contain either $p$ or $g$ as factor, by the number 13·596. This number, which is nothing more than the specific gravity of mercury at 0° C., compared with water at its maximum density, will for the sake of brevity be represented by $k$*.

This change of the formulæ, however, scarcely increases the calculation, inasmuch as it is equivalent to substituting everywhere, in place of the constant factor $\frac{1}{A}$,—which, according to

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rate one calculated from the above equation, that it may without hesitation be employed in calculations connected with the steam-engine.

With respect to temperatures between 0° and 100°, Regnault employed the following formula for calculating the vapour-tensions:—

$$\text{Log}\, p = a + b\alpha^t - c\beta^t.$$

The constants, according to the improved calculations of Moritz, have the following values:—

$$a = 4{\cdot}7393707,$$
$$\text{Log}\, b = \bar{2}{\cdot}1319907112,$$
$$\text{Log}\, c = 0{\cdot}6117407675,$$
$$\text{Log}\, \alpha = 0{\cdot}006864937152,$$
$$\text{Log}\, \beta = \bar{1}{\cdot}996725536856.$$

From this formula an equation for $\frac{dp}{dt}$ may be again deduced, of the form

$$\frac{1}{p} \cdot \frac{dp}{dt} = \text{A}\alpha^t + \text{B}\beta^t,$$

wherein the constants $\alpha, \beta$ have the values above indicated, and A and B are given by the formulæ

$$\text{Log A} = \bar{4}{\cdot}6930586,$$
$$\text{Log B} = \bar{2}{\cdot}8513123.$$

On calculating from this equation the value of $\frac{dp}{dt}$ corresponding, for instance, to a temperature of 70°, we find

$$\left(\frac{dp}{dt}\right)_{70} = 10{\cdot}1112,$$

and by the approximate method of determination we have

$$\frac{p_{71} - p_{69}}{2} = 10{\cdot}113\,;$$

a number which again agrees satisfactorily with the one calculated from the more accurate equation.—1864.]

* [To express a pressure of $p$ millimetres of mercury, in kilogrammes per square metre, the number $p$ must be multiplied by the weight of a column of mercury, having a height of one millimetre and a base equal to one square

Joule, has the value 423·55 already mentioned,—the other constant,

$$\frac{1}{\mathrm{A}k}=\frac{423\cdot55}{13\cdot596}=31\cdot1525\,; \quad . \quad . \quad . \quad . \quad (46)$$

when, instead of the work W, the magnitude $\frac{\mathrm{W}}{k}$ will be found in the first instance, and will subsequently merely have to be multiplied by $k$.

47. Let us now return to the equations (XVII), and consider first the second of them.

This equation may be written in the following form :—

$$\mathrm{T}_2 g_2=\mathrm{C}+a(t_1-t_2)-b(p_1-p_2), \quad . \quad . \quad . \quad (47)$$

wherein the magnitudes C, $a$, and $b$ are independent of $t_2$, and have the following values :—

$$\left.\begin{aligned} \mathrm{C}&=\frac{1}{e\mathrm{V}-l\sigma}\left[\frac{r_1}{\mathrm{A}k}+\epsilon\mathrm{V}\left(\frac{r_0-c(\mathrm{T}_1-\mathrm{T}_0)}{\mathrm{A}ku_0}+p_1-p_0\right)\right] \\ a&=\frac{c\left(l+\frac{\epsilon\mathrm{V}}{u_0}\right)}{\mathrm{A}k(e\mathrm{V}-l\sigma)}, \\ b&=\frac{\epsilon\mathrm{V}-l\sigma}{e\mathrm{V}-l\sigma} \end{aligned}\right\} \quad . \quad . \quad (47\,a)$$

Of the three terms on the right-hand side of (47), the first far exceeds the others; hence it will be possible, by successive approximation, to determine the product $\mathrm{T}_2 g_2$, and thence also the temperature $t_2$.

In order to obtain the first approximate value of the product, which we will call $\mathrm{T}'g'$, let us on the right side of (47) set $t_1$ in the place of $t_2$, and corresponding thereto $p_1$ in place of $p_2$, then

$$\mathrm{T}'g'=\mathrm{C}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

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metre. The volume of such a column is the $\frac{1}{1000}$th part of a cubic metre, in other words a cubic decimetre. Now a cubic decimetre of water at the maximum density weighs 1 kilogramme, and consequently a cubic decimetre of mercury at 0° weighs 13·596 kilogrammes. This is the factor, therefore, with which the number $p$ must be multiplied in the case under consideration. In our equations, however, it will of course amount to the same thing if, instead of multiplying the terms which contain the factor $p$, or the differential coefficient of $p$ by 13·596, we divide the remaining terms by the same number.—1864.]

The temperature $t'$, corresponding to this value of the product, can be sought in the Table. In order to find a second approximate value of the product, the value of $t'$ just found, and the corresponding value of the pressure $p'$, are introduced into (47) in the places of $t_2$ and $p_2$, whereby, having regard to the former equation, we have

$$T''g''=T'g'+a(t_1-t')-b(p_1-p'). \quad . \quad . \quad . \qquad (48\,a)$$

As before, the temperature $t''$, corresponding to this value of the product, is given by the Table. If this does not with sufficient exactitude represent the required temperature $t_2$, the same method must be repeated. The newly-found values $t''$ and $p''$ must be substituted in (47) in place of $t_2$ and $p_2$, whereby with the assistance of the two last equations, we have

$$T'''g'''=T''g''+a(t'-t'')-b(p'-p''), \quad . \quad . \quad . \qquad (48\,b)$$

and in the table we can find the new temperature $t'''$.

We might proceed in this manner for any length of time, though we shall find that the third approximation is already within $\frac{1}{100}$dth, and the fourth within $\frac{1}{1000}$dth of a degree of the true value of the temperature $t_2$.

48. The treatment of the third of the equations (XVII) is precisely similar. If we divide by $V-l\sigma$, and for facility of calculation introduce Briggs's logarithms (Log) in place of natural logarithms (log) by dividing by M the modulus of this system, the equation will take the form

$$g_3=C+a\,\mathrm{Log}\frac{T_2}{T_3}, \quad . \quad . \quad . \quad . \quad . \qquad (49)$$

wherein C and $a$ are independent of $T_3$, and have the following values :—

$$\left.\begin{aligned} C&=\frac{eV-l\sigma}{V-l\sigma}\cdot g_2, \\ a&=\frac{c\left(l+\frac{\epsilon V}{u_0}\right)}{M\,.\,Ak(V-l\sigma)}. \end{aligned}\right\} \quad . \quad . \quad . \qquad (49\,a)$$

Again, in equation (49) the first term on the right is greatest, so that we can apply the method of successive approximation.

In the first place, $T_2$ is put in the place of $T_3$, and we obtain the first approximate value of $g_3$, viz.

$$g' = C, \quad \ldots \ldots \quad (50)$$

from which we can find the corresponding temperature $t'$ in the Tables, and thence the absolute temperature $T'$. This is now substituted for $T_3$ in (49), and gives

$$g'' = g' + a \operatorname{Log} \frac{T_2}{T'}, \quad \ldots \ldots \quad (50\,a)$$

whence $T''$ is found. Similarly we obtain

$$g''' = g'' + a \operatorname{Log} \frac{T'}{T''}, \quad \ldots \ldots \quad (50\,b)$$

and so forth.

49. Before proceeding to the numerical application of the equations (XVII), the magnitudes $c$ and $r$ alone remain to be determined.

The magnitude $c$, which is the specific heat of the liquid, has hitherto been treated as constant in our development. Of course this is not quite correct, for the specific heat increases a little with increasing temperature. If, however, we select as a common value the one which is correct for about the middle of the interval over which the temperatures involved in the investigation extend, the deviations cannot be important ones. In machines driven by steam, this mean temperature may be taken at 100° C.; this being, in ordinary high-pressure engines, about equally distant from the temperature of the boiler and that of the condenser. In the case of water, therefore, we will employ the number which, according to Regnault, expresses its specific heat at 100°, and thus set

$$c = 1{\cdot}0130. \quad \ldots \ldots \quad (51)$$

In the determination of $r$ we shall start from the equation

$$\lambda = 606{\cdot}5 + 0{\cdot}305 \, . \, t,$$

given by Regnault as expressing the whole quantity of heat necessary to raise the unit of weight of water from 0° to the temperature $t$, and afterwards to evaporate it at that temperature. According to this definition, however,

$$\lambda = \int_0^t c\,dt + r,$$

so that

$$r=606{\cdot}5+0{\cdot}305\,.\,t-\int_0^t cdt.$$

In order to obtain precisely Regnault's value of $r$, we ought to substitute for $c$ in the above integral, the function of the temperature which Regnault determined. For our present purpose, however, I think it will suffice to give to $c$ the constant value above selected, by means of which

$$\int_0^t cdt=1{\cdot}013\,.\,t,$$

and the two terms in the above equation involving $t$ combine to form the single one $-0{\cdot}708\,.\,t$.

At the same time we must alter the constant term of the equation a little, and determine it so that the formula will correctly express that observed value of $r$ which in all probability is most accurate. As a mean of thirty-eight observations, Regnault found the value of $\lambda$ at 100° to be 636·67. Deducting the quantity of heat necessary to raise the unit of weight of water from 0° to 100°, which, according to Regnault, amounts to 100·5 units of heat, and contenting ourselves with one decimal, there remains

$$r_{100}=536{\cdot}2^{*}.$$

Employing this value, we obtain the following formula:—

$$r=607-0{\cdot}708\,.\,t. \quad . \quad . \quad . \quad . \quad . \quad (52)$$

The following comparison of a few values calculated herefrom, with the corresponding ones given by Regnault in his tables†, will show that this simplified formula agrees sufficiently well with the more accurate method of calculation above alluded to:—

| *t*. | 0°. | 50°. | 100°. | 150°. | 200°. |
|---|---|---|---|---|---|
| *r* according to equation (52) | 607·0 | 571·6 | 536·2 | 500·8 | 465·4 |
| *r* according to Regnault ... | 606·5 | 571·6 | 536·5 | 500·7 | 464·3 |

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* In his tables Regnault gives, instead of this, the number 536·5; the reason is, however, that instead of the above value 636·67 for $\lambda$ at 100°, he used the round number 637 in his calculations.

† *Mém. de l'Acad. des Sciences*, vol. xxi. p. 748.

50. In order to be able to distinguish between the effects of the two different kinds of expansions to which the two last of the equations (XVII) refer, it will perhaps be best to consider in the first place a steam-engine in which only one of them takes place. We will commence, therefore, with one of the machines which are said to work *without expansion*.

In this case, $e$, which expresses the relation of the volumes before and after expansion, equals 1, and at the same time $T_3 = T_2$; so that the equations (XVII) assume a simpler form.

The last of these equations becomes an identity, and therefore vanishes. Further, many terms of the first will admit of elimination, because they now become like the corresponding terms of the second, from which they before differed only by containing $T_3$ instead of $T_2$. Introducing the above-mentioned quantity $k$ at the same time, we now obtain

$$\left.\begin{aligned}&\frac{W}{k} = V(1-\epsilon)(p_2 - p_0) - l\sigma(p_1 - p_0),\\&(V - l\sigma)T_2 g_2 = \frac{r_1 + lc(T_1 - T_2)}{Ak} + \epsilon V\left(\frac{r_0 - c(T_2 - T_0)}{Aku_0} + p_2 - p_0\right)\\&\qquad + l\sigma(p_1 - p_2)^*.\end{aligned}\right\} \text{(XVIII)}$$

The first of these two equations is exactly the same as the one which we also obtain by Pambour's theory, if in (XII) we make $e = 1$, and introduce V instead of B. The second equation, however, differs from and replaces the simple relation between volume and pressure assumed by Pambour.

51. To the quantity $\epsilon$, which occurs in these equations and represents the vicious space as a fractional part of the whole space set free to the vapour, we will give the value 0·05. The quantity of liquid which the vapour carries with it on entering

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* [If in the two first equations in (XVII) we make $e = 1$, $T_3 = T_2$, and introduce the quantity $k$, the second equation at once reduces itself to the second equation in (XVIII). The first equation, however, assumes at first the form

$$\frac{W}{k} = \frac{r_1 + lc(T_1 - T_2)}{Ak} - (V - l\sigma)(T_2 g_2 - p_2 + p_0) + \epsilon V \frac{r_0 - c(T_2 - T_0)}{Aku_0}.$$

But if in place of $(V - l\sigma)\,T_2 g_2$ we here substitute the value given by the second equation, all terms disappear which contain $Ak$ as divisor, and the remaining terms have merely to be arranged according to the factors V and $l\sigma$, in order to obtain the first equation in (XVIII).—1864.]

the cylinder varies in different machines. Pambour states that it amounts on the average to 0·25 in locomotives, but in stationary engines to much less, probably only to 0·05 of the whole mass entering the cylinder. In our example we will make use of the latter number, according to which the ratio of the whole mass entering the cylinder is to the vaporous part of the same as 1 : 0·95. Further, let the pressure in the boiler be five atmospheres, to which the temperature 152°·22 belongs, and let us suppose that the machine has no condenser, or, in other words, let it have a condenser with the pressure of one atmosphere. The mean reaction in the cylinder is accordingly greater than one atmosphere. As before mentioned, the difference in locomotives may be considerable, but in stationary engines it is smaller. With respect to stationary engines, Pambour has altogether neglected this difference; and as our only object at present is to compare the new formulæ with those of Pambour, we will also disregard the difference, and let $p_0$ equal one atmosphere.

In this example, therefore, the following values will have to be made use of in equations (XVIII) :—

$$\left.\begin{aligned} \epsilon &= 0{\cdot}05, \\ l &= \frac{1}{0{\cdot}95} = 1{\cdot}053, \\ p_1 &= 3800, \\ p_0 &= 760. \end{aligned}\right\} \quad \ldots \ldots \quad (53)$$

To these must be added the values

$$k = 13{\cdot}596,$$
$$\sigma = 0{\cdot}001,$$

which are the same for all cases; and then in the first of the equations (XVIII), besides the required value of W, the magnitudes V and $p_2$ alone will remain undetermined.

52. We must now examine, in the first place, the *least possible* value of V.

This value corresponds to the case where the pressure in the cylinder is the same as that in the boiler, so that we have merely to put $p_1$ in the place of $p_2$ in the last of equations (XVIII) in order to obtain

$$V=\frac{\frac{r_1}{Ak}+l\sigma\,.\,T_1g_1}{T_1g_1-\epsilon\left(\frac{r_0-c(T_1-T_0)}{Aku_0}+p_1-p_0\right)}\quad .\quad .\quad .\quad .\qquad (54)$$

In order at once to give an example of the influence of the vicious space, I have calculated two values of this expression, corresponding respectively to the cases where no vicious space exists ($\epsilon=0$), and where, according to supposition, $\epsilon=0{\cdot}05$. These values, expressed as fractions of a cubic metre to one kilogramme of vapour from the boiler, are

0·3637 and 0·3690.

The latter value is greater than the former, because, first, the vapour entering the vicious space with great velocity, the *vis viva* of its motion is converted into heat, which in its turn causes the evaporation of a part of the accompanying liquid; and secondly, because the vapour before present in the vicious space, contributes to the increase of the ultimate quantity of vapour.

Substituting both the above values of V in the first of equations (XVIII), and in the one case again making $\epsilon=0$, whilst in the other $\epsilon=0{\cdot}05$, we have as the corresponding quantities of work expressed in kilogramme-metres, the numbers

14990 and 14450.

According to Pambour's theory, it makes no difference whether a part of the volume is vicious space or not; in both cases this volume is determined from the equation (29 *b*) by giving to $p$ the particular value $p_1$. By so doing we obtain

0·3883.

This value is greater than the one (0·3637) before found for the same quantity of vapour, because hitherto the volume of vapour at its maximum density was esteemed greater than, according to the mechanical theory of heat, it can be, and this former estimate also finds expression in equation (29 *b*).

If, by means of this volume, we determine the work under the two suppositions $\epsilon=0$ and $\epsilon=0{\cdot}05$, we have

16000 and 15200.

As might have been concluded immediately from the greater volume, these quantities of work are both greater than those before found, but not in the same ratio; for, according to our equations, the loss of work occasioned by vicious space is less than it would be according to Pambour's theory.

53. In a machine of the kind here considered, which Pambour actually examined, the velocity which the machine actually possessed, compared with the minimum velocity calculated, according to his theory, for the same intensity of evaporation and the same pressure in the boiler, gave the ratio 1·275 : 1 in one experiment, and in another, where the charge was less, 1·70 : 1. These velocities would in our case correspond to the volumes 0·495 and 0·660. As an example of the determination of work, we will now choose a velocity between these two, and set simply,

$$V = 0{\cdot}6.$$

In order next to find the temperature $t_2$ corresponding to this value of V, we employ the equation (47) under the following special form:—

$$T_2 g_2 = 26577 + 56{\cdot}42 \,.\, (t_1 - t_2) - 0{\cdot}0483 \,.\, (p_1 - p_2). \qquad (55)$$

Effecting, by means of this equation, the successive determinations of $t_2$ described in Art. 47, we obtain the following series of approximate values:—

$$\begin{aligned} t' &= 13\overset{\circ}{3}{\cdot}01, \\ t'' &= 134{\cdot}43, \\ t''' &= 134{\cdot}32, \\ t'''' &= 134{\cdot}33. \end{aligned}$$

Further approximate values would only differ from each other in higher decimal places; so that, contenting ourselves with two decimal places, the last number may be considered as the true value of $t_2$. The corresponding pressure is

$$p_2 = 2308{\cdot}30.$$

Applying these values of V and $p_2$, as well as those given in Art. 51, to the first of the equations (XVIII), we obtain

$$W = 11960.$$

Pambour's equation (XII) gives for the same volume 0·6, the work

$$W = 12520.$$

54. In order to show more clearly the dependence of the work upon the volume, and at the same time the difference which exists between Pambour's and my own theory in this respect, I have made a calculation, similar to the last, for a series of other volumes increasing uniformly. The results are comprised in the following Table. The first horizontal row of numbers, separated from the rest by a line, contains the values found for a machine without vicious space. In other respects the arrangement of the Table will be easily understood.

| V. | $t_2$. | W. | According to Pambour. | |
|---|---|---|---|---|
| | | | V. | W. |
| 0·3637 | 152°·22 | 14990 | 0·3883 | 16000 |
| 0·3690 | 152·22 | 14450 | 0·3883 | 15200 |
| 0·4 | 149·12 | 14100 | 0·4 | 15050 |
| 0·5 | 140·83 | 13020 | 0·5 | 13780 |
| 0·6 | 134·33 | 11960 | 0·6 | 12520 |
| 0·7 | 129·03 | 10910 | 0·7 | 11250 |
| 0·8 | 124·55 | 9880 | 0·8 | 9980 |
| 0·9 | 120·72 | 8860 | 0·9 | 8710 |
| 1 | 117·36 | 7840 | 1 | 7440 |

We see that the quantities of work calculated according to Pambour's theory diminish more quickly with increasing volume than those calculated from our equations; for at first the former are considerably greater than the latter, afterwards they approach thereto, and finally they are actually less than the latter. The reason is, that according to Pambour's theory, the same mass, as at first, always remains vaporous during expansion; whilst, according to our theory, a part of the liquid accompanying the vaporous mass afterwards evaporates, and the more so the greater the expansion.

55. In a similar manner we will now consider a machine which works with expansion, and we will further select one with a condenser.

With reference to the magnitude of the expansion, we will suppose that the cylinder is cut off from the boiler when the piston has completed one-third of its journey. Then for the determination of $e$ we have the equation

$$e-\epsilon=\frac{1}{3}(1-\epsilon)\,;$$

whence, retaining the former value, 0·05, of $\epsilon$,

$$e=\frac{1\cdot 1}{3}=0\cdot 3666\ldots$$

As before, let the pressure in the boiler be five atmospheres. By good arrangement the pressure in the condenser may be kept below one-tenth of an atmosphere. As it is not always so small, however, and as the reacting pressure in the cylinder always exceeds it a little, we will assume the mean reaction to be one-fifth of an atmosphere (or 152 millims.), to which the temperature $t_0=60^\circ\cdot 46$ corresponds. Retaining the former assumed value of $l$, therefore, the quantities requiring application in this example are

$$\left.\begin{aligned} e&=0\cdot 36667,\\ \epsilon&=0\cdot 05,\\ l&=1\cdot 053,\\ p_1&=3800,\\ p_0&=152.\end{aligned}\right\}\quad\ldots\ldots\ldots\quad (56)$$

In order to calculate the work, we now only require the value of V to be given. To guide our choice, we must first know the least possible value of V, which we can find, as before, from the second of the equations (XVII.) by putting $p_1$ in the place of $p_2$, and changing the other quantities dependent on $p$ accordingly. In this manner we find for the present case the value

1·010.

Starting from this, we will assume, as a first example, that the actual velocity of the machine's motion has to this minimum a ratio of 3 : 2 nearly; so that setting

$$V=1\cdot 5,$$

we will determine the work for this velocity.

56. The temperatures $t_2$ and $t_3$ must now be determined by setting this value of V in the two last of equations (XVII). For the machine without a condenser, the determination of $t_2$ has been sufficiently explained; and as the present case differs from

that one only by a different value for *e*, which was there equal to 1, it will be sufficient to state here that the final result is

$$t_2 = 137^\circ{\cdot}43.$$

The equation (49), which serves to determine $t_3$, now takes the form

$$g_3 = 26{\cdot}604 + 51{\cdot}515 \operatorname{Log} \frac{T_2}{T_3}, \quad . \quad . \quad . \quad . \quad (57)$$

and from it we obtain the following approximate values:—

$$\begin{aligned} t' &= \overset{\circ}{9}9{\cdot}24, \\ t'' &= 101{\cdot}93, \\ t''' &= 101{\cdot}74, \\ t'''' &= 101{\cdot}76. \end{aligned}$$

We may consider the last of these values, from which the following ones would only differ in higher places of decimals, as the proper value of $t_3$; and we may use it, together with the known values of $t_1$ and $t_0$, in the first of the equations (XVII). By so doing we find

$$W = 31080.$$

When, assuming the same value of V, we calculate the work according to Pambour's equation (XII),—whereby, however, the values of B and *b* are not taken from equation (29 *b*), as in the machine without condenser, but from equation (29 *a*) intended for machines with condensers,—we find

$$W = 32640.$$

57. In a manner similar to the foregoing I have also calculated the work for the volumes 1·2, 1·8, and 2·1. Besides this, in order to illustrate by an example the influence which the several imperfections have upon the work, I have added the following cases:—

(1) The case of a machine having no vicious space, and where at the same time the pressure in the cylinder during the entrance of the vapour is equal to that in the boiler, and the expansion is carried so far that the pressure diminishes from its original value $p_1$ to $p_0$. If we further suppose that $p_0$ is exactly the pressure in the condenser, this case will be the one to which equation (XI) refers, and which for a given quantity of heat—

the temperatures at which the heat is received and imparted being also considered as given—furnishes the greatest possible quantity of work.

(2) The case of a machine, again, having no vicious space, and when the pressure in the cylinder is again equal to that in the boiler, but where the expansion is not, as before, complete, but only continued until the ratio $e:1$ is obtained. This is the case to which equation (X) refers; only in order to determine the amount of expansion, the change caused by the same in the temperature of the vapour was before supposed to be known, whilst here the expansion is determined according to the volume, and the change of temperature must be afterwards calculated therefrom.

(3) The case of a machine with vicious space and incomplete expansion, and where, of the former favourable conditions, the only one which remains is, that during the entrance of the vapour the pressure in the cylinder is the same as in the boiler, so that the volume has its smallest possible value.

To these cases may be added the one already mentioned, where the last favourable condition is relinquished, and the volume has a greater than its minimum value.

For the sake of comparison, all these cases, with the exception of the first, are also calculated according to Pambour's theory. The reason of the exception is, that the equations (29 *a*) and (29 *b*) do not here suffice; for even the one which is intended for small pressures cannot be applied below one-half, or at most one-third of an atmosphere, whereas here the pressure ought to decrease to one-fifth of an atmosphere.

The following are the numbers given by our equations in the first of the above cases:—

| Volume before expansion. | Volume after expansion. | W. |
|---|---|---|
| 0·3637 | 6·345 | 50460 |

For all the rest of the above cases the results are given in the following Table, where the numbers referring to a machine without vicious space, are again separated from the rest by a horizontal line. The volumes after expansion are alone given, because the corresponding ones before expansion, being in all cases smaller in the proportion of $e : 1$, may be easily found:—

| V. | $t_2$. | $t_3$. | W. | According to Pambour. | |
|---|---|---|---|---|---|
| | | | | V. | W. |
| | ° | ° | | | |
| 0·992 | 152·22 | 113·71 | 34300 | 1·032 | 36650 |
| 1·010 | 152·22 | 113·68 | 32430 | 1·032 | 34090 |
| 1·2 | 145·63 | 108·38 | 31870 | 1·2 | 33570 |
| 1·5 | 137·43 | 101·76 | 31080 | 1·5 | 32640 |
| 1·8 | 131·02 | 96·55 | 30280 | 1·8 | 31710 |
| 2·1 | 125·79 | 92·30 | 29490 | 2·1 | 30780 |

58. The quantities of work in this Table, as well as those in the former Table for machines without condensers, refer to a kilogramme of vapour coming from the boiler. It is easy, however, to refer the work to a *unit of heat* furnished by the source of heat; for every kilogramme of vapour requires as much heat as is necessary, first to raise the mass $l$ (somewhat more than one kilogramme) from the temperature it had when entering the boiler up to the general temperature of the same, and then at that temperature to convert a kilogramme of it into vapour. This quantity of heat can be calculated from former data.

59. In conclusion, I will add a few remarks on *friction*, restricting myself, however, to a justification of my having hitherto disregarded friction in the developed equations, by showing that instead of introducing the same at once into the first general expressions for the work, as Pambour has done, it may also, according to the same principles, and according to the manner of other authors, be afterwards brought into calculation.

The forces which the machine has to overcome during its action may be thus distinguished:—(1) The resistance externally opposed to it, and in overcoming which it performs the required *useful* work. Pambour calls this resistance the charge of the machine. (2) The resistances which have their source in the machine itself, so that the work expended in overcoming them is not externally of use. All these resistances are included in the term *friction*; although, besides friction in its more limited sense, they comprise other forces, particularly the resistances caused by pumps belonging to the machine, exclusive of the one which feeds the boiler, and which has already been considered.

Pambour brings both these kinds of resistances into calculation as forces opposing the motion of the piston; and in order conveniently to combine them with the pressures of the vapour on both sides of the piston, he also adopts a notation similar to the one ordinarily used for vapour pressures; that is to say, the symbol denotes, not the whole force, but that part of it which corresponds to a unit of surface of the piston. In this sense let the letter R represent the charge.

A further distinction must still be made in the case of friction, for it has not a constant value in each machine, but increases with the charge. Accordingly Pambour divides it into two parts: that which is already present when the machine moves without charge, and that which the charge itself occasions. With respect to the last, he assumes that it is proportional to the charge. Accordingly, the friction referred to the unit of surface is expressed by

$$f+\delta \cdot \mathrm{R},$$

where $f$ and $\delta$ are magnitudes which, although dependent upon the construction and dimensions of the machine, are, according to Pambour, to be considered as constant in any given machine.

We can now refer the work of the machine to these *resisting* forces instead of, as before, to the *driving* force of steam; for the negative work done by the former must be equal to the positive work done by the latter, otherwise an acceleration or retardation of motion would ensue, which would be contradictory to the hypothesis of uniform motion hitherto made. During the time that a unit of weight of vapour enters the cylinder, the surface of the piston describes the space $(1-\epsilon)\mathrm{V}$, hence for the work W we obtain the expression

$$\mathrm{W}=(1-\epsilon)\mathrm{V}[(1+\delta) \cdot \mathrm{R}+f].$$

On the other hand, the *useful* part of this work, which for distinction from the whole work shall be symbolized by (W), is expressed thus,

$$(\mathrm{W})=(1-\epsilon)\mathrm{V} \cdot \mathrm{R}.$$

Eliminating R from this equation by means of the former, we have the equation

$$(W)=\frac{W-(1-\epsilon)V\,.\,f}{1+\delta}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (58)$$

by means of which, V being known, the useful work (W) can be deduced from the whole work W as soon as the quantities $f$ and $\delta$ are given.

I will not here enter into Pambour's method of finding the latter quantities, as this determination still rests upon a too insecure basis, and as friction is altogether foreign to the subject of this memoir.

TABLE CONTAINING THE VALUES, FOR STEAM, OF $p$, ITS DIFFERENTIAL COEFFICIENT $\frac{dp}{dt}=g$, AND THE PRODUCT $T\,.\,g$ EXPRESSED IN MILLIMETRES OF MERCURY.

| $t$ in Centigrade degrees. | $p$. | Δ. | $g$. | Δ. | $T\,.\,g$. | Δ. |
|---|---|---|---|---|---|---|
| 40° | 54·906 | 3·003 | 2·935 | 0·139 | 919 | 46 |
| 41 | 57·909 | 3·145 | 3·074 | 0·144 | 965 | 49 |
| 42 | 61·054 | 3·291 | 3·218 | 0·149 | 1014 | 50 |
| 43 | 64·345 | 3·444 | 3·367 | 0·155 | 1064 | 52 |
| 44 | 67·789 | 3·601 | 3·522 | 0·161 | 1116 | 55 |
| 45 | 71·390 | 3·766 | 3·683 | 0·167 | 1171 | 57 |
| 46 | 75·156 | 3·935 | 3·850 | 0·173 | 1228 | 59 |
| 47 | 79·091 | 4·112 | 4·023 | 0·180 | 1287 | 62 |
| 48 | 83·203 | 4·294 | 4·203 | 0·185 | 1349 | 64 |
| 49 | 87·497 | 4·483 | 4·388 | 0·193 | 1413 | 67 |
| 50 | 91·980 | 4·679 | 4·581 | 0·199 | 1480 | 69 |
| 51 | 96·659 | 4·882 | 4·780 | 0·207 | 1549 | 72 |
| 52 | 101·541 | 5·092 | 4·987 | 0·213 | 1621 | 74 |
| 53 | 106·633 | 5·309 | 5·200 | 0·221 | 1695 | 78 |
| 54 | 111·942 | 5·533 | 5·421 | 0·228 | 1773 | 80 |
| 55 | 117·475 | 5·766 | 5·649 | 0·237 | 1853 | 83 |
| 56 | 123·241 | 6·006 | 5·886 | 0·244 | 1936 | 87 |
| 57 | 129·247 | 6·254 | 6·130 | 0·252 | 2023 | 89 |
| 58 | 135·501 | 6·510 | 6·382 | 0·260 | 2112 | 93 |
| 59 | 142·011 | 6·775 | 6·642 | 0·269 | 2205 | 96 |
| 60 | 148·786 | 7·048 | 6·911 | 0·278 | 2301 | 100 |
| 61 | 155·834 | 7·330 | 7·189 | 0·286 | 2401 | 103 |
| 62 | 163·164 | 7·621 | 7·475 | 0·296 | 2504 | 107 |
| 63 | 170·785 | 7·922 | 7·771 | 0·305 | 2611 | 111 |
| 64 | 178·707 | 8·231 | 8·076 | 0·314 | 2722 | 114 |
| 65 | 186·938 |  | 8·390 |  | 2836 |  |

### TABLE (*continued*).

| *t* in Centigrade degrees. | *p*. | Δ. | *g*. | Δ. | T.*g*. | Δ. |
|---|---|---|---|---|---|---|
| 65° | 186·938 | 8·550 | 8·390 | 0·325 | 2836 | 118 |
| 66 | 195·488 | 8·880 | 8·715 | 0·334 | 2954 | 123 |
| 67 | 204·368 | 9·218 | 9·049 | 0·344 | 3077 | 126 |
| 68 | 213·586 | 9·568 | 9·393 | 0·355 | 3203 | 131 |
| 69 | 223·154 | 9·928 | 9·748 | 0·365 | 3334 | 135 |
| 70 | 233·082 | 10·298 | 10·113 | 0·376 | 3469 | 139 |
| 71 | 243·380 | 10·680 | 10·489 | 0·387 | 3608 | 144 |
| 72 | 254·060 | 11·072 | 10·876 | 0·398 | 3752 | 149 |
| 73 | 265·132 | 11·476 | 11·274 | 0·410 | 3901 | 153 |
| 74 | 276·608 | 11·892 | 11·684 | 0·422 | 4054 | 159 |
| 75 | 288·500 | 12·320 | 12·106 | 0·433 | 4213 | 163 |
| 76 | 300·820 | 12·759 | 12·539 | 0·445 | 4376 | 168 |
| 77 | 313·579 | 13·210 | 12·984 | 0·458 | 4544 | 174 |
| 78 | 326·789 | 13·675 | 13·442 | 0·471 | 4718 | 179 |
| 79 | 340·464 | 14·152 | 13·913 | 0·484 | 4897 | 185 |
| 80 | 354·616 | 14·642 | 14·397 | 0·497 | 5082 | 190 |
| 81 | 369·258 | 15·146 | 14·894 | 0·511 | 5272 | 197 |
| 82 | 384·404 | 15·664 | 15·405 | 0·524 | 5469 | 202 |
| 83 | 400·068 | 16·194 | 15·929 | 0·538 | 5671 | 208 |
| 84 | 416·262 | 16·740 | 16·467 | 0·552 | 5879 | 214 |
| 85 | 433·002 | 17·299 | 17·019 | 0·577 | 6093 | 220 |
| 86 | 450·301 | 17·874 | 17·586 | 0·582 | 6313 | 227 |
| 87 | 468·175 | 18·463 | 18·168 | 0·597 | 6540 | 234 |
| 88 | 486·638 | 19·067 | 18·765 | 0·612 | 6774 | 240 |
| 89 | 505·705 | 19·687 | 19·377 | 0·628 | 7014 | 248 |
| 90 | 525·392 | 20·323 | 20·005 | 0·644 | 7262 | 254 |
| 91 | 545·715 | 20·975 | 20·649 | 0·660 | 7516 | 262 |
| 92 | 566·690 | 21·643 | 21·309 | 0·676 | 7778 | 269 |
| 93 | 588·333 | 22·328 | 21·985 | 0·694 | 8047 | 276 |
| 94 | 610·661 | 23·031 | 22·679 | 0·712 | 8323 | 285 |
| 95 | 633·692 | 23·751 | 23·391 | 0·728 | 8608 | 292 |
| 96 | 657·443 | 24·488 | 24·119 | 0·747 | 8900 | 300 |
| 97 | 681·931 | 25·243 | 24·865 | 0·765 | 9200 | 309 |
| 98 | 707·174 | 26·017 | 25·630 | 0·783 | 9509 | 317 |
| 99 | 733·191 | 26·809 | 26·413 | 0·787 | 9826 | 320 |
| 100 | 760·00 | 27·59 | 27·200 | 0·805 | 10146 | 328 |
| 101 | 787·59 | 28·42 | 28·005 | 0·840 | 10474 | 343 |
| 102 | 816·01 | 29·27 | 28·845 | 0·855 | 10817 | 350 |
| 103 | 845·28 | 30·13 | 29·700 | 0·865 | 11167 | 356 |
| 104 | 875·41 | 31·00 | 30·565 | 0·885 | 11523 | 367 |
| 105 | 906·41 | 31·90 | 31·450 | 0·915 | 11888 | 378 |
| 106 | 938·31 | 32·83 | 32·365 | 0·935 | 12266 | 388 |
| 107 | 971·14 | 33·77 | 33·300 | 0·955 | 12654 | 397 |
| 108 | 1004·91 | 34·74 | 34·255 | 0·975 | 13051 | 407 |
| 109 | 1039·65 | 35·72 | 35·230 | 0·990 | 13458 | 414 |
| 110 | 1075·37 | 36·72 | 36·220 | 1·010 | 13872 | 424 |
| 111 | 1112·09 | 37·74 | 37·230 | 1·030 | 14296 | 434 |
| 112 | 1149·83 | 38·78 | 38·260 | 1·060 | 14730 | 448 |
| 113 | 1188·61 | 39·86 | 39·320 | 1·080 | 15178 | 457 |
| 114 | 1228·47 | 40·94 | 40·400 | 1·100 | 15635 | 467 |
| 115 | 1269·41 |  | 41·500 |  | 16102 |  |

## TABLE (*continued*).

| *t* in Centigrade degrees. | *p*. | Δ. | *g*. | Δ. | T.*g*. | Δ. |
|---|---|---|---|---|---|---|
| 115° | 1269·41 | 42·06 | 41.500 | 1·125 | 16102 | 479 |
| 116 | 1311·47 | 43·19 | 42·625 | 1·150 | 16581 | 491 |
| 117 | 1354·66 | 44·36 | 43·775 | 1·170 | 17072 | 502 |
| 118 | 1399·02 | 45·53 | 44·945 | 1·185 | 17574 | 509 |
| 119 | 1444·55 | 46·73 | 46·130 | 1·220 | 18083 | 526 |
| 120 | 1491·28 | 47·97 | 47·350 | 1·245 | 18609 | 537 |
| 121 | 1539·25 | 49·22 | 48·595 | 1·260 | 19146 | 547 |
| 122 | 1588·47 | 50·49 | 49·855 | 1·290 | 19693 | 560 |
| 123 | 1638·96 | 51·80 | 51·145 | 1·315 | 20253 | 574 |
| 124 | 1690·76 | 53·12 | 52·460 | 1·335 | 20827 | 583 |
| 125 | 1743·88 | 54·47 | 53·795 | 1·365 | 21410 | 599 |
| 126 | 1798·35 | 55·85 | 55·160 | 1·400 | 22009 | 615 |
| 127 | 1854·20 | 57·27 | 56·560 | 1·415 | 22624 | 624 |
| 128 | 1911·47 | 58·68 | 57·975 | 1·430 | 23248 | 633 |
| 129 | 1970·15 | 60·13 | 59·405 | 1·470 | 23881 | 652 |
| 130 | 2030·28 | 61·62 | 60·875 | 1·500 | 24533 | 666 |
| 131 | 2091·90 | 63·13 | 62·375 | 1·520 | 25199 | 678 |
| 132 | 2155·03 | 64·66 | 63·895 | 1·550 | 25877 | 694 |
| 133 | 2219·69 | 66·23 | 65·445 | 1·575 | 26571 | 706 |
| 134 | 2285·92 | 67·81 | 67·020 | 1·600 | 27277 | 720 |
| 135 | 2353·73 | 69·43 | 68·620 | 1·630 | 27997 | 735 |
| 136 | 2423·16 | 71·07 | 70·250 | 1·670 | 28732 | 755 |
| 137 | 2494·23 | 72·77 | 71·920 | 1·685 | 29487 | 765 |
| 138 | 2567·00 | 74·44 | 73·605 | 1·710 | 30252 | 778 |
| 139 | 2641·44 | 76·19 | 75·315 | 1·750 | 31030 | 798 |
| 140 | 2717·63 | 77·94 | 77·065 | 1·770 | 31828 | 810 |
| 141 | 2795·57 | 79·73 | 78·835 | 1·810 | 32638 | 830 |
| 142 | 2875·30 | 81·56 | 80·645 | 1·835 | 33468 | 844 |
| 143 | 2956·86 | 83·40 | 82·480 | 1·865 | 34312 | 860 |
| 144 | 3040·26 | 85·29 | 84·345 | 1·895 | 35172 | 876 |
| 145 | 3125·55 | 87·19 | 86·240 | 1·920 | 36048 | 891 |
| 146 | 3212·74 | 89·13 | 88·160 | 1·960 | 36939 | 911 |
| 147 | 3301·87 | 91·11 | 90·120 | 1·990 | 37850 | 928 |
| 148 | 3392·98 | 93·11 | 92·110 | 2·015 | 38778 | 943 |
| 149 | 3486·09 | 95·14 | 94·125 | 2·045 | 39721 | 959 |
| 150 | 3581·23 | 97·20 | 96·170 | 2·085 | 40680 | 980 |
| 151 | 3678·43 | 99·31 | 98·255 | 2·120 | 41660 | 999 |
| 152 | 3777·74 | 101·44 | 100·375 | 2·140 | 42659 | 1012 |
| 153 | 3879·18 | 103·59 | 102·515 | 2·175 | 43671 | 1032 |
| 154 | 3982·77 | 105·79 | 104·690 | 2·220 | 44703 | 1054 |
| 155 | 4088·56 | 108·03 | 106·910 | 2·250 | 45757 | 1073 |
| 156 | 4196·59 | 110·29 | 109·160 | 2·270 | 46830 | 1085 |
| 157 | 4306·88 | 112·57 | 111·430 | 2·310 | 47915 | 1107 |
| 158 | 4419·45 | 114·91 | 113·740 | 2·345 | 49022 | 1127 |
| 159 | 4534·36 | 117·26 | 116·085 | 2·375 | 50149 | 1144 |
| 160 | 4651·62 | 119·66 | 118·460 | 2·410 | 51293 | 1165 |
| 161 | 4771·28 | 122·08 | 120·870 | 2·445 | 52458 | 1184 |
| 162 | 4893·36 | 124·55 | 123·315 | 2·490 | 53642 | 1209 |
| 163 | 5017·91 | 127·06 | 125·805 | 2·510 | 54851 | 1222 |
| 164 | 5144·97 | 129·57 | 128·315 | 2·545 | 56073 | 1244 |
| 165 | 5274·54 |  | 130·860 |  | 57317 |  |

## TABLE (*continued*).

| *t* in Centigrade degrees. | *p*. | Δ. | *g*. | Δ. | T.*g*. | Δ |
|---|---|---|---|---|---|---|
| 165° | 5274·54 | 132·15 | 130·860 | 2·585 | 57317 | 1265 |
| 166 | 5406·69 | 134·74 | 133·445 | 2·620 | 58582 | 1286 |
| 167 | 5541·43 | 137·39 | 136·065 | 2·670 | 59868 | 1314 |
| 168 | 5678·82 | 140·08 | 138·735 | 2·685 | 61182 | 1326 |
| 169 | 5818·90 | 142·76 | 141·420 | 2·725 | 62508 | 1348 |
| 170 | 5961·66 | 145·53 | 144·145 | 2·765 | 63856 | 1372 |
| 171 | 6107·19 | 148·29 | 146·910 | 2·795 | 65228 | 1390 |
| 172 | 6255·48 | 151·12 | 149·705 | 2·830 | 66618 | 1412 |
| 173 | 6406·60 | 153·95 | 152·535 | 2·880 | 68030 | 1440 |
| 174 | 6560·55 | 156·88 | 155·415 | 2·920 | 69470 | 1464 |
| 175 | 6717·43 | 159·79 | 158·335 | 2·935 | 70934 | 1476 |
| 176 | 6877·22 | 162·75 | 161·270 | 2·980 | 72410 | 1502 |
| 177 | 7039·97 | 165·75 | 164·250 | 3·025 | 73912 | 1529 |
| 178 | 7205·72 | 168·80 | 167·275 | 3·060 | 75441 | 1550 |
| 179 | 7374·52 | 171·87 | 170·335 | 3·090 | 76991 | 1570 |
| 180 | 7546·39 | 174·98 | 173·425 | 3·140 | 78561 | 1599 |
| 181 | 7721·37 | 178·15 | 176·565 | 3·170 | 80160 | 1619 |
| 182 | 7899·52 | 181·32 | 179·735 | 3·205 | 81779 | 1642 |
| 183 | 8080·84 | 184·56 | 182·940 | 3·255 | 83421 | 1670 |
| 184 | 8265·40 | 187·83 | 186·195 | 3·280 | 85091 | 1688 |
| 185 | 8453·23 | 191·12 | 189·425 | 3·320 | 86779 | 1714 |
| 186 | 8644·35 | 194·47 | 192·795 | 3·370 | 88493 | 1743 |
| 187 | 8838·82 | 197·86 | 196·165 | 3·400 | 90236 | 1763 |
| 188 | 9036·68 | 201·27 | 199·565 | 3·445 | 91999 | 1792 |
| 189 | 9237·95 | 204·75 | 203·010 | 3·480 | 93791 | 1814 |
| 190 | 9442·70 | 208·23 | 206·490 | 3·515 | 95605 | 1837 |
| 191 | 9650·93 | 211·78 | 210·005 | 3·550 | 97442 | 1861 |
| 192 | 9862·71 | 215·33 | 213·555 | 3·595 | 99303 | 1889 |
| 193 | 10078·04 | 218·97 | 217·150 | 3·645 | 101192 | 1919 |
| 194 | 10297·01 | 222·62 | 220·795 | 3·675 | 103111 | 1941 |
| 195 | 10519·63 | 226·32 | 224·470 | 3·715 | 105052 | 1966 |
| 196 | 10745·95 | 230·05 | 228·185 | 3·750 | 107018 | 1991 |
| 197 | 10976·00 | 233·82 | 231·935 | 3·795 | 109009 | 2020 |
| 198 | 11209·82 | 237·64 | 235·730 | 3·840 | 111029 | 2048 |
| 199 | 11447·46 | 241·50 | 239·570 | 3·885 | 113077 | 2077 |
| 200 | 11688·96 |  | 243·455 |  | 115154 |  |

# APPENDIX TO FIFTH MEMOIR [1864].

## ON SOME APPROXIMATE FORMULÆ EMPLOYED TO FACILITATE CALCULATIONS.

With a view of elucidating the mechanical theory of heat and its applications to the phenomena which present themselves in the steam-engine, Zeuner, in his work on the subject*, has treated a series of problems having, for the most part, reference to the same cases which have been treated by me in the immediately preceding (p. 151 to 157), and in the Second Memoir. In doing so, Zeuner enters into somewhat greater detail than I have done, and he seeks to facilitate the calculations by introducing approximate formulæ; of some of the latter, however, I cannot approve.

Zeuner thus enunciates the *Problem* I:—"A cylinder contains $m_1$ kilogrammes of vapour, and $(M-m_1)$ kilogrammes of water. Suppose the mass to expand slowly, so that the pressure on the piston which has to be overcome by the vapour is at each moment equal to the tension of the latter; the temperature of the mass falls from $t_1$ to $t_2$, and the tension from $p_1$ to $p_2$. What work does the vapour perform, and how much heat must be received or given off *in order that the quantity of vapour* $\mathrm{m}_1$ *may remain constant, and consequently that neither condensation of vapour nor evaporation of water may take place during expansion?*"

The quantity of heat which must be imparted to the mass within the cylinder during its expansion and consequent change of temperature in order to prevent both condensation and evaporation, may be at once expressed by means of the specific heat of water, say $c$, and the specific heat of saturated vapour, for which latter I have already used the symbol $h$. For an infinitesimal change of temperature $dt$ we have

$$dQ=(M-m_1)c\,dt+m_1h\,dt, \quad . \quad . \quad . \quad . \quad (a)$$

and for a finite change, say from $t_1$ to $t_2$,

$$Q=(M-m_1)\int_{t_1}^{t_2}c\,dt+m_1\int_{t_1}^{t_2}h\,dt. \quad . \quad . \quad . \quad . \quad . \quad (b)$$

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* *Grundzüge der mechanischen Wärmetheorie*, von G. Zeuner. Freiberg, 1860.

The first term on the right, which has reference to the liquid water, is self-intelligible, since the specific heat of water is a magnitude given immediately by observation; we may consequently leave this term out of consideration. The quantity $h$ which appears in the second term has been determined by the equation

$$h=\frac{dr}{dt}+c-\frac{r}{a+t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(c)}$$

which is numbered (32) in my First Memoir (p. 65). In it we have merely, as is there done, to put, for $c$ and $r$, the values given by Regnault's experiments, in order to have $h$ expressed as a function of the temperature. It will be readily seen that we have here to do with the case which I have already treated as the *first* case in the Second Memoir (p. 91 *et seq.*), and where, by way of example, I actually calculated the integral for two expansions; that is to say, for expansions whereby the pressure diminishes from five and from ten atmospheres, respectively, down to one atmosphere, and consequently the temperature falls from 152°·2 and from 180°·3, respectively, down to 100°.

Zeuner, on the other hand, by introducing various simplifications in order to facilitate his calculations, arrives at the following equation, numbered (122) in his work:—

$$Q=(2{\cdot}0433m_1-1{\cdot}0224M)(t_1-t_2). \quad . \quad . \quad . \quad . \quad \text{(d)}$$

He remarks that this equation only holds, immediately, for those temperatures which are more fully defined in § 30 of his work. Now in this paragraph he states that a certain approximate formula there given holds perfectly between the temperatures 100° and 150°, and that beyond these limits even, from about 60° to 180°, the deviations are small. After referring to this paragraph he adds, "I believe that our present experimental knowledge of the deportment of vapour is so uncertain and fluctuating, particularly beyond the limits of temperature stated in § 30, that, provisionally, the above expression, deduced by methods of approximation, may without hesitation be generally applied."

I propose, by a numerical example, to compare Zeuner's approximate formula with my expression. To do so we will take the case where precisely the whole mass in the cylinder is vaporous. In this case we have $m_1 = \mathrm{M}$, and Zeuner's equation (d) becomes

$$\mathrm{Q} = 1{\cdot}0209\,\mathrm{M}(t_1 - t_2), \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(e)}$$

whilst the preceding equation (b) becomes

$$\mathrm{Q} = \mathrm{M}\int_{t_1}^{t_2} h\,dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(f)}$$

Suppose now the initial temperature to be 180°, and that the vapour expands so that its temperature falls successively to 170°, 160°, 150°, and so on to 60°. During this expansion heat must be imparted to the vapour in order to prevent its partial precipitation; let us calculate how much must be imparted during the successive falls of ten degrees on the assumption that M = 1.

For each of these intervals Zeuner's equation gives the value

10·209;

my equation, on the other hand, gives the following series of values :—

7·73; 8·14; 8·57; 9·01; 9·49; 9·98;
10·50; 11·04; 11·62; 12·22; 12·87; 13·55.

From this it will be seen that in the interval from 180° to 60°, within which according to Zeuner the deviations should be small, the true values, instead of being constant and equal to 10·209, vary between 7·73 and 13·55. Even in the small interval between 150° and 100°, within which Zeuner considers his formula to be perfectly true, the true values vary between 9·01 and 11·04.

Although I quite admit that to render the mechanical theory of heat useful to practical mechanicians it is necessary to simplify its use by the calculation of tables, and the establishment of the simplest possible approximate formulæ, and consequently that Zeuner's efforts to that end must be very welcome to them, still I cannot think that they will be satisfied with formulæ which correspond so little with the actual state of things as does that here adduced.

The questions discussed in Zeuner's *Problem* II. are those to which the equations (VII) and (IX) of the preceding memoir refer. The same expansion as in Problem I. is assumed to take place, but with this difference, that no heat is thereby imparted to, or abstracted from the mass in the cylinder, and under these circumstances it is required to determine in what manner the quantity of vapour present is changed through expansion, and what work is performed.

After giving my equations (VII) and (IX) (the latter in a somewhat modified form), Zeuner again proceeds to simplifications, and arrives at two approximate formulæ, one for the quantity of vapour $\mu$ which is newly developed or, if negative, precipitated during the expansion, and the other for the heat L consumed by exterior work. If in the first of these formulæ we substitute for a quantity $\rho$ which therein occurs, Zeuner's own expression for that quantity, in exactly the same manner as he himself has done in the second formula, the two become

$$\mu=(M-2m_1)\beta\frac{t_1-t_2}{\alpha-\beta t_2}, \quad \ldots \ldots \quad (g)$$

$$L=[Mc-(M-m_1)\beta](t_1-t_2), \quad \ldots \ldots \quad (h)$$

wherein $\alpha$, $\beta$, $c$ are three constants having the respective values

$$\left.\begin{aligned}\alpha&=575{\cdot}03,\\ \beta&=0{\cdot}7882,\\ c&=1{\cdot}0224.\end{aligned}\right\} \quad \ldots \ldots \quad (i)$$

In order to compare the results of these formulæ with those which follow from my own equations, we will suppose that at the commencement of the expansion precisely the whole mass in the cylinder is vaporous, so that $m_1=M$; and we will further introduce into the equation (h), in place of the heat L consumed by work, the work W itself in accordance with the relation $W=\frac{L}{A}$. The two equations then are

$$\mu=-M\beta\frac{t_1-t_2}{\alpha-\beta t_2} \quad \ldots \ldots \quad (k)$$

$$W=\frac{Mc}{A}(t_1-t_2). \quad \ldots \ldots \quad (l)$$

Assuming 150° to be the initial, and 125°, 100°, 75°, successively, the final temperatures, we may, for the purpose of comparison, employ the numerical values already calculated from my equations, and collected in the small tables on pp. 154 & 157. If $m$ denote the quantity of vapour present at the end of the expansion, we have, in fact, to put $\mu = m - \mathrm{M}$, and hence $\frac{\mu}{\mathrm{M}} = \frac{m}{\mathrm{M}} - 1$; and in this equation we may substitute the values of $\frac{m}{\mathrm{M}}$ given in the first Table. The Tables in question extend beyond the interval now under consideration, in fact reach down to 25°, but in this comparison we will only employ the numbers down to a temperature of 75°, in order not to overstep the limits for which Zeuner has determined his formulæ. By so doing the following corresponding numbers are obtained:—

| Final temperature. | | 125°. | 100°. | 75°. |
|---|---|---|---|---|
| $\frac{\mu}{\mathrm{M}}$ | according to equation (VII) | −0·044 | −0·089 | −0·134 |
| | according to equation (k) | −0·041 | −0·079 | −0·115 |
| $\frac{\mathrm{W}}{\mathrm{M}}$ | according to equation (IX) | 11300 | 23200 | 35900 |
| | according to equation (l) | 10800 | 21700 | 32500 |

Here, therefore, within the small interval from 150° to 75°, not inconsiderable deviations already manifest themselves. Zeuner expresses the opinion that it is on the equations, representing work, which he has established, that a new theory of the steam-engine may be based; and that their simplicity and convenient form, as well as the circumstance that the results which they furnish agree quite satisfactorily with those which follow from my own equations, certainly recommend them as suitable for this object. I must confess, however, that in the preceding numbers I find no agreement sufficiently satisfactory to convince me that the equations in question would form a suitable foundation for the new theory of the steam-engine.

In his *Problem* III. Zeuner considers the case where a quantity of vapour and water contained in a vessel is suddenly exposed to a pressure different from that which exists in that vessel; this occurs, for instance, when a vessel in which the pressure exceeds one atmosphere is suddenly put in communication with the atmosphere so that the vapour can issue therefrom. The question now is how much heat must be imparted to the mass during its change of volume, and the associated change of temperature, in order that neither precipitation of vapour nor evaporation of water may take place, but that exactly the original quantity of vapour may preserve its state of vapour at the maximum density.

This case allies itself to those which I have treated in the Second Memoir as second and third cases. I have there distinguished the two cases where the vessel contains vapour solely, and where (like the boiler of a steam-engine) it contains not only vapour, but likewise water, which during the efflux of the former further evaporates, and thus replaces the vapour lost. Zeuner thinks he is able to represent these two cases in a very simple manner, by one equation.

In fact, the equation (144) of his book contains an expression for the heat to be imparted to the mass which essentially agrees with the one developed by me for the second case, and given in equation (3) of my memoir (p. 95), although its form is somewhat different in consequence of the modified notation therein adopted. To this quantity of heat, however, is added that which must be imparted to the water in order to change its temperature from $t_1$ to $t_2$, and in this manner is formed the expression for the total quantity of heat, which must be imparted to the mass consisting of vapour and water. By the addition of this term, having reference to the water, Zeuner imagines he has rendered the equation, developed by me for the second case, also applicable to the third case. I cannot, however, agree with him.

The equation formed by Zeuner implies that the water contained in the vessel changes its temperature in the same manner as the vapour. If we consider a boiler, however, from which steam issues through an aperture, for instance, through the safety valve, the issuing vapour will suffer on expanding a very quick and considerable diminution of temperature, in which diminution the mass in the boiler takes no part. The issuing vapour, therefore, must be considered separately on deciding whether, when no heat is communicated to it or withdrawn from it, it is overheated or partially precipitated, and on determining how much heat must be imparted to, or withdrawn from it in order to maintain it exactly at its maximum density. For this purpose I hold that the procedure adopted by me is quite appropriate; namely that of considering the issuing vapour between two surfaces, in the first of which exists the pressure prevailing in the interior of the vessel, whilst in the second the pressure is equal to that of the atmosphere, and the velocity of efflux has already so far diminished that the *vis viva* corresponding to the motion of the stream of vapour may be neglected.

# SIXTH MEMOIR.

## ON THE APPLICATION OF THE THEOREM OF THE EQUIVALENCE OF TRANSFORMATIONS TO INTERIOR WORK*.

In a memoir published in the year 1854†, wherein I sought to simplify to some extent the form of the developments I had previously published, I deduced, from my fundamental proposition *that heat cannot, by itself, pass from a colder into a warmer body,* a theorem which is closely allied to, but does not entirely coincide with, the one first deduced by S. Carnot from considerations of a different kind, based upon the older views of the nature of heat. It has reference to the circumstances under which work can be transformed into heat, and conversely, heat converted into work; and I have called it the *Theorem of the Equivalence of Transformations.* I did not, however, there communicate the entire theorem in the general form in which I had deduced it, but confined myself on that occasion to the publication of a part which can be treated separately from the rest, and is capable of more strict proof.

In general, when a body changes its state, work is performed *externally* and *internally* at the same time,—the exterior work having reference to the forces which extraneous bodies exert upon the body under consideration, and the interior work to the forces exerted by the constituent molecules of the body in question upon each other. The interior work is for the most part so little known, and connected with another equally unknown quantity‡ in such a way, that in treating of it we are obliged in

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* Communicated to the *Naturforschende Gesellschaft* of Zurich, Jan. 27th, 1862; published in the Vierteljahrschrift of this Society, vol. vii. p. 48; in Poggendorff's *Annalen,* May 1862, vol. cxvi. p. 73; in the Philosophical Magazine, S. 4. vol. xxiv. pp. 81, 201; and in the *Journal des Mathématiques* of Paris, S. 2. vol. vii. p. 209.

† "On a modified form of the second Fundamental Theorem in the Mechanical Theory of heat." [Fourth Memoir of this collection, p. 116.]

‡ [In fact with the increase of the heat actually present in the body.—1864.]

some measure to trust to probabilities; whereas the exterior work is immediately accessible to observation and measurement, and thus admits of more strict treatment. Accordingly, since, in my former paper, I wished to avoid everything that was hypothetical, I entirely excluded the interior work, which I was able to do by confining myself to the consideration of *cyclical processes*—that is to say, operations in which the modifications which the body undergoes are so arranged that the body finally returns to its original condition. In such operations the interior work which is performed during the several modifications, partly in a positive sense and partly in a negative sense, neutralizes itself, so that nothing but exterior work remains, for which the theorem in question can then be demonstrated with mathematical strictness, starting from the above-mentioned fundamental proposition.

I have delayed till now the publication of the remainder of my theorem, because it leads to a consequence which is considerably at variance with the ideas hitherto generally entertained of the heat contained in bodies, and I therefore thought it desirable to make still further trial of it. But as I have become more and more convinced in the course of years that we must not attach too great weight to such ideas, which in part are founded more upon usage than upon a scientific basis, I feel that I ought to hesitate no longer, but to submit to the scientific public the theorem of the equivalence of transformations in its complete form, with the theorems which attach themselves to it. I venture to hope that the importance which these theorems, supposing them to be true, possess in connexion with the theory of heat will be thought to justify their publication in their present hypothetical form.

I will, however, at once distinctly observe that, whatever hesitation may be felt in admitting the truth of the following theorems, the conclusions arrived at in my former paper, in reference to cyclical processes, are not at all impaired.

1. I will begin by briefly stating the theorem of the equivalence of transformations, as I have already developed it, in order to be able to connect with it the following considerations.

When a body goes through a cyclical process, a certain amount of exterior work may be produced, in which case a certain quantity of heat must be simultaneously expended; or, conversely, work may be expended and a corresponding quantity of heat may be gained. This may be expressed by saying:—*Heat can be transformed into work, or work into heat, by a cyclical process.*

There may also be another effect of a cyclical process: heat may be transferred from one body to another, by the body which is undergoing modification absorbing heat from the one body and giving it out again to the other. In this case the bodies between which the transfer of heat takes place are to be viewed merely as heat reservoirs, of which we are not concerned to know anything except the temperatures. If the temperatures of the two bodies differ, heat passes, either from a warmer to a colder body, or from a colder to a warmer body, according to the direction in which the transference of heat takes place. Such a transfer of heat may also be designated, for the sake of uniformity, a *transformation,* inasmuch as it may be said that *heat of one temperature is transformed into heat of another temperature.*

The two kinds of transformations that have been mentioned are related in such a way that one presupposes the other, and that they can mutually replace each other. If we call transformations which can replace each other *equivalent,* and seek the mathematical expressions which determine the amount of the transformations in such a manner that equivalent transformations become equal in magnitude, we arrive at the following expression:—*If the quantity of heat* Q *of the temperature* t *is produced from work, the equivalence-value of this transformation is*

$$\frac{Q}{T};$$

*and if the quantity of heat* Q *passes from a body whose temperature is* $t_1$ *into another whose temperature is* $t_2$, *the equivalence-value of this transformation is*

$$Q\left(\frac{1}{T_2}-\frac{1}{T_1}\right),$$

where T is a function of the temperature which is independent of the kind of process by means of which the transformation is effected, and $T_1$ and $T_2$ denote the values of this function which correspond to the temperatures $t_1$ and $t_2$. I have shown by separate considerations that T is in all probability nothing more than the *absolute temperature*.

These two expressions further enable us to recognize the positive or negative sense of the transformations. In the first, Q is taken as positive when work is transformed into heat, and as negative when heat is transformed into work. In the second, we may always take Q as positive, since the opposite senses of the transformations are indicated by the possibility of the difference $\frac{1}{T_2}-\frac{1}{T_1}$ being either positive or negative. It will thus be seen that the passage of heat from a higher to a lower temperature is to be looked upon as a positive transformation, and its passage from a lower to a higher temperature as a negative transformation.

If we represent the transformations which occur in a cyclical process by these expressions, the relation existing between them can be stated in a simple and definite manner. If the cyclical process is *reversible,* the transformations which occur therein must be partly positive and partly negative, and the equivalence-values of the positive transformations must be together equal to those of the negative transformations, so that the algebraic sum of all the equivalence-values becomes $=0$. If the cyclical process is *not reversible,* the equivalence-values of the positive and negative transformations are not necessarily equal, but they can only differ in such a way that the positive transformations predominate. The theorem respecting the equivalence-values of the transformations may accordingly be stated thus :—*The algebraic sum of all the transformations occurring in a cyclical process can only be positive, or, as an extreme case, equal to nothing.*

The mathematical expression for this theorem is as follows. Let $dQ$ be an element of the heat given up by the body to any reservoir of heat during its own changes (heat which it may absorb from a reservoir being here reckoned as negative), and T the absolute temperature of the body at the moment of giving up this heat, then the equation

$$\int\frac{dQ}{T}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(I)}$$

must be true for every reversible cyclical process, and the relation

$$\int\frac{dQ}{T}\geqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{I}\,a)$$

must hold good for every cyclical process which is in any way possible.

2. Although the necessity of this theorem admits of strict mathematical proof if we start from the fundamental proposition above quoted, it thereby nevertheless retains an abstract form, in which it is with difficulty embraced by the mind, and we feel compelled to seek for the precise physical cause, of which this theorem is a consequence. Moreover, since there is no essential difference between interior and exterior work, we may assume almost with certainty that a theorem which is so generally applicable to exterior work cannot be restricted to this alone, but that, where exterior work is combined with interior work, it must be capable of application to the latter also.

Considerations of this nature led me, in my first investigations on the mechanical theory of heat, to assume a general law respecting the dependence of the active force of heat on temperature, among the immediate consequences of which is the theorem of the equivalence of transformations in its more complete form, and which at the same time leads to other important conclusions. This law I will at once quote, and will endeavour to make its meaning clear by the addition of a few comments. As for the reasons for supposing it to be true, such as do not at once appear from its internal probability will gradually become apparent in the course of this paper. It is as follows:—

*In all cases in which the heat contained in a body does mechanical work by overcoming resistances, the magnitude of the resistances which it is capable of overcoming is proportional to the absolute temperature.*

In order to understand the significance of this law, we require to consider more closely the processes by which heat can perform mechanical work. These processes always admit of being reduced to the alteration in some way or another of the arrangement of the constituent parts of a body. For instance, bodies are expanded by heat, their molecules being thus separated from each other: in this case the mutual attractions of the molecules on the one hand, and external opposing forces on the other, in so far as any such are in operation, have to be overcome. Again, the state of aggregation of bodies is altered by heat, solid bodies being rendered liquid, and both solid and liquid bodies being rendered aëriform: here likewise internal forces, and in general external forces also, have to be overcome. Another case which I will also mention, because it differs so widely from the foregoing, and therefore shows how various are the modes of action which have here to be considered, is the transfer of electricity from one body to the other, constituting the thermo-electric current, which takes place by the action of heat on two heterogeneous bodies in contact.

In the cases first mentioned, the arrangement of the molecules is altered. Since, even while a body remains in the same state of aggregation, its molecules do not retain fixed unvarying positions, but are constantly in a state of more or less extended motion, we may, when speaking of the *arrangement of the molecules* at any particular time, understand either the arrangement which would result from the molecules being fixed in the actual positions they occupy at the instant in question, or we may suppose such an arrangement that each molecule occupies its mean position. Now the effect of heat always tends to loosen the connexion between the molecules, and so to increase their mean distances from one another. In order to be able to represent this mathematically, we will express the degree in which the molecules of a body are separated from each other, by introducing a new magnitude, which we will call the *disgregation* of the body, and by help of which we can define the effect of heat as simply *tending to increase the disgregation.* The way in which a definite measure of this magnitude can be arrived at will appear from the sequel.

In the case last mentioned, an alteration in the arrangement of the electricity takes place, an alteration which can be represented and taken into calculation in a way corresponding to the alteration of the position of the molecules, and which, when it occurs, we will consider as always included in the general expression *change of arrangement,* or *change of disgregation.*

It is evident that each of the changes that have been named may also take place in the reverse sense, if the effect of the opposing forces is greater than that of the heat. We will assume as likewise self-evident that, for the production of work, a corresponding quantity of heat must always be expended, and conversely, that, by the expenditure of work, an equivalent quantity of heat must be produced.

3. If we now consider more closely the various cases which occur in relation to the forces which are operative in each of them, the case of the expansion of a permanent gas presents itself as particularly simple. We may conclude from certain properties of the gases that the mutual attraction of their molecules at their mean distances is very small, and therefore that only a very slight resistance is offered to the expansion of a gas, so that the resistance of the sides of the containing vessel must maintain equilibrium with almost the whole effect of the heat. Accordingly the externally sensible pressure of a gas forms an approximate measure of the separative force of the heat contained in the gas; and hence, according to the foregoing law, this pressure must be nearly proportional to the absolute temperature. The internal probability of the truth of this result is indeed so great, that many physicists since Gay-Lussac and Dalton have without hesitation presupposed this proportionality, and have employed it for calculating the absolute temperature.

In the above-mentioned case of thermo-electric action, the force which exerts an action contrary to that of the heat is likewise simple and easily determined. For at the point of contact of two heterogeneous substances, such a quantity of electricity is driven from the one to the other by the action of the heat, that the opposing force resulting from the electric tension suffices to hold the force exerted by the heat in equilibrium. Now in a former memoir "On the application of the Mechanical Theory of Heat to the Phenomena of Thermal Electricity"*, I have shown that, in so far as changes in the arrangement of the molecules are not produced at the same time by the changes of temperature, the difference of tension produced by heat must be proportional to the absolute temperature, as is required by the foregoing law.

In the other cases that are quoted, as well as in most others, the relations are less simple, because in them an essential part is played by the forces exerted by the molecules upon one another, forces which, as yet, are quite unknown. It results, however,

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* Poggendorff's *Annalen*, vol. xc. p. 513.

from the mere consideration of the external resistances which heat is capable of overcoming, that in general its force increases with the temperature. If we wish, for instance, to prevent the expansion of a body by means of external pressure, we are obliged to employ a greater pressure the more the body is heated; hence we may conclude, without having a knowledge of the interior forces, that the total amount of the resistances which can be overcome in expansion, increases with the temperature. We cannot, however, directly ascertain whether it increases exactly in the proportion required by the foregoing law, without knowing the interior forces. On the other hand, if this law be regarded as proved on other grounds, we may reverse the process, and employ it for the determination of the interior forces exerted by the molecules.

The forces exerted upon one another by the molecules are not of so simple a kind that each molecule can be replaced by a mere point; for many cases occur in which it can be easily seen that we have not merely to consider the distances of the molecules, but also their relative positions. If we take, for example, the melting of ice, there is no doubt that interior forces, exerted by the molecules upon each other, are overcome, and accordingly increase of disgregation takes place; nevertheless the centres of gravity of the molecules are on the average not so far removed from each other in the liquid water as they were in the ice, for the water is the more dense of the two. Again, the peculiar behaviour of water in contracting when heated above 0° C., and only beginning to expand when its temperature exceeds 4°, shows that likewise in liquid water, in the neighbourhood of its melting-point, increase of disgregation is not accompanied by increase of the mean distances of its molecules.

In the case of the interior forces, it would accordingly be difficult—even if we did not want to measure them, but only to represent them mathematically—to find a fitting expression for them which would admit of a simple determination of magnitude. This difficulty, however, disappears if we take into calculation, not the forces themselves, but the *mechanical work* which, in any change of arrangement, is required to overcome them. The expressions for the quantities of work are simpler than those for the corresponding forces; for the quantities of work can be all expressed, without further secondary statements, by numbers which, having reference to the same unit, can be added together, or subtracted from one another, however various the forces may be to which they refer.

It is therefore convenient to alter the form of the above law by introducing, instead of the forces themselves, the work done in overcoming them. In this form it reads as follows :—

*The mechanical work which can be done by heat during any change of the arrangement of a body is proportional to the absolute temperature at which this change occurs.*

4. The law does not speak of the work which the heat *does*, but of the work which it *can do*; and similarly, in the first form of the law, it is not of the resistances which the heat overcomes, but of those which it *can overcome* that mention is made. This distinction is necessary for the following reasons :—

Since the exterior forces which act upon a body while it is undergoing a change of arrangement may vary very greatly, it may happen that the heat, while causing a change of arrangement, has not to overcome the whole resistance which it would be possible for it to overcome. A well-known and often-quoted example of this is afforded by a gas which expands under such conditions that it has not to overcome an opposing pressure equal to its own expansive force, as, for instance, when the space filled by the gas is made to communicate with another which is empty, or contains a gas of lower pressure. In order in such cases to determine the force of the heat, we must evidently not consider the resistance which actually is overcome, but that which can be overcome.

Also in changes of arrangement of the opposite kind, that is, where the action of heat is overcome by the opposing forces, a similar distinction may require to be made, but in this case only as far as this—that the total amount of the forces by which the action of the heat is overcome may be greater than the active force of the heat, but not smaller.

Cases in which these differences occur may be thus characterized. When a change of arrangement takes place so that the force and counterforce are equal, the change can likewise take place in the reverse direction under the influence of the same forces. But if it occurs so that the overcoming force is greater than that which is overcome, the change cannot take place in the opposite direction under the influence of the same forces. We may say that the change has occurred in the first case in a *reversible* manner, and in the second case in an *irreversible* manner.

Strictly speaking, the overcoming force must always be more powerful than the force which it overcomes; but as the excess of force does not require to have any assignable value, we may think of it as becoming continually smaller and smaller, so that its value may approach to nought as nearly as we please. Hence it may be seen that the case in which the changes take place reversibly is a limit which in reality is never quite reached, but to which we can approach as nearly as we please. We may therefore, in theoretical discussions, still speak of this case as one which really exists; indeed, as a limiting case it possesses special theoretical importance.

I will take this opportunity of mentioning another process in which this distinction is likewise to be observed. In order for one body to impart heat to another by conduction or radiation (in the case of radiation, wherein mutual communication of heat takes place, it is to be understood that we speak here of a body which gives out more heat than it receives), the body which parts with heat must be warmer than the body which takes up heat; and hence the passage of heat between two bodies of different temperature can take place in one direction only, and not in the contrary direction. The only case in which the passage of heat can occur equally in both directions is when it takes place between bodies of equal temperature. Strictly speaking, however, the communication of heat from one body to another of the same temperature is not possible; but since the difference of temperature may be as small as we please, the case in which it is equal to nothing, and the passage of heat accordingly reversible, is a limiting case which may be regarded as theoretically possible.

5. We will now deduce the mathematical expression for the above law, treating in the first place the case in which the change of condition undergone by the body under consideration takes place *reversibly*. The result at which we shall arrive for this case will easily admit of subsequent generalization, so as to include also the cases in which a change occurs irreversibly.

Let the body be supposed to undergo an infinitely small change of condition, whereby the quantity of heat contained in it, and also the arrangement of its constituent particles, may be altered. Let the quantity of heat contained in it be expressed by H, and the change of this quantity by $dH$. Further, let the work, both interior and exterior together, performed by the heat in the change of arrangement be denoted by $dL$, a magnitude which may be either positive or negative according as the active force of the heat overcomes the forces acting in the contrary direction, or is overcome by them. We obtain the heat expended to produce this quantity of work by multiplying the work by the thermal-equivalent of a unit of work which we may call A; hence it is $AdL$.

The sum $dH+AdL$ is the quantity of heat which the body must receive from without, and must accordingly withdraw from another body during the change of condition. We have, however, already represented by $dQ$ the infinitely small quantity of heat imparted to another body by the one which is undergoing modification, hence we must represent in a corresponding manner, by $-dQ$, the heat which it withdraws from another body. We thus obtain the equation

$$-dQ=dH+AdL,$$

or

$$dQ+dH+AdL=0^*. \quad . \quad . \quad . \quad . \quad (1)$$

In order now to be able to introduce the disgregation also into the formulæ, we must first settle how we are to determine it as a mathematical quantity.

By disgregation is represented, as stated in Art. 2, the degree

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* In my previous memoirs I have separated from one another the *interior* and the *exterior* work performed by the heat during the change of condition of the body. If the former be denoted by $dI$, and the latter by $dW$, the above equation becomes

$$dQ+dH+AdI+AdW=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Since, however, the increase in the quantity of heat actually contained in a body, and the heat consumed by interior work during a change of condition, are magnitudes of which we commonly do not know the individual values, but only the sum of those values, and which resemble each other in being fully determined as soon as we know the initial and final conditions of the body, without our requiring to know how it has passed from the one to the other, I have thought it advisable to introduce a function which shall of dispersion of the body. Thus, for example, the disgregation of a body is greater in the liquid state than in the solid, and greater in the aëriform than in the liquid state. Further, if part of a given quantity of matter is solid and the rest liquid, the disgregation is greater the greater the proportion of the whole mass that is liquid; and similarly, if one part is liquid and the remainder aëriform, the disgregation is greater the larger the aëriform portion. The disgregation of a body is fully determined when the arrangement of its constituent particles is given; but, on the other hand, we cannot say conversely that the arrangement of the constituent particles is determined when the magnitude of the disgregation is known. It might, for example, happen that the disgregation of a given quantity of matter should be the same when one part was solid and one part aëriform, as when the whole mass was liquid.

We will now suppose that, with the aid of heat, the body changes its condition, and we will provisionally confine ourselves to such changes of condition as can occur in a continuous and

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represent the sum of these two magnitudes, and which I have denoted by U. Accordingly

$$dU = dH + AdI, \quad \ldots\ldots \quad (b)$$

and hence the foregoing equation becomes

$$dQ + dU + AdW = 0; \quad \ldots\ldots \quad (c)$$

and if we suppose the last equation integrated for any finite alteration of condition, we have

$$Q + U + AW = 0. \quad \ldots\ldots \quad (d)$$

These are the equations which I have used in my memoirs published in 1850 and in 1854, partly in the particular form which they assume for the permanent gases, and partly in the general form in which they are here given, with no other difference than that I there took the positive and negative quantities of heat in the opposite sense to what I have done here, in order to attain greater correspondence with the equation (I) given in Art. 1. The function U which I introduced is capable of manifold application in the theory of heat, and, since its introduction, has been the subject of very interesting mathematical developments by W. Thomson and by Kirchhoff (see Philosophical Magazine, S. 4. vol. ix. p. 523, and Poggendorff's *Annalen*, vol. ciii. p. 177). Thomson has called it "the mechanical energy of a body in a given state," and Kirchhoff "Wirkungsfunction." Although I consider my original definition of it as representing the *sum of the heat added to the quantity already present and of that expended in interior work*, starting from any given initial state (pp. 29 and 113), as perfectly exact, I can still have no objection to make against an abbreviated mode of expression. [See the Appendix A. On Terminology at the end of this memoir] reversible manner, and we will also assume that the body has a uniform temperature throughout. Since the increase of disgregation is the action by means of which heat performs work, it follows that the quantity of work must bear a definite ratio to the quantity by which the disgregation is increased; we will therefore fix the still arbitrary determination of the magnitude of disgregation so that, at any given temperature, the increase of disgregation shall be proportional to the work which the heat can thereby perform. The influence of the temperature is determined by the foregoing law. For if the same change of disgregation takes place at different temperatures, the corresponding work must be proportional to the absolute temperature. Accordingly, let Z be the disgregation of the body, and $dZ$ an infinitely small change of it, and let $dL$ be the corresponding infinitely small quantity of work, we can then put

$$dL = KTdZ,$$

or

$$dZ = \frac{dL}{KT},$$

where K is a constant dependent on the unit, hitherto left undetermined, according to which Z is to be measured. We will choose this unit of measure so that $K = \frac{1}{A}$, and the equation becomes

$$dZ = \frac{AdL}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we suppose this expression integrated, from any initial condition in which Z has the value $Z_0$, we get

$$Z = Z_0 + A\int\frac{dL}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The magnitude Z is thus determined, with the exception of a constant dependent upon the initial condition that is chosen.

If the temperature of the body is not everywhere the same, we can regard it as divided into any number we choose of separate parts, refer the elements $dZ$ and $dL$ in equation (2) to any one of them, and at once substitute for T the value of the absolute temperature of that part. If we then unite by summation the infinitely small changes of disgregation of the separate parts, or by integration, if there is an infinite number of them, we obtain the similarly infinitely small change of disgregation of the entire body, and from this we can obtain, likewise by integration, any desired finite change of disgregation.

We will now return to equation (1), and by help of equation (2) we will eliminate from it the element of work $dL$. Thus we get

$$dQ+dH+TdZ=0; \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or, dividing by T,

$$\frac{dQ+dH}{T}+dZ=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we suppose this equation integrated for a finite change of condition, we have

$$\int\frac{dQ+dH}{T}+\int dZ=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

Supposing the body not to be of uniform temperature throughout, we may imagine it broken up again into separate parts, make the elements $dQ$, $dH$, and $dZ$ in equation (5) refer, in the first instance, to one part only, and for T put the absolute temperature of this part. The symbols of integration in (II) are then to be understood as embracing the changes of all the parts. We must here remark that cases in which one continuous body is of different temperatures at different parts, so that a passage of heat immediately takes place by conduction from the warmer to the colder parts, must be for the present disregarded, because such a passage of heat is not reversible, and we have provisionally confined ourselves to the consideration of reversible changes.

Equation (II) is the required mathematical expression of the above law, *for all reversible changes of condition of a body*; and it is clearly evident that it also remains applicable, if a series of successive changes of condition be considered instead of a single one.

6. The differential equation (4), whence equation (II) is derived, is connected with a differential equation which results from the already known principles of the mechanical theory of heat, and which transforms itself directly into (4) for the particular case in which the body under consideration is a perfect gas.

We will suppose that there is given any body of variable volume, upon which the only active external force is the pressure exerted on the surface. Let the volume which it assumes under this pressure $p$, at the temperature T (reckoned from the absolute zero) be $v$, and let us suppose that the condition of the body is fully determined by the magnitudes T and $v$. If we now denote by $\frac{dQ}{dv}dv$ the quantity of heat which the body must take up in order to expand to the extent of $dv$, without change of temperature (for the sake of conformity with the mode in which the signs are used in the other equations occurring in this section, the positive sense of the quantity of heat is here taken differently from what it is in equation (4), in which heat given up by the body, and not heat communicated to it, is reckoned positive), the following well-known equation, from the mechanical theory of heat, will hold good:—

$$\frac{dQ}{dv}=AT\frac{dp}{dT}.$$

Let us now suppose that the temperature of the body is changed by $dT$, and its volume by $dv$, and let us call the quantity of heat which it then takes up $dQ$; we may then write

$$dQ=\frac{dQ}{dT}dT+\frac{dQ}{dv}dv.$$

For the magnitude here denoted by $\frac{dQ}{dT}$, which represents the specific heat under constant volume*, we can put the letter $c$, and for $\frac{dQ}{dv}$ the expression already given. Then we have

$$dQ=c\,dT+AT\frac{dp}{dT}dv. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The only external force which the body has to overcome on expanding, being $p$, the work which it performs in so doing is $pdv$, and the magnitude $\frac{dp}{dT}dv$ indicates the increase of this work with the temperature.

If we now apply this equation to a perfect gas, the specific heat under constant volume is in this case to be regarded as the real specific heat [capacity for heat] †, which gives the increase

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* [Provided the weight of the body under consideration be regarded as a unit of weight.—1864.]

† [I must here say a few words relative to the expressions *real specific heat* and *real capacity for heat.*

According to the mechanical theory of heat, it is not necessary that the in the quantity of heat actually present in the gas; for here no heat is consumed in work, since exterior work is only performed

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heat imparted to a body should afterwards be actually present in the form of heat in that body; a portion of the heat, in fact, may be consumed on interior or exterior work. Accordingly it is necessary to consider, not only the different specific heats of bodies, which indicate how much heat must be imparted to a body for the purpose of heating it under different circumstances (*e.g.* the specific heat of a solid or liquid body at the ordinary atmospheric pressure, the specific heat of a gas at constant volume or under constant pressure, and the specific heat of a vapour at its maximum density), but also another magnitude indicating by how much the heat actually present in a unit-weight of the substance in question—in other words, the *vis viva* of its molecular motions—is increased by an elevation of one degree in temperature.

Hitherto I have, in accordance with Rankine's custom, called this magnitude the *real specific heat*; I must confess, however, that to me the expression does not appear to be quite appropriate. It implies, in fact, that the other magnitudes above named—for instance the specific heat of a gas under constant pressure—have improperly received the name specific heat. But in the words *specific heat* there is nothing whatever on which to found the objection that the quantity of heat which must be imparted to a unit-weight of gas, under constant pressure, in order to raise its temperature one degree ought not to be termed the specific heat under constant pressure. It is otherwise, however, with the expression capacity for heat. These words clearly indicate that the heat in question is that which the body can contain. Accordingly the expression is a very appropriate one for denoting by how much the heat actually present in the body is increased by the elevation of temperature; whilst, strictly speaking, it is not applicable to the total quantity of heat which must be imparted to a body during its elevation of temperature, of which quantity a portion is transformed into work, and the remaining portion alone remains *as* heat in the body.

I should deem it advantageous, therefore, to distinguish the two expressions *specific heat* and *capacity for heat*, which have hitherto been employed synonymously in physical treatises; to give the name *specific heat* to the total quantity of heat which must be imparted to the body to elevate its temperature, so that there will be different kinds of specific heat according to the different conditions under which this elevation occurs, and to reserve the name *capacity for heat* for the heat actually present in a body. Since this distinction, however, has not yet been made, the term *real* may provisionally be added, and the expression *real capacity for heat* used to denote the magnitude which indicates by how much the heat actually present in a unit-weight of the substance is increased by an elevation of one degree in temperature.

In order to introduce this terminology, I have in the text employed the words *real capacity for heat* wherever the expression *real specific heat* appears in the original. This is of course a merely verbal alteration and has no effect on the meaning, since, hitherto, physicists have drawn no distinction whatever between *specific heat* and *capacity for heat*; to indicate the alteration, however, the latter of these expressions, whenever it is substituted for the former, is placed between square brackets.—1864.]

when increase of volume occurs, and interior work has no existence in the case of perfect gases. We may therefore regard $cd\mathrm{T}$ as identical with $d\mathrm{H}$. We have further, for the perfect gases, the equation

$$pv = \mathrm{RT},$$

where R is a constant, and hence we get

$$\frac{dp}{d\mathrm{T}}dv = \frac{\mathrm{R}}{v}dv = \mathrm{R}d \, . \log v.$$

Equation (6) is thus transformed into

$$d\mathrm{Q} = d\mathrm{H} + \mathrm{ART}d \, . \log v^{*}. \quad . \quad . \quad . \quad . \quad (7)$$

This equation agrees, disregarding the difference in the sign of $d$Q (which is caused only by the different way in which we have chosen to employ the signs + and − in this case), with equation (4), and the function there represented by the general symbol Z has, in this particular case, the form $\mathrm{AR} \log v$.

Rankine, who has written several interesting memoirs on the transformation of heat into work†, has proposed a transformation of equation (6), for all other bodies, similar to that above given for perfect gases only‡. To this end he writes, only with slightly different letters,

$$d\mathrm{Q} = kd\mathrm{T} + \mathrm{AT}d\mathrm{F}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $k$ denotes the real [capacity for heat] of the body, and F is a magnitude to the determination of which Rankine appears to have been led chiefly by the circumstance mentioned above, that the quantity $\frac{dp}{d\mathrm{T}}dv$ which occurs in equation (6) represents the increase of exterior work done during the infinitely small change of volume which accompanies an increase of temperature. Rankine defines the magnitude F as "the rate of variation of

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* [If we retain for $d$H the product $cd$T, and for $d \log v$ the expression $\frac{dv}{v}$, the equation (7) will have the form

$$d\mathrm{Q} = cd\mathrm{T} + \mathrm{AR}\frac{\mathrm{T}}{v}dv,$$

and become the same as the equation (II $b$) which presented itself in the First Memoir, at p. 38.—1864.]

† Philosophical Magazine, S. 4, vol. v. p. 106; Edinburgh New Philosophical Journal, New Series, vol. ii. p. 120; Manual of the Steam-engine.

‡ Manual of the Steam-engine, p. 310.

performed effective work with temperature;" and denoting the exterior work which the body can do in passing, at a given temperature, from a given former condition into its present one, by U, he puts

$$F=\frac{dU}{dT}. \qquad (9)$$

In the discussion which immediately follows, of the case in which the exterior work consists only in overcoming an external pressure, he gives the equation

$$U=\int pdv,$$

whence follows

$$F=\int\frac{dp}{dT}dv. \qquad (10)$$

The integals which here occur are to be taken from a given initial volume to the actually existing volume, the temperature being supposed constant. Introducing this value of F into equation (8), he writes it in the following form:—

$$dQ=\left(k+AT\int_{\infty}^{v}\frac{d^2p}{dT^2}dv\right)dT+AT\frac{dp}{dT}dv. \qquad (11)$$

His reason for taking an infinitely large volume as the initial volume is not stated, although the choice of the initial volume is evidently not a matter of indifference.

It is easy to see that this manner of modifying equation (6) is very different from my development; the results are also discordant; for the quantity F is not identical with the corresponding quantity $\frac{1}{A}Z$ in my equations, but only coincides with it in that part which could be deduced from data already known; that is to say, the last term of equation (6) gives the differential coefficient, according to $v$, of the magnitude which has to be introduced, since, to secure the coincidence of this term and the last in the modified equation, we must in any case put

$$\frac{dF}{dv}=\frac{1}{A}\frac{dZ}{dv}=\frac{dp}{dT}[*]. \qquad (12)$$

Rankine has, however, as may be seen from equation (10),

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[*] [Conceive a function of T and $v$ to be introduced; it may be denoted at

formed the magnitude F by simply integrating, according to $v$, this expression for the differential coefficient of F according to $v$. In order to see in what way the magnitude $\frac{1}{A}$ Z differs from this, we will modify somewhat the expression for Z given in the preceding Art.

According to equation (2),

$$\frac{T}{A}dZ=dL.$$

$d$L denotes here the interior and exterior work, taken together, which is performed when the body undergoes an infinitely slight change of condition. We will denote the interior work by $d$I; and since when the condition of the body is determined by its temperature T and its volume $v$, I must be a function of these two quantities, we may write

$$dI=\frac{dI}{dT}dT+\frac{dI}{dv}dv.$$

The exterior work, assuming it to consist merely in overcoming an external pressure, is represented by $pdv$. Hence, if we further decompose the differential $dZ$ into its two parts, we may write the above equation thus :—

$$\frac{T}{A}\frac{dZ}{dT}dT+\frac{T}{A}\frac{dZ}{dv}dv=\frac{dI}{dT}dT+\left(\frac{dI}{dv}+p\right)dv,$$

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pleasure by either F or by $\frac{1}{A}$Z, but in either case let it have the property of satisfying the equation

$$dQ=kdT+ATdF,$$

or

$$dQ=kdT+TdZ.$$

These equations may then be written in the form

$$dQ=\left(k+AT\frac{dF}{dT}\right)dT+AT\frac{dF}{dv}dv,$$

or

$$dQ=\left(k+T\frac{dZ}{dT}\right)dT+T\frac{dZ}{dv}dv;$$

and on supposing them to exist simultaneously with (6), and remembering that the factors of $dv$ must be the same in all three equations, we at once conclude that the magnitudes F and $\frac{1}{A}$Z must satisfy the condition expressed in (12).—1864.]

whence we have

$$\left.\begin{aligned}\frac{\mathrm{T}}{\mathrm{A}}\frac{d\mathrm{Z}}{d\mathrm{T}}&=\frac{d\mathrm{I}}{d\mathrm{T}},\\ \frac{\mathrm{T}}{\mathrm{A}}\frac{d\mathrm{Z}}{dv}&=\frac{d\mathrm{I}}{dv}+p.\end{aligned}\right\}\quad\ldots\ldots\quad(13)$$

Differentiating the first of these equations according to $v$, and the second according to T, we get

$$\frac{\mathrm{T}}{\mathrm{A}}\frac{d^2\mathrm{Z}}{d\mathrm{T}dv}=\frac{d^2\mathrm{I}}{d\mathrm{T}dv},$$

$$\frac{1}{\mathrm{A}}\frac{d\mathrm{Z}}{dv}+\frac{\mathrm{T}}{\mathrm{A}}\frac{d^2\mathrm{Z}}{d\mathrm{T}dv}=\frac{d^2\mathrm{I}}{d\mathrm{T}dv}+\frac{dp}{d\mathrm{T}}.$$

The first of these equations subtracted from the second, gives

$$\frac{1}{\mathrm{A}}\frac{d\mathrm{Z}}{dv}=\frac{dp}{d\mathrm{T}}.$$

The differential coefficient of Z according to $v$ consequently fulfils the condition given in (12); the first of the equations (13) gives at the same time the differential coefficient according to T; and putting these two together, we obtain the complete differential equation

$$\frac{1}{\mathrm{A}}d\mathrm{Z}=\frac{1}{\mathrm{T}}\frac{d\mathrm{I}}{d\mathrm{T}}d\mathrm{T}+\frac{dp}{d\mathrm{T}}dv.\quad\ldots\ldots\quad(14)$$

To obtain the quantity $\frac{1}{\mathrm{A}}\mathrm{Z}$, we must integrate this equation. It is easy to see that this integral will in general differ by a function of T from that which would be obtained by integrating only the last term*. It is only when $\frac{d\mathrm{I}}{d\mathrm{T}}=0$ that the two integrals may at once be regarded as equal, and then, in order that the foregoing equation may be integrable, it follows that $\frac{d^2p}{d\mathrm{T}^2}=0$; this case occurs in perfect gases.

I believe that what I can claim as new in my equation (II)

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* [In order to integrate the equation (14), we will assume an initial condition in which the temperature and volume have the values $\mathrm{T}_0$ and $v_0$, and denote by $\mathrm{Z}_0$ the corresponding value of Z. Let us suppose then that the temperature first changes from $\mathrm{T}_0$ to any given value T, and that, subsequently, the volume changes, without further alteration of temperature, from

is just this, that the magnitude Z which there occurs has acquired, through my developments, a definite physical meaning, whence it follows that it is fully determined by the arrangement of the constituent particles of the body which exist at any given instant. Thus only does it become possible to deduce from this equation the important conclusion which follows.

7. We will now investigate the manner in which, from equation (II), it is possible to arrive at the equation (I) previously given in Art. 1, which equation must hold, according to the fundamental theorem that I have already enunciated, for every *reversible cyclical process.*

When the successive changes of condition constitute a *cyclical process,* the disgregation of the body is the same at the end of the operation as it was at the beginning, and hence the following equation must hold good :—

$$\int dZ=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Equation (II) is hereby transformed into

$$\int\frac{dQ+dH}{T}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In order that this equation may accord with equation (I), namely,

$$\int\frac{dQ}{T}=0,$$

the following equation must hold for every reversible cyclical process :—

$$\int\frac{dH}{T}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

It is this equation which leads to the consequence referred to

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$v_0$ to $v$. By pursuing this course of changes we obtain by integration the following equation

$$Z=Z_0+A\int_{T_0}^{T}\left(\frac{1}{T}\cdot\frac{dJ}{dT}\right)_{v=v_0}dT+A\int_{v_0}^{v}\frac{dp}{dT}dv.$$

It is manifest that the integral

$$\int_{T_0}^{T}\left(\frac{1}{T}\cdot\frac{dJ}{dT}\right)_{v=v_0}dT$$

which here presents itself is the function of T, mentioned in the text, as that by which the magnitude $\frac{1}{A}Z$ differs from the magnitude F, as defined by the equation (10).—1866.]

in the introductory Art.* as at variance with commonly received views. It can, in fact, be proved that, in order that this equation may be true, it is at once *necessary* and *sufficient* to assume the following theorem:—

*The quantity of heat actually present in a body depends only on its temperature, and not on the arrangement of its constituent particles.*

It is at once evident that the assumption of this theorem *suffices* for equation (III); for if H is a function of the temperature only, the differential expression $\frac{dH}{T}$ takes the form $f(T)\,dT$, in which $f(T)$ is obviously a real function which can have but one value for each value of T, and the integral of this expression must obviously vanish if the initial and final values of T are the same.

The *necessity* of this theorem may be demonstrated thus.

In order to be able to refer the changes of condition to changes of certain magnitudes, we will assume that the manner in which the body changes its condition is not altogether arbitrary, but is such that the condition of the body is determined by its temperature, and by any second magnitude which is independent of the temperature. This second magnitude must plainly be connected with the arrangement of the constituent particles: we may, for example, consider the disgregation of the body as such a magnitude; it may, however, be any other magnitude dependent on the arrangement of the constituent particles. A case which often occurs, and one which has been frequently discussed, is that in which the *volume* of the body is the second magnitude, which can be altered independently of the temperature, and which, together with the temperature, determines the condition of the body. We will take X as a general expression for the second magnitude, so that the two magnitudes T and X together determine the condition of the body.

Since, however, the quantity of heat H, present in the body, is a magnitude which in any case is completely determined by the condition of the body at any instant, it must here, where the condition of the body is determined by the magnitudes T

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* [See p. 216.]

and X, be a function of these two magnitudes. Accordingly, we may write the differential $d$H in the following form,

$$dH = M\,dT + N\,dX, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

where M and N are functions of T and X, which must satisfy the well-known equation of condition to which the differential coefficients of a function of two independent variables are subject; that is, the equation

$$\frac{dM}{dX} = \frac{dN}{dT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

Again, if the integral $\int \frac{dH}{T}$ is to become equal to nothing each time that the magnitudes T and X return to the same values as they had at the beginning, $\frac{dH}{T}$ must also be the complete differential of a function of T and X. And since we may write, as a consequence of (17),

$$\frac{dH}{T} = \frac{M}{T}dT + \frac{N}{T}dX, \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

we obtain, for the differential coefficients which here occur, the equation of condition

$$\frac{d}{dX}\left(\frac{M}{T}\right) = \frac{d}{dT}\left(\frac{N}{T}\right), \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

which exactly corresponds to equation (18).

By effecting the differentiations, this equation becomes

$$\frac{1}{T}\frac{dM}{dX} = \frac{1}{T}\frac{dN}{dT} - \frac{N}{T^2}; \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

and, by applying equation (18) to this, we get

$$N = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

According to (17), N is the differential coefficient of H according to X; and if this differential coefficient is to be generally equal to nothing, H itself must be independent of X; and since we may understand by X any magnitude whatever which is independent of T, and together with T determines the condition of the body, it follows that H can only be a function of T.

8. This last conclusion appears, according to commonly received opinions, to be opposed to well-known facts.

I will choose as an illustrative example, in the first place, a case which is very familiar, and in which the discrepancy is particularly great, namely, water in its various states. We may have water in the liquid state, and in the solid state in the form of ice, at the same temperature; and the above theorem asserts that the quantity of heat contained in it is in both cases the same. This appears to be contradicted by experience. The specific heat of ice is only about half as great as that of liquid water, and this appears to furnish grounds for the following conclusion. If at any given temperature a unit-weight of ice and a unit-weight of water in reality contained the same quantity of heat, we must, in order to heat or cool them both, impart to or withdraw from the water more heat than we impart to or withdraw from the ice, so that the equality in the quantity of heat could not be maintained at any other temperatures. A similar difference to that existing between water and ice also exists between water and steam, inasmuch as the specific heat of steam is much smaller than that of water.

To explain this difference, I must recall the fact that only part of the heat which a body takes up when heated goes to increase the quantity of heat actually present in it, the remainder being consumed as work. Now, I believe that the differences in the specific heat of water in its three states of aggregation are caused by great differences in the proportion which is consumed as work, and that this proportion is considerably greater in the liquid state than in the other two states*. We must, accordingly, here distinguish between the observed specific heat and

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* I have already enunciated this view in my first memoir on the Mechanical Theory of Heat, having, in fact, inserted the following in a note [p. 20], which has reference to the diminution of the cohesion of water with increase of temperature:—"Hence it follows, at once, that only part of the quantity of heat which water receives from without when heated, is to be regarded as heat in the free state, the rest being consumed in diminishing cohesion. This view is in accordance with the circumstance that water has so much higher a specific heat than ice, and probably also than steam." At that time the experiments of Regnault on the specific heat of gases were not yet published, and we still found in the text-books the number 0·847, obtained by De la Roche and Bérard, for the specific heat of steam. I had, however, already concluded, on the theoretical grounds which are the subject of the present discussion, that this number must be much too high; and it is to this conclusion that the concluding words "and probably also than steam" refer.

the real [capacity for heat] with which the change of temperature $dT$ must be multiplied, in order that we may obtain the corresponding increase of the quantity of heat actually present; and, in accordance with the above theorem, I believe we must admit that the real [capacity for heat] of water is the same in all three states of aggregation; and the same considerations which apply to water must naturally also apply in like manner to other substances. In order to determine experimentally the real [capacity for heat] of a substance, it must be taken in the form of strongly overheated vapour, in such a state of expansion, in fact, that the vapour may, without sensible error, be regarded as a perfect gas; and its specific heat must then be determined under constant volume*.

Rankine is not of my opinion in relation to the real [capacity for heat] of bodies in different states of aggregation. At page 307 of his 'Manual of the Steam-Engine,' he says, "The real specific heat of each substance is constant at all densities, so long as the substance retains the same condition, solid, liquid, or gaseous; but a change of real specific heat, sometimes considerable, often accompanies the change between any two of these conditions."

In the case of water in particular, he says, on the same page, that the real specific heat of liquid water is "sensibly equal" to the apparent specific heat; whereas, according to the view above put forth by myself, it must amount to less than half the apparent specific heat.

If Rankine admits that the real [capacity for heat] may be different in different states of aggregation, I do not see what reason there is for supposing it to remain constant within the same state of aggregation. Within one and the same state of aggregation, *e.g.* within the solid state, alterations in the arrangement of the molecules occur, which, though without doubt less considerable, are still essentially of the same kind as the alterations which accompany the passage from one state of aggregation to another; and it therefore seems to me that there is something arbitrary in denying for the smaller changes what

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* [In the *Appendix* B. to this memoir will be found a Table containing the specific heats at constant volume, calculated according to the principles of the mechanical theory of heat, for those gases and vapours whose specific heats under constant pressure have been observed by Regnault.—1864.]

is admitted in respect to the greater. On this point I cannot agree with the way in which the talented English mathematician treats the subject; relying simply on the law established by myself in relation to the working force of heat, it appears to me that but one of the following cases can be possible. Either the above law is correct, in which case the real [capacity for heat] remains the same, not only for the same state of aggregation, but for the different states of aggregation, or the law is not correct, and in this case we have no definite knowledge whatever concerning the real [capacity for heat], and it may equally well be variable within the same state of aggregation as in different states of aggregation.

9. I believe, indeed, that we must extend the application of this law, supposing it to be correct, still further, and especially to *chemical combinations and decompositions.*

The separation of chemically combined substances is likewise an increase of the disgregation, and the chemical combination of previously isolated substances is a diminution of their disgregation; and consequently these processes may be brought under considerations of the same class as the formation or precipitation of vapour. That in this case also the effect of heat is to increase the disgregation, results from many well-known phenomena, many compounds being decomposable by heat into their constituents—as, for example, mercuric oxide, and, at very high temperatures, even water. To this it might perhaps be objected that, in other cases, the effect of increased temperature is to favour the union of two substances—that, for instance, hydrogen and oxygen do not combine at low temperatures, but do so easily at higher temperatures. I believe, however, that the heat exerts here only a secondary influence, contributing to bring the atoms into such relative positions that their inherent forces, by virtue of which they strive to unite, are able to come into operation. Heat itself can never, in my opinion, tend to produce combination, but only, and in every case, decomposition.

Another circumstance which renders the consideration of this case more difficult is this, that the conclusions we have been accustomed to draw always imply that the alterations in question can take place in a continuous and reversible manner; this, however, is not usually the case under the circumstances which accompany our chemical operations. Nevertheless cases do occur in which this condition is fulfilled, especially in the chemical changes brought about by the action of electric force. The galvanic current affords us a simple means of causing combination or decomposition; and in this case the cell in which the chemical change takes place itself forms a galvanic element, the electromotive force of which either contributes to intensify the current, or has to be overcome by other electromotive forces; so that in the one case there is a production, and in the other a consumption of work.

Similarly, I believe that we could in all cases, by producing or expending work, cause the combination or separation of substances at pleasure, provided we possessed the means of acting at will on the individual atoms, and of bringing them into whatever position we pleased. At the same time I am of opinion that heat, leaving out of view its secondary effects, tends in a definite manner, in all cases of chemical change, to render the combination of atoms more difficult, and to facilitate their separation, and that the energy of its action is likewise regulated by the general law above given.

Supposing this to be the case, the theorem which we have deduced from this law must also be applicable here, and a chemical compound must contain exactly the same quantity of heat as its constituents would contain at the same temperature in the uncombined state. Hence it follows that the real [capacity for heat] of every compound must admit of being simply calculated from the real [capacities] of the simple bodies*. If, further, the well-known relation between the specific heats of the simple bodies and their atomic weights be taken into consideration (a relation which I believe not only to be approximately, but, in the case of real [capacities for heat], absolutely exact), it will be apparent what enormous simplifications the law which we have established is capable, supposing it to be true, of introducing into the doctrine of heat.

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* [The *Appendix B*, already referred to, also contains the principal portions of a Note, published by me in the *Annalen der Chemie und Pharmacie*, which offers an opportunity of testing how far the specific heats, at constant volume, of a series of gases (calculated according to Regnault's observations) correspond to the theorem, deduced in the text, relative to the true capacities for heat.—1864.]

10. After these expositions, I can now state the more extended form of the theorem of the equivalence of transformations.

In Art. 1 I have mentioned two kinds of transformations: first, the transformation of work into heat, and *vice versâ*; and secondly, the passage of heat between bodies of different temperatures. In addition to these, we will now take, as a third kind of transformation, the change in the disgregation of a body, assuming the increase of disgregation to be a positive, and the diminution of it to be a negative transformation.

We will now, in the first place, bring the first and last transformations into relation with each other; and here the same circumstances have to be taken into consideration as have already been discussed in Art. 5. If a body changes its disgregation in a reversible manner, the change is accompanied by a transformation of heat into work, or of work into heat, and we can determine the equivalent values of the two kinds of transformations by comparing together the transformations which take place simultaneously.

Let us first assume that *the same change of arrangement takes place at different temperatures*; the quantity of heat which is thereby converted into work, or is produced from work, will then vary; in fact, according to the above law, it will be proportional to the absolute temperature. If, now, we regard as equivalent the transformations which correspond to one and the same change of arrangement, it results that, for the determination of the equivalence-values of these transformations, we must divide the several quantities of heat by the absolute temperatures respectively corresponding to them. The production of the quantity of heat Q from work must, therefore, if it takes place at the temperature T, have the equivalence-value

$$\frac{Q}{T} \text{ const.};$$

and if we here take the constant, which can be assumed at will, as equal to unity, we obtain the expression given in Art. 1.

We will assume, in the second place, that *different changes of arrangement take place at one and the same temperature,* these changes being accompanied by increase of disgregation; and if we adopt as a principle that increments of disgregation wherein the same quantity of heat is converted into work shall be regarded as equivalent to each other, and that their equivalence-value shall be equal, when taken absolutely, to that of the simultaneously occurring transformation from heat into work, but that they shall have the opposite sign, we thus acquire a starting-point for the determination of the equivalence-values of changes of disgregation.

By combining these two rules, we can determine also the equivalence-value of a change of disgregation occurring at various temperatures, and we thus obtain the expression given in Art. 5. Let, for instance, $dL$ be an element of the work performed during a change of disgregation, in effecting which the quantity of heat $AdL$ is consumed, and let the equivalence-value of the change of disgregation be denoted by $Z-Z_0$, we then have

$$Z-Z_0=A\int\frac{dL}{T}.$$

Finally, as to the process cited above as the second kind of transformation—namely, the passage of heat between bodies of different temperatures,—in the case of reversible changes of condition it can be brought about only by heat being converted into work at the one temperature, and work back again into heat at the other; it is therefore already comprised among the transformations of the first kind. And, as I have mentioned in my previous memoir, we may in all cases regard a transformation of the second kind as a combination of two transformations of the first kind.

We will now return to equation (II), namely,

$$\int\frac{dQ+dH}{T}+\int dZ=0.$$

$dH$ is here the increment of the quantity of heat present in the body corresponding to an infinitely small change of condition, and $dQ$ is the quantity of heat simultaneously given up to external bodies. The sum $dQ+dH$ is therefore the new quantity of heat which, supposing it to be positive, must be produced from work, or if it is negative, must be converted into work. Accordingly, the first integral in the above equation is the equivalence-value of all the transformations which have occurred of the first kind;

the second integral represents the transformations of the third kind; and the sum of all these transformations must be, as is expressed by the equation, equal to nothing.

Hence, in so far as *reversible* alterations of condition are concerned, the theorem may be expressed in the following form:—

*If the equivalence-value* $\frac{Q}{T}$ *be assumed for the production of the quantity of heat* Q *from work at the temperature* T, *a magnitude admits of being introduced, as a second transformation corresponding thereto, which has relation to changes in the arrangement of the particles of the body, is completely determined by the initial and final conditions of the body, and fulfils the condition that in every reversible change of condition the algebraic sum of the transformations is equal to nothing.*

11. We must now examine the manner in which the foregoing theorem is modified when we give up the condition that all changes of condition are to take place reversibly.

From what has been said in Art. 4 concerning non-reversible changes of condition, it is easy to perceive that the following must be a general property of all three kinds of transformations. A negative transformation can never occur without a simultaneous positive transformation whose equivalence-value is at least as great; on the other hand, positive transformations are not necessarily accompanied by negative transformations of equal value, but may take place in conjunction with smaller negative transformations, or even without any at all.

If heat is to be transformed into work, which is a negative transformation, a positive change of disgregation must take place at the same time, which cannot be smaller in amount than that determinate magnitude which we regard as equivalent. In the positive transformation of work into heat, on the other hand, the state of things is different. If the force of heat is overcome by opposing forces, so that a negative change of disgregation is brought about, we know that in this case the overcoming forces may be greater than is required to produce the particular result. The excess of force may then give rise to motions of considerable velocity in the parts of the body under consideration, and these motions may subsequently be changed into the molecular motions which we call heat, so that in the end more work comes to be transformed into heat than corresponds to the negative change of disgregation brought about. In many operations, especially in friction, the transformation of work into heat may take place even quite independently of any simultaneous negative transformation.

The relation in which the third kind of transformation, namely change of disgregation, stands to considerations of this nature, is implied in what has been already said. The positive change of disgregation may indeed be greater, but cannot be smaller, than the accompanying transformation of heat into work; and the negative change of disgregation may be smaller, but cannot be greater, than the transformation of work into heat.

Finally, in so far as regards the second kind of transformation, or the passage of heat between bodies of different temperatures, I have thought myself justified in assuming as a fundamental proposition what, according to all that we know of heat, must be regarded as well-established, namely, that the passage from a lower to a higher temperature, which counts as a negative transformation, cannot take place of itself—that is, without a simultaneous positive transformation. On the other hand, the passage of heat in the contrary direction, from a higher to a lower temperature, may very well take place without a simultaneous negative transformation.

Taking these circumstances into consideration, we will now return once more to the consideration of the development by means of which we arrived at equation (II) in Art. 5. Equation (2), which occurs in the same Article, expresses the relation in which an infinitely small change of disgregation must stand to the work simultaneously performed by the heat, under the condition that the change takes place in a reversible manner. In case this last condition need not be fulfilled, the change of disgregation may be greater, provided it is positive, than the value calculated from the work; and if negative, it may be, when taken absolutely, smaller than that value, but in this case also it would algebraically have to be stated as greater. Instead of equation (2), we must therefore write

$$dZ \geqq \frac{AdL}{T} \quad \ldots\ldots\ldots\ldots \quad (2\,a)$$

Applying this to equation (1), we obtain, instead of equation (5),

$$\frac{dQ+dH}{T}+dZ\geqq 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5\,a)$$

The further question now arises, what influence would it have on the formulæ, if a direct passage of heat took place between parts of different temperature within the body in question.

In case the body is not of uniform temperature throughout, the differential expression occurring in equation ($5a$) must not be referred to the entire body, but only to a portion whose temperature may be considered as the same throughout; so that if the temperature of the body varies continuously, the number of parts must be assumed as infinite. In integrating, the expressions which apply to the separate parts may be united again to a single expression for the whole body, by extending the integral, not only to the changes of one part, but to the changes of all the parts. In forming this integral, we must now have regard to the passage of heat taking place between the different parts.

It must here be remarked that $dQ$ is an element of the heat which the body under consideration gives up to, or absorbs from, an external body which serves only as a reservoir of heat, and that this element does not come into question now that we are discussing the passage of heat between the different parts of the body itself. This transfer of heat is mathematically expressed by a decrease in the quantity of heat H in one part, and an equivalent increase in another part; and accordingly we require to direct our attention only to the term $\frac{dH}{T}$ in the differential expression ($5\,a$). If we now suppose that the infinitely small quantity of heat $dH$ leaves one part of the body whose temperature is $T_1$, and passes into another part whose temperature is $T_2$, there result the two following infinitely small terms,

$$-\frac{dH}{T_1} \text{ and } +\frac{dH}{T_2},$$

which must be contained in the integral; and since $T_1$ must be greater than $T_2$, it follows that the positive term must in any case be greater than the negative term, and that consequently the algebraic sum of both is positive. The same thing applies equally to every other element of heat transferred from one part to another; and the change which the integral of the whole differential expression occurring in (5 *a*) undergoes, on account of this transfer of heat, can therefore only consist in the addition of a positive quantity to the value which would else have been obtained. But since, as results from equation (5 *a*), the last value which would be obtained, without taking this direct transfer of heat into consideration, cannot be less than nothing, this can still less be the case when it has been increased by another positive quantity.

We may therefore write as a general expression, including all the circumstances which occur in non-reversible changes, the following, instead of equation (II) :—

$$\int\frac{dQ+dH}{T}+\int dZ \geqq 0. \quad . \quad . \quad . \quad . \quad . \qquad (\mathrm{II}\,a)$$

The theorem which in Art. 1 was enunciated in reference to cyclical processes only, and was represented by the expression (I *a*), has thus assumed a more general form, and may be enunciated thus :—

*The algebraic sum of all the transformations occurring during any change of condition whatever can only be positive, or, as an extreme case, equal to nothing.*

In my previous paper I have spoken of two transformations with opposite signs, which neutralize each other in the algebraic sum, as *compensating* transformations. The foregoing theorem may therefore be enunciated still more briefly as follows :—

*Uncompensated transformations can only be positive**.

12. In conclusion, we will submit the integral

$$\int\frac{dH}{T},$$

which has been frequently used above, to a somewhat closer consideration. We will call this integral, when it is taken from any

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* [I will here say a word as to the manner in which I have defined positive and negative transformations, since, without anticipating matters, I could not on first making choice of these signs, in the Fourth Memoir, p. 123, state the reasons which determined my choice.

If transfers of heat between bodies of different temperatures were alone the subject of contemplation, it might perhaps be thought more appropriate to call the transfer of heat from a colder to a warmer body a positive, and the given initial condition to the condition actually existing, *the transformation-value of the heat actually present in the body when calculated from the given initial condition.* That is, when in any way whatever work is transformed into heat, or heat into work, and the quantity of heat present in the body is thereby altered, the increment or decrement of this integral gives the equivalence-value of the transformations which have taken place. Further, if transfers of heat take place between parts of different temperature within the body itself, or within a system of bodies, the equivalence-value of these transfers of heat is likewise expressed by the increment or decrement of this integral, if it is extended to the whole system of bodies under consideration.

In order to be able actually to perform the integration which has been indicated, we must know the relation between the quantity of heat H and the temperature T. If we call the mass of the body $m$, and its real [capacity for heat] $c$, we have, for a change of temperature throughout amounting to $d$T, the equation

$$dH = mc\,dT. \qquad (23)$$

According to what has been said above, the real [capacity for heat] of a body is independent of the arrangement of its particles; and since *an arrangement* is known, namely, that in perfect gases, for which we must regard it as established, partly by existing experimental data, and partly as the result of theoretical considerations, that the real [capacity for heat] is independent of temperature, we may assume the same thing for the other states of aggregation, and may regard the real [capacity

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transfer from a warmer to a colder body a negative transformation. Since we have to consider, however, not only transference of heat but likewise two other kinds of transformation connected therewith, our point of view on proceeding to a choice of signs must not be limited to making provision for the ordinary notions regarding transfers of heat; we must, on the contrary, seek for an appropriate distinctive feature common to all three kinds of transformations. The theorem enunciated in the text furnishes this feature. Each of the three kinds of transformation can take place, in one direction, of itself or without compensation, but in the opposite direction only with compensation. In nature, therefore, there is a general tendency to transformations of a definite direction. I have taken this tendency as the normal one, and called the transformations which occur in accordance with this tendency, positive, and those which occur in opposition to this tendency, negative.—1864.]

for heat] as always *constant*. Thence it follows that the amount of heat present in a body is simply proportional to its absolute temperature, inasmuch as we can write

$$H=mcT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Even when the body is not homogeneous, but consists of different substances, all, however, at the temperature T, the foregoing equation will still remain applicable, if for $c$ we substitute the corresponding mean value. On the other hand, if different parts of the body have different temperatures, we must in the first instance apply the equation to the separate parts, and then unite the various equations by summation. If, for the sake of generality, we assume that the temperature varies continuously, so that the body must be conceived as divided into an infinite number of parts, the equation takes the following form:

$$H=\int cTdm. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Applying these expressions to the integral given above for the transformation-value of the heat in the body, and denoting the initial temperature by $T_0$, we obtain, for the more simple case in which the temperature is uniform throughout,

$$\int\frac{dH}{T}=mc\int_{T_0}^{T}\frac{dT}{T}=mc\log\frac{T}{T_0}, \quad . \quad . \quad . \quad . \quad (26)$$

and, as a general expression embracing all cases,

$$\int\frac{dH}{T}=\int c\log\frac{T}{T_0}\cdot dm. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

If the disgregation of a body is changed, without heat being supplied to or withdrawn from it, by an external object, the amount of heat contained in the body must be changed in consequence of the production or consumption of heat attendant on the change of disgregation, and a rise or fall of temperature must be the result; consequently the question may be raised, How great must the change of disgregation be in order to bring about a given change of temperature, it being assumed that all changes of condition take place reversibly? In this case we must apply equation (II), putting $dQ=0$, whereby it is transformed into

$$\int\frac{dH}{T}+\int dZ=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

If we assume, for the sake of simplicity, that the temperature of the entire body varies uniformly, so that T has the same value for all parts, we may apply equation (26) to the determination of the first of the two integrals; and we thus obtain, for the required change of disgregation, the equation

$$Z-Z_0=mc\log\frac{T_0}{T}*. \quad . \quad . \quad . \quad . \quad . \quad (29)$$

If we desired to cool a body down to the absolute zero of temperature, the corresponding change of disgregation, as shown by the foregoing formula, in which we should then have $T=0$, would be infinitely great. Hereon is based the argument by which it may be proved to be impossible practically to arrive at the absolute zero of temperature by any alteration of the condition of a body.

## APPENDICES TO SIXTH MEMOIR [1864].

### APPENDIX A. (Page 226.)

### ON TERMINOLOGY.

The new conceptions which the mechanical theory of heat has introduced into science present themselves so frequently in all investigations on heat, that it has become desirable to possess simple and characteristic names for them.

I have divided into the following three parts the heat which must be imparted to a body in order to change its condition in any manner whatever: *first*, the increased amount of heat actually present in the body; *second*, the heat consumed by interior work; and *third*, the heat consumed by exterior work. Of these three quantities of heat the last can only be determined when all the changes are known which the body has suffered;

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* [If the above simplifying hypothesis—that the temperature is the same in all parts of the body and changes in the same manner—be not made, we shall have the equation

$$Z-Z_0=\int c\log\frac{T_0}{T}\,dm,$$

instead of the equation (29).—1864.]

for the determination of the two first quantities, however, a knowledge of the entire series of changes is not necessary, an acquaintance with the initial and final conditions of the body suffices. Given, therefore, the initial condition, proceeding from which the body arrives successively at any other conditions whatever, the first and second of the above quantities of heat may be regarded as two magnitudes which are perfectly defined by the condition of the body at the moment under consideration. The same remark applies, of course, to the sum of these two quantities which I have represented by U, and which is of great importance, inasmuch as it presents itself in the first fundamental equation of the mechanical theory of heat*.

The definition I have given of this magnitude—*the sum of the increment of actually present heat, and of the heat consumed by interior work*—being for general purposes too long to serve as the name of the quantity, several more convenient ones have been proposed. As already remarked in the note on p. 226, Thomson has to this end employed the expression "*the mechanical energy of a body in a given state,*" and Kirchhoff the term "*Wirkungsfunction.*" Zeuner, again, in his "*Grundzüge der mechanischen Wärmetheorie,*" has called U "die innere Wärme des Körpers" (interior heat of the body).

The latter name does not appear to me to correspond quite to the signification of the magnitude U, since only a portion of the latter represents heat actually present in the body, in other words, *vis viva* of its molecular motions, the other portion having reference to heat which has been consumed by interior work, and which, therefore, no longer exists as heat. I do not for a moment imagine that Zeuner had any intention to imply, by that name, that all the heat represented by U was actually present as heat in the body; nevertheless the name might easily be interpreted in this sense.

Of the two other expressions mentionod above, the term *energy* employed by Thomson appears to me to be very appropriate; it has in its favour, too, the circumstance that it corresponds to the proposition of Rankine to include under the common name energy, both heat and everything that heat can

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* See equation (II *a*) of the First Memoir, p. 28, and equation (I) of the Fourth Memoir, p. 113.

replace. I have no hesitation, therefore, in adopting, for the quantity U, the expression *energy of the body*.

It must be here observed, however, that the total energy of a body cannot be measured, it is only the increment of energy, due to the passage of the body from any initial state to its present condition, that is susceptible of measurement. The initial condition being assumed as given, the increment of energy is a perfectly defined magnitude for every other condition of the body. The question is, are we to understand by the *energy of a body* merely the increment of energy estimated from a given initial condition, or is the energy which the body possessed at the beginning to be included in the term? In the latter case, where the *total* energy of the body is implied, we must conceive the increment of energy to be supplemented by the addition of an unknown constant having reference to the initial condition. It will not always be necessary, of course, to mention this constant expressly; we may tacitly assume that it is included.

Since the magnitude U consists of two parts which have frequently to be considered individually, it will not suffice to have an appropriate name for U merely, we must also be able to refer conveniently to these its constituent parts.

The first part presents no difficulty whatever; the heat actually present in the body may be simply called *the heat of the body*, or the *thermal content of the body* (*Wärmeinhalt des Körpers*).

In giving a name to the second part of U, however, we are at once inconvenienced by a circumstance which embarrasses the whole mechanical theory of heat,—the fact that heat and work are measured by different units. The unit of heat is the quantity of heat which is necessary to raise the temperature of a unit-weight of water from 0° to 1°, and the unit of work is the quantity which is represented by the product of the unit of weight into the unit of length,—in French measure, therefore, a kilogramme-metre.

Now in the mechanical theory of heat, after admitting that heat can be transformed into work and work into heat, in other words, that either of these may replace the other, it becomes frequently necessary to form a magnitude of which heat and work are constituent parts. But heat and work being measured by different units, we cannot in such a case say, simply, the magnitude is the *sum of heat and work*; we are compelled to say either *the sum of the heat and the heat-equivalent of the work*, or *the sum of the work and the work-equivalent of the heat.*

Rankine has avoided this inconvenient mode of expression in his memoirs by assuming as his unit of heat the quantity which is equivalent to a unit of work. Nevertheless, although perfectly appropriate on theoretic grounds, it must be admitted that great difficulties oppose themselves to the general introduction of this measure of heat. On the one hand it is always difficult to change a unit when once adopted, and on the other there is here the additional circumstance that the heat-unit hitherto used is a magnitude intimately connected with ordinary calorimetric methods, and the latter being mostly based on the heating of water, necessitate only slight reductions, and these founded on very trustworthy measurements; the heat-unit adopted by Rankine, however, besides requiring the same reductions, assumes the mechanical equivalent of heat to be known,—an assumption which is only approximately correct. Accordingly, since we cannot expect the mechanical measure for heat to be universally adopted, we must always, when quantities of heat enter into an equation, first state whether these quantities are measured in the ordinary manner or by the mechanical unit, and consequently the above-mentioned inconvenience would not be removed by Rankine's procedure.

For this purpose, therefore, I will venture another proposition. Let heat and work continue to be measured each according to its most convenient unit, that is to say, heat according to the thermal unit, and work according to the mechanical one. But besides the work measured according to the mechanical unit, let another magnitude be introduced denoting *the work measured according to the thermal unit,* that is to say, *the numerical value of the work when the unit of work is that which is equivalent to the thermal unit.* For the work thus expressed a particular name is requisite. I propose to adopt for it the Greek word (*ἔργον*) *ergon**.

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* The author has used the German word *Werk,* which is almost synonymous with *Arbeit,* but he proposes the term *Ergon* as more suitable for introduction into other languages. The Greek word ἔργον is so closely allied to the English word work, that both are quite well suited to designate two

The processes which are considered in the mechanical theory of heat may be very conveniently described by means of this new term. Heat and ergon are, in fact, two magnitudes which admit of mutual transformation and substitution, without any alteration in the numerical values of the respective quantities being thereby involved. Accordingly, heat and ergon may, without preparation, be added to, or subtracted from, one another.

When we consider the work produced during any change in the condition of a body, we must call it the *ergon produced*, if it be measured by the unit of heat, and here again we distinguish *interior ergon* and *exterior ergon*. The latter, as already stated in the memoirs, is dependent upon the entire series of successive changes, whilst the former is completely determined when the initial and final conditions, solely, are known. Assuming the initial condition to be given, therefore, the interior ergon may be regarded as a magnitude which depends solely upon the condition of the body at the moment under consideration.

Analogous to the expression *thermal content of the body*, we may introduce the expression *ergonal content of the body*. With reference to the last conception, however, the same remark applies which was previously made with reference to energy. We may understand by ergonal content, either the increment of ergon reckoned from a given initial condition, or the *total* ergonal content. In the latter case we have merely to conceive an unknown constant, having reference to the initial state, added to the increment of ergon; this is so obvious, however, that in such cases we may usually assume tacitly that the constant has been included.

The same remark also applies to the thermal content of a body. By this term we may likewise understand either the increment of heat calculated from an arbitrarily assumed initial condition, or the *total* thermal content. In the latter case a constant associated with that initial condition is to be added to the heat-increment. The only difference is that in the case of the ergonal content, the added constant is quite unknown, whilst

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magnitudes which are essentially the same, but measured according to different units.—T. A. H.

in the case of the thermal content, the constant may be approximately determined, seeing that the absolute zero of temperature is to a certain extent known.

Now the quantity U is the sum of the thermal content and ergonal content, so that in place of the word *energy*, we may use if we please the somewhat longer expression, *thermal and ergonal content*.

In connexion with these remarks on Terminology I will venture another suggestion. Hitherto the heat which disappears when a body is fused or evaporated has been termed *latent heat*. This name originated when it was thought that the heat which can no longer be detected by our senses, when a body fuses or evaporates, still exists in the body in a peculiar concealed condition. According to the mechanical theory of heat, this notion is no longer tenable. All heat actually present in a body is sensible heat; the heat which disappears during fusion or evaporation is converted into work, and consequently exists no longer as heat; I propose, therefore, in place of *latent heat*, to substitute the term *ergonized heat*.

In order to distinguish, in a similar manner, the two parts of the latent heat which I have stated to be expended, respectively, on interior and on exterior work, the expressions *interior* and *exterior ergonized heat* might be used.

It must further be observed that of the heat which must be imparted to a body in order to raise its temperature without changing its state of aggregation (all of which was formerly regarded as *free*), a great portion falls in the same category as that which has hitherto been called latent heat, and for which I now propose the term ergonized heat. For, in general, the heating of a body involves a change in the arrangement of its molecules. This change usually occasions a sensible alteration in volume, but it may occur even when the volume of the body remains the same. For every change in molecular arrangement, a certain amount of ergon is requisite, which may be partly interior and partly exterior, and in producing this ergon, heat is consumed. Only a part of the heat communicated to a body, therefore, serves to increase the heat actually present therein; the remaining part constitutes the ergonized heat.

In certain cases, such as those of evaporation and fusion, where the proposed term ergonized heat frequently presents itself, a more abbreviated form of expression may, of course, be adopted, should it be found convenient to do so. For instance, instead of using the expressions *ergonized heat of evaporation*, and *ergonized heat of fusion*, we may simply say, as I have done in my memoirs, *heat of evaporation* and *heat of fusion*.

## APPENDIX B. (Page 239.)

### ON THE SPECIFIC HEAT OF GASES AT CONSTANT VOLUME.

In the foregoing memoir it was stated that, in order to obtain the *true heat-capacity* of a substance, it must be used as a strongly over-heated vapour, and in fact in such a condition of expansion, that the vapour without appreciable error may be regarded as a perfect gas, and then its specific heat at constant volume must be determined. Now in reality this is not, strictly speaking, quite practicable, since permanent gases themselves, which are furthest removed from their point of condensation, do not exactly follow the laws of a perfect gas; and hence we must certainly assume that at the temperatures at which they can be observed, condensible gases, and still more substances, which at the atmospheric pressure and at ordinary temperatures are either liquid or solid, and only become gaseous at higher temperatures, deviate still more considerably from those laws. To this must be added the circumstance that, with chemically constituted substances, and particularly with those of a complicated and not very permanent constitution, partial chemical changes accompany the processes of heating and cooling; such changes, even if they took place to so small an extent as to be with difficulty detected, might cause the quantities of heat taken up or given off by the gas during its heating or cooling at constant volume to deviate considerably from the true heat-capacity. Notwithstanding these imperfections, which are more or less unavoidable, the specific heat at constant volume corresponding to the gaseous condition of a body is always, of all the several specific heats of the substance, that which is most suited to serve as the approximate measure of the true heat-capacity, and consequently it is, in a theoretical point of view, a magnitude of some interest.

Now Regnault having recently determined experimentally the specific heats at constant pressures of a considerable number of gases and vapours, it was easy to calculate from these numbers, according to the principles of the mechanical theory of heat, the specific heats at constant volumes. Accordingly, immediately after the first publication of Regnault's results, I made these calculations and registered the results in a table for my own use. With reference thereto, it must be again remarked that the method of calculation employed is only strictly correct for a *perfect* gas; nevertheless the tables give at least approximate results for other gases. It must also be observed that the observation of the specific heat of a gas is the more difficult, and consequently the corresponding observation-number the less trustworthy the less permanent the gas is, and consequently the more its deportment deviates from the laws of a perfect gas. Since, then, no greater exactitude can be demanded from the calculation than that which the observation-numbers themselves possess, the method of calculation employed may be regarded as perfectly suited to its object. In forming my Table, I have thought it advisable to introduce a small change in one of the two series of numbers which Regnault has given for the specific heats at constant pressures. I have referred the numbers there to a unit somewhat different from that employed by Regnault, and I have likewise chosen a corresponding different unit in one of the two series containing specific heats at constant volumes. Regnault, in fact, gives us the specific heats of gases in two different ways. He first compares the weights of the gases, and states the quantity of heat which a unit-weight of each gas requires in order to have its temperature raised one degree; this he expresses in ordinary heat-units, that is to say, in terms of the quantity of heat which a unit-weight of water absorbs on being heated from 0° to 1°. In the second place he compares the volumes of the gases, and here he again uses the ordinary unit of heat; the volume to which the numbers refer being that which a unit-weight of atmospheric air occupies when it is of the same temperature and under the same pressure as the gas itself under consideration.

By this choice of units the second series of numbers clearly possesses a rather complicated signification, and its application is thereby embarrassed. When we compare the volumes of the gases with those of atmospheric air, it is best to choose a unit of heat in a corresponding manner, that is to say, so as to compare the quantity of heat, which the heating of a certain volume of gas by 1° requires, with that quantity which an equal volume of atmospheric air at the same temperature and under the same pressure requires when equally heated. This method of expressing the specific heats of gases was formerly generally employed, and consequently I have deemed it advisable to supplement the numbers given by Regnault under the rubric "*en volume*" by a series of numbers, which have reference to the last-named unit of heat; this was easily done, inasmuch as it was merely necessary to divide those numbers by the specific heat of a unit-weight of atmospheric air expressed in ordinary heat-units. In a similar manner I have also expressed in both ways the specific heats at constant volumes calculated by myself; so that, on the one hand, gases are compared with equal weights of water (the ordinary heat-unit having reference to the unit-weight of water), and on the other hand, they are compared with equal volumes of atmospheric air.

The Tables which I calculated for myself in this manner were published in the year 1861, in a paper which appeared in the *Annalen der Chemie und Pharmacie*, vol. cxviii. p. 106, and which originated in a previous note by Buff; in this paper the method of calculation was more fully described. The great importance of the able physical investigations of Regnault justify me, I think, in here entering on this subject, and communicating the Tables in question. To do so, however, I must once more recalculate the Tables; for Regnault published the results of his investigations on the specific heats of gases provisionally in the year 1853, in the *Comptes Rendus*, vol. xxxvi. p. 676, and in the year 1862 his investigations appeared in a complete form in the second volume of his *Relation des Expériences*, which likewise forms the twenty-sixth volume of the Memoirs of the Academy of Paris. The numbers in this volume, however, are not quite the same as those which first appeared in the *Comptes Rendus*; they were somewhat changed by subsequent corrections.

My previously published Tables having been calculated from the numbers first published by Regnault, I have now to apply my calculations to the corrected numbers.

In order to explain the calculation of the Tables, it will perhaps be best first to collect briefly the principal equations having reference to perfect gases.

The first characteristic equation of perfect gases, is that which expresses the law of Mariotte and Gay-Lussac, and is given in equation (I) of the First Memoir, page 21. If we introduce therein the absolute temperature T instead of the temperature $t$, calculated from the freezing-point, and represent, as before, by $p$ and $v$ the pressure and the volume referred to the unit of weight, the equation will take the form

$$pv = RT, \qquad \text{(A)}$$

wherein R is a constant to be specially determined for each gas.

The other equation which here enters into consideration is that which expresses the first fundamental theorem of the mechanical theory of heat when applied to a perfect gas. It is given in the equation (II) of the First Memoir, p. 38, and on again introducing the absolute temperature instead of the temperature counted from the freezing-point, takes the form

$$dQ = c\,dT + AR\frac{T}{v}dv, \qquad \text{(B)}$$

wherein A denotes the calorific equivalent of work, and $c$, as is manifest from the equation, *the specific heat of the gas at constant volume*, which may now without hesitation be regarded as a constant, since the conclusions drawn in that memoir have been confirmed by the experiments of Regnault.

In the First Memoir it was stated that a relation being established by the equation (A) between the pressure, volume, and temperature, any two of these magnitudes may be chosen arbitrarily as independent variables, and the third then regarded as a function thereof. The two magnitudes thus chosen, then, determine the condition of the gas, and by their variations the changes which the gas suffers, and consequently also the quantities of heat which the gas must thereby absorb may be expressed; provided, of course, that we assume, as we always did in the equations of the First Memoir, that the changes of the gas take place in a reversible manner .In the differential equation (B) the temperature and volume are chosen as independent variables; by the help of equation (A) we may at once deduce from this differential equation the two other corresponding ones, which contain on their right-hand sides, instead of the temperature and volume, either the temperature and pressure or the pressure and volume.

After introducing the variables T and $p$, the equation becomes

$$dQ=(c+AR)dT-AR\frac{T}{p}dp, \quad . \quad . \quad . \quad . \quad (B_1)$$

and on introducing $p$ and $v$ as variables it takes the form

$$dQ=\frac{c}{R}vdp+\frac{c+AR}{R}pdv. \quad . \quad . \quad . \quad . \quad . \quad (B_2)$$

From equation ($B_1$) we see that the sum

$$c+AR$$

denotes *the specific heat of the gas at constant pressure.* Representing this by $c'$ and replacing in a corresponding manner AR by the difference $c'-c$, the foregoing three equations become

$$dQ=cdT+(c'-c)\frac{T}{v}dv, \quad . \quad . \quad . \quad . \quad . \quad (B')$$

$$dQ=c'dT-(c'-c)\frac{T}{p}dp, \quad . \quad . \quad . \quad . \quad . \quad (B'_1)$$

$$dQ=\frac{c}{R}vdp+\frac{c'}{R}pdv. \quad . \quad . \quad . \quad . \quad . \quad . \quad (B'_2)$$

I take this opportunity of remarking that in my memoirs I have employed for the two specific heats, a notation different from the usual one. Formerly, in fact, it was customary to denote the specific heat of a gas at constant pressure by $c$, and the specific heat at constant volume by $c'$. But since from the point of view reached by the mechanical theory of heat, the specific heat at constant volume presents itself as a simpler magnitude (inasmuch as for a perfect gas the specific heat at constant volume is the true capacity for heat, whilst the specific heat at constant pressure is the sum of the true heat-capacity, and of the heat consumed by the work of expansion, that is to say, a magnitude composed of two essentially different parts), it appeared to me to be desirable to select the simpler symbol for the simpler magnitude, and I have therefore denoted the specific heat at constant volume by $c$, and the specific heat at constant pressure by $c'$.

Each of the three differential equations, (B), ($B_1$), ($B_2$), may serve for the calculations corresponding to the changes of condition of a gas, and we may always select from the three different forms the one which is most convenient for the required calculation. All three differential equations are *unintegrable* so long as the two variables on the right-hand side are regarded as independent of each other, and they will only become *integrable* when some further relation is given, between the variables which they involve, by means of which it will be possible to reduce the differential equations involving three variables to differential equations between two variables. The nature of the changes which the gas suffers is so determined by this relation, that the whole series of changes become known.

The particular relation which exists between the two *specific heats* is now manifest from what has been already stated. For by the equation (10 *a*) of the First Memoir (p. 39), we have

$$c' = c + AR, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

whence, on substituting for R the fraction $\frac{pv}{T}$, in accordance with equation (A), and at the same time removing the magnitude $c$ to the left-hand side, and $c'$ to the right-hand side, we obtain

$$c = c' - \frac{Ap}{T}v. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Let us suppose this equation to be specially formed for *atmospheric air*, and let us denote by $c_1$, $c_1'$ and $v_1$ the values of $c$, $c'$ and $v$ for atmospheric air; the equation then gives

$$c_1 = c'_1 - \frac{Ap}{T}v_1,$$

whence follows

$$\frac{Ap}{T} = \frac{c'_1 - c_1}{v_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

This substituted in equation (b) gives

$$c=c'-(c'_1-c_1)\frac{v}{v_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(d)}$$

The fraction $\frac{v}{v_1}$ is the reciprocal of the density of the gas compared with air at the same temperature and under the same pressure; hence, on denoting this density by $d$, we have

$$c=c'-\frac{c'_1-c_1}{d}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(e)}$$

The difference $c'_1-c_1$ which here makes its appearance may also be determined, and to do so the ratio $\frac{c'_1}{c_1}$ must first be calculated from the observed velocity of sound. In my First Memoir I employed for this ratio the value 1·421 assumed by Dulong; the value 1·41, however, appears to be a more correct one, the third decimal being for the present omitted, since if introduced it would be uncertain. Employing the latter value, therefore, we will put

$$\frac{c'_1}{c_1}=1{\cdot}41, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(f)}$$

whence it will follow that

$$c_1=\frac{c'_1}{1{\cdot}41}.$$

Substituting now the value $c'_1=0{\cdot}2375$ as found experimentally by Regnault*, we have

$$c_1=\frac{0{\cdot}2375}{1{\cdot}41}=0{\cdot}1684, \quad . \quad . \quad . \quad . \qquad \text{(g)}$$

and from this we deduce

$$c'_1-c_1=0{\cdot}2375-0{\cdot}1684=0{\cdot}0691. \quad . \quad . \quad . \qquad \text{(h)}$$

On substituting this numerical value in the equation (e), we have

$$c=c'-\frac{0{\cdot}0691}{d}, \text{ or}$$

$$c=\frac{c'd-0{\cdot}0691}{d}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(i)}$$

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[*] In the second volume of his *Relation des Expériences*, p. 108, Regnault gives the following numbers corresponding to different limits of temperature:

between $-30°$ and $+10°$ ........ 0·23771.
" $0°$ " $+100°$ ........ 0·23741.
" $0°$ " $+200°$ ........ 0·23751.

With respect to the specific heats at constant volumes corresponding to the *unit of volume*, I denoted them by $\gamma$ in my First Memoir. They are obtained by dividing the specific heats $c$ corresponding to the unit of weight by the volume which a unit of weight of the gas, at the particular temperature and pressure, assumes. We may put therefore

$$\gamma=\frac{c}{v}; \quad \text{(k)}$$

and for atmospheric air,

$$\gamma_1=\frac{c_1}{v_1}. \quad \text{(l)}$$

The magnitude with which we are at present interested, and by which the quantity of heat consumed in heating the gas at constant volume is compared with the quantity which an equal volume of atmospheric air requires when equally heated under the same circumstances, is obtained on finding, from the above two equations, the value of the fraction $\frac{\gamma}{\gamma_1}$. We have, in fact,

$$\frac{\gamma}{\gamma_1}=\frac{c}{c_1}\cdot\frac{v_1}{v}; \quad \text{(m)}$$

or substituting for $c_1$ its value, and for the fraction $\frac{v_1}{v}$ the letter $d$ as before,

$$\frac{\gamma}{\gamma_1}=\frac{c}{0{\cdot}1684}\cdot d. \quad \text{(n)}$$

Lastly, on substituting for $c$ the expression given in (i), we have

$$\frac{\gamma}{\gamma_1}=\frac{c'd-0{\cdot}0691}{0{\cdot}1684}. \quad \text{(o)}$$

The product $c'd$, which occurs in the equations (i) and (o), is the above-named magnitude, given by Regnault, for the several gases, in the column headed "*en volume.*" In order therefore to obtain the specific heat of a gas at constant volume, expressed in either of the two ways above alluded to, viz., as compared with that of an equal weight of water or as compared with that of an equal volume of air, it is merely necessary to deduct the number 0·0691 from the number standing in the column in question, and then to divide the remainder either by the density of the gas or by the number 0·1684.

I have collected the numbers so calculated in a Table (p. 266), wherein the several columns have the following significations:—

*Column* I. The *name* of the gas.

*Column* II. The *chemical constitution* expressed in such a manner that the diminution of volume accompanying the combination is at once visible. In fact the volumes of the simple gases which are stated, are those which must combine in order to produce *two* volumes of the compound gas. The hypothetical volume of carbon gas which appears therein, is that which must be assumed in order to say that a volume of carbon gas combines with a volume of oxygen to produce carbonic oxide gas, and with two volumes of oxygen to produce carbonic acid. Accordingly, when in the Table alcohol, for instance, is denoted by $C_2 H_6 O$, it indicates that 2 volumes of the hypothetical carbon gas, 6 volumes of hydrogen and 1 volume of oxygen, give 2 volumes of alcohol vapour. In determining the volume of sulphur gas, I have employed the specific gravity 2·23 found, at very high temperatures, by Sainte-Claire Deville and Troost. The ordinary chemical symbols are used, irrespective of their volumes in a gaseous condition, for the elements silicon, phosphorus, arsenic, titanium and tin, which enter into the five last combinations of the Table. Since the gas-volumes of these elements are either still unknown or affected with certain, not yet sufficiently explained irregularities.

*Column* III. The *density* of the gas as given by Regnault.

*Column* IV. The *specific heat under constant pressure, compared with that of an equal weight of water,* or what amounts to the same thing, referred to the unit-weight of gas and expressed in ordinary thermal units. These are the numbers which Regnault has given in the column headed "*en poids.*"

*Column* V. *The specific heat under constant pressure, compared with that of an equal volume of air,* and calculated by dividing the numbers given by Regnault under the heading "*en volume,*" by the number 0·2375.

*Column* VI. The *specific heat at constant volume, compared with that of an equal weight of water,* and calculated according to equation (i).

*Column* VII. The *specific heat at constant volume, compared* *with that of an equal volume of air,* and calculated according to equation (o).

In the Tables published in the *Ann. der Chem. und Pharm.,* I added an eighth column, giving the *true thermal capacity* of the compounds, as compared with the true thermal capacity of an equal volume of a simple gas.

The numbers contained in this column depend on the supposition more accurately laid down in the preceding memoir, according to which a chemically compounded substance contains just as much heat as the constituents would do if separated and at the same temperature. According to this supposition, we may very easily calculate the true thermal capacity, corresponding to the unit of volume, of a compound gas, from the changes of volume which occur during the combination, provided we know the true thermal capacities, corresponding to the same unit of volume, of the simple gases. For instance, let us consider the three simple gases, oxygen, hydrogen, and nitrogen, whose specific heats at constant volume may be considered as very nearly equal to one another; so that we may also assume that their true thermal capacities are also equal. (The small deviations arising from the circumstance that the gases are not quite perfect ones are here neglected.) Now if we consider the gaseous compounds of the gases and compare the true thermal capacities of a unit of volume of each compound with the true thermal capacities of the simple gases, the numerical ratios are immediately given by the changes of volume which occur during combination. We thus obtain for binoxide of nitrogen, where no change of volume occurs, the true thermal capacity 1; for protoxide of nitrogen and for aqueous vapour, where the diminution of volume is in ratio $1 : \frac{2}{3}$, the thermal capacity $\frac{3}{2}$; and for ammonia, where the diminution of volume is in the ratio of $1 : \frac{1}{2}$, the thermal capacity 2. In a similar manner the true thermal capacity of any other compound gas may be determined by the theorem under consideration.

My reasons for omitting this column completely from the following Table, were twofold. In the first place the true thermal capacity corresponding to the unit of volume, of each simple component gas being known, the method of determining that of the compound gas is so simple that the required numbers may be immediately read from the chemical formulæ, and consequently it is scarcely necessary to print them specially; and in the second place, since uncertainties still exist as to the true thermal capacities, corresponding to the unit of volume, of some of the simple gases, a discussion thereof ought to precede any numerical statement. I propose to return to this subject on some future occasion.

| I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|
| | | | Specific heat under constant pressure | | Specific heat at constant volume | |
| Names of the gases. | Chemical constitution. | Density. | compared with that of an equal weight of water. | compared with that of an equal volume of air. | compared with that of an equal weight of water. | compared with that of an equal volume of air. |
| Atmospheric air | ...... | 1 | 0·2375 | 1 | 0·1684 | 1 |
| Oxygen | $O_2$ | 1·1056 | 0·21751 | 1·013 | 0·1551 | 1·018 |
| Nitrogen | $N_2$ | 0·9713 | 0·24380 | 0·997 | 0·1727 | 0·996 |
| Hydrogen | $H_2$ | 0·0692 | 3·40900 | 0·993 | 2·411 | 0·990 |
| Chlorine | $Cl_2$ | 2·4502 | 0·12099 | 1·248 | 0·0928 | 1·350 |
| Bromine | $Br_2$ | 5·4772 | 0·05552 | 1·280 | 0·0429 | 1·395 |
| Binoxide of nitrogen | $N\,O$ | 1·0384 | 0·2317 | 1·013 | 0·1652 | 1·018 |
| Carbonic oxide | $C\,O$ | 0·9673 | 0·2450 | 0·998 | 0·1736 | 0·997 |
| Hydrochloric acid | $H\,Cl$ | 1·2596 | 0·1852 | 0·982 | 0·1304 | 0·975 |
| Carbonic acid | $C\,O_2$ | 1·5201 | 0·2169 | 1·39 | 0·172 | 1·55. |
| Protoxide of nitrogen | $N_2\,O$ | 1·5241 | 0·2262 | 1·45 | 0·181 | 1·64 |
| Aqueous vapour | $H_2\,O$ | 0·6219 | 0·4805 | 1·26 | 0·370 | 1·36 |
| Sulphurous acid | $S\,O_2$ | 2·2113 | 0·1544 | 1·44 | 0·123 | 1·62 |
| Sulphuretted hydrogen | $H_2\,S$ | 1·1747 | 0·2432 | 1·20 | 0·184 | 1·29 |
| Bisulphide of carbon | $C\,S_2$ | 2·6258 | 0·1569 | 1·74 | 0·131 | 2·04 |
| Marsh-gas | $C\,H_4$ | 0·5527 | 0·5929 | 1·38 | 0·468 | 1·54 |
| Chloroform | $C\,H\,Cl_3$ | 4·1244 | 0·1567 | 2·72 | 0·140 | 3·43 |
| Olefiant gas | $C_2\,H_4$ | 0·9672 | 0·4040 | 1·75 | 0·359 | 2·06 |
| Ammonia | $N\,H_3$ | 0·5894 | 0·5084 | 1·26 | 0·391 | 1·37 |
| Benzole | $C_6\,H_6$ | 2·6942 | 0·3754 | 4·26 | 0·350 | 5·60 |
| Oil of turpentine | $C_{10}\,H_{16}$ | 4·6978 | 0·5061 | 10·01 | 0·491 | 13·71 |
| Wood-spirit | $C\,H_4\,O$ | 1·1055 | 0·4580 | 2·13 | 0·395 | 2·60 |
| Alcohol | $C_2\,H_6\,O$ | 1·5890 | 0·4534 | 3·03 | 0·410 | 3·87 |
| Ether | $C_4\,H_{10}\,O$ | 2·5573 | 0·4797 | 5·16 | 0·453 | 6·87 |
| Sulphide of ethyle | $C_4\,H_{10}\,S$ | 3·1101 | 0·4008 | 5·25 | 0·379 | 6·99 |
| Chloride of ethyle | $C_2\,H_5\,Cl$ | 2·2269 | 0·2738 | 2·57 | 0·243 | 3·21 |
| Bromide of ethyle | $C_2\,H_5\,Br$ | 3·7058 | 0·1896 | 2·96 | 0·171 | 3·76 |
| Dutch liquid | $C_2\,H_4\,Cl_2$ | 3·4174 | 0·2293 | 3·30 | 0·209 | 4·24 |
| Acetone | $C_3\,H_6\,O$ | 2·0036 | 0·4125 | 3·48 | 0·378 | 4·50 |
| Acetic-ether | $C_4\,H_8\,O_2$ | 3·0400 | 0·4008 | 5·13 | 0·378 | 6·82 |
| Terchloride of silicon | $Si\,Cl_3$ | 5·8833 | 0·1322 | 3·27 | 0·120 | 4·21 |
| Terchloride of phosphorus | $P\,Cl_3$ | 4·7464 | 0·1347 | 2·69 | 0·120 | 3·39 |
| Terchloride of arsenic | $As\,Cl_3$ | 6·2667 | 0·1122 | 2·96 | 0·101 | 3·77 |
| Chloride of titanium | $Ti\,Cl_4$ | 6·6402 | 0·1290 | 3·61 | 0·119 | 4·67 |
| Chloride of tin | $Sn\,Cl_4$ | 8·9654 | 0·0939 | 3·54 | 0·086 | 4·59 |

# SEVENTH MEMOIR.

## ON AN AXIOM IN THE MECHANICAL THEORY OF HEAT[*].

1. When I wrote my First Memoir on the Mechanical Theory of Heat[†], two different views were entertained relative to the deportment of heat in the production of mechanical work. One was based on the old and widely spread notion, that heat is a peculiar substance, which may be present in greater or less quantity in a body, and thus determine the variations of temperature. Conformably with this notion was the opinion that, although heat could change its mode of distribution by passing from one body into another, and could further exist in different conditions, to which the terms *latent* and *free* were applied, yet the quantity of heat in the whole mass could neither increase nor diminish, since matter can neither be created nor destroyed.

Upon this view is based the paper published by S. Carnot[‡], in the year 1824, wherein machines driven by heat are subjected to a general theoretical treatment. Carnot, in investigating more closely the circumstances under which moving force can be produced by heat, found that in all cases there is a passage of heat from a body of higher into one of a lower temperature; as in the case of a steam-engine where, by means of steam, heat passes from the fire or from a body of very high temperature, to the condenser, a space containing bodies of lower temperature. He compared this manner of producing work with that which occurs when a mass of water falls from a higher to a lower level, and consequently, in correspondence with the expression *"une chute d'eau,"* he described the fall of heat

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[*] Read at a Meeting of the Swiss Association, held at Samaden, August 25th, 1863, and published in Poggendorff's *Annalen*, November 1863, vol. cxx. p. 426.

[†] On the Moving force of Heat, &c. (First Memoir of this collection).

[‡] Réflexions sur la puissance motrice du feu.

from a higher to a lower temperature as "*une chute du calorique*"*.

Regarding the subject from this point of view, he lays down the theorem that the magnitude of the work produced always bears a certain general relation to the simultaneous transfer of heat, *i.e.* to the quantity of heat which passes over, and to the temperatures of the bodies between which the transfer takes place, and that this relation is independent of the nature of the substances through which the production of work and the transfer of heat are effected. His proof of the necessity of such a relation is based on the axiom *that it is impossible to create a moving force out of nothing*, or in other words, *that perpetual motion is impossible.*

The other view above referred to is that heat is not invariable in quantity; but that when mechanical work is produced by heat, heat must be consumed, and that, on the contrary, by the expenditure of work a corresponding quantity of heat can be produced. This view stands in immediate connexion with the new theory respecting the nature of heat, according to which heat is not a substance but a motion. Since the end of the last century various writers, amongst whom Rumford, Davy, and Seguin may be mentioned, have accepted this theory; but it is only since 1842 that Mayer of Heilbronn, Colding of Copenhagen, and Joule of Manchester examined the theory more closely, founded it, and established with certainty the law of the equivalence of heat and work.

According to this theory, the causal relation involved in the process of the production of work by heat is quite different from that which Carnot assumed. Mechanical work ensues from the conversion of existing heat into work, just in the same manner as, by the ordinary laws of mechanics, force is overcome, and work thereby produced, by motion which already exists; in the latter case the motion suffers a loss, in *vis viva,* equivalent to the work done, so that we may say that the *vis viva* of motion has been converted into work. Carnot's comparison, therefore, in accordance with which the production of work by heat corresponds to the production of work by the falling of a mass of

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* See page 28 of Carnot's paper.

water,—and, in fact, the fall of a certain quantity of heat from a higher to a lower temperature may be regarded as a cause of the work produced, was no longer admissible according to modern views. On this account it was thought that one of two alternatives must necessarily be accepted; either Carnot's theory must be retained and the modern view rejected, according to which heat is consumed in the production of work, or, on the contrary, Carnot's theory must be rejected and the modern view adopted.

2. When at the same period I entered on the investigation of this subject, I did not hesitate to accept the view that heat must be consumed in order to produce work. Nevertheless I did not think that Carnot's theory, which had found in Clapeyron a very expert analytical expositor, required total rejection; on the contrary, it appeared to me that the theorem established by Carnot, after separating one part and properly formulising the rest, might be brought into accordance with the more modern law of the equivalence of heat and work, and thus be employed together with it for the deduction of important conclusions. The theorem of Carnot thus modified was treated by me in the second part of the above-cited memoir, in the first part of which I had considered the law of the equivalence of heat and work.

In my later memoirs I succeeded in establishing simpler and at the same time more comprehensive theorems by pursuing further the same considerations which had led me to the first modification of Carnot's theorem. I will not now enter, however, upon these extensions of the theory, but will limit myself for the present to the question how, in accordance with the law of the equivalence of heat and work, the necessity can be demonstrated of the other theorem in its modified form.

The axiom employed by Carnot in the proof of his theorem, and which consists in the impossibility of creating moving force, or, more properly expressed, mechanical work out of nothing, could no longer be employed in establishing the modified theorem. In fact, since in the latter it is already assumed that to produce mechanical work an equivalent amount of heat must be consumed, it follows that the supposition of the creation of work is altogether out of the question, no matter whether a transfer of heat from a warm to a colder body does or does not accompany the consumption of heat.

On the other hand, I found that another and, in my opinion, a more certain basis can be secured for the proof by reversing the sequence of reasoning pursued by Carnot, and by accepting as an axiom a theorem, in a somewhat modified form, which may be regarded as a consequence of his assumptions.

In fact, after establishing from the axiom that work cannot be produced from nothing, the theorem that in order to produce work a corresponding quantity of heat must be transferred from a warmer to a colder body, Carnot to be consistent could not but conclude that, in order to transfer heat from a colder to a warmer body, work must be expended. Although we must now abandon the argument which led to this result, and notwithstanding the fact that the result itself in its original form is not quite admissible, it is nevertheless manifest that an essential difference exists between the transfer of heat from a warmer to a colder body and the transfer from a colder to a warmer, since the first may take place spontaneously under circumstances which render the latter impossible.

On investigating the subject more closely, and taking into consideration the known properties and actions of heat, I came to the conviction that the difference in question had its origin in the nature of heat itself, inasmuch as by its very nature it must tend to equalize existing differences of temperature. Heat accordingly incessantly strives to pass from warmer to colder bodies, and a passage in a contrary direction can only take place under circumstances where simultaneously another quantity of heat passes from a warmer to a colder body, or when some change occurs which has the peculiarity of not being reversible without causing on its part such a transfer from a warmer to a colder body. This change which simultaneously takes place is consequently to be regarded as the equivalent of that transfer of heat from a colder to a warmer body, so that it cannot be said that the transfer has taken place *of itself* (von selbst).

I thought it permissible, therefore, to lay down the axiom, that

*Heat cannot of itself pass from a colder to a warmer body,*

and to employ it in demonstrating the second fundamental theorem of the mechanical theory of heat.

3. This axiom has met with very different receptions on the part of the scientific public. To some it appeared to be so self-evident as to render its express statement unnecessary, to others, on the contrary, its correctness appeared to be doubtful.

The first opinion is, I find, expressed in the very meritorious paper published by Zeuner in 1860, under the title "Grundzüge der Mechanischen Wärmetheorie," in which he seeks to expound this theory, so far as at that time developed, in as connected and simple a manner as possible, in order to extend an acquaintance with the principal results of this theory to those to whom the original memoirs were either not accessible, or were difficult of perusal in consequence of the mathematical developments therein contained.

In this work Zeuner gives my proof of the second fundamental theorem essentially in the form in which it was reproduced by Reech*. In one point, however, his exposition differs from the latter; for Reech gives the theorem that heat cannot of itself pass from a colder to a warmer body, expressly as an axiom laid down by me, and he bases his demonstration thereon. Zeuner, however, does not mention this theorem at all, but merely shows that, if for any two bodies the second fundamental theorem of the mechanical theory of heat were not true, it would be possible by means of two cyclical processes performed in opposite ways with these two bodies, to transfer heat from a colder to a warmer body without any other change; and he then remarks†, "since we can repeat both processes any number of times by employing the two bodies alternately in the manner described, it would follow that, without expending either work or heat, we could continually transfer heat from a body of lower to a body of higher temperature; which is absurd." Few readers, I believe, will admit that the impossibility here alluded to of the transfer, without any other change, of heat from a colder to a warmer body is as self-evident as the words "which is absurd" would imply. In the conduction of heat as well

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* Récapitulation très-succinte des recherches algébriques faites sur la théorie des effets mécaniques de la chaleur par différents auteurs.—Journ. de Liouville, S. 2. vol. i. p. 58.

† Page 24 of his work.

as in its radiation under ordinary circumstances, we may certainly say that this impossibility is established by daily experience. But even in the radiation of heat, the question may arise whether it would not be possible, by artificially concentrating rays of heat by means of mirrors or lenses, to generate a temperature higher than that possessed by the bodies which emit the rays, and thus to cause heat to pass into a warmer body*. The subject is still more complicated in cases where heat is transformed into work and work into heat, either by processes such as friction and resistance of the air, or by the circumstance that one or more bodies suffer changes of condition in which are involved both positive and negative, interior and exterior work,—where, in fact, according to the customary mode of expression, heat is rendered *latent* or *free*; which heat the changing bodies may withdraw from or communicate to other bodies of different temperatures.

I cannot but think that when in such cases, and however complicated the processes may be, it is asserted that heat never passes from a colder to a warmer body without some permanent change occurring which may be regarded as an equivalent thereof, this theorem ought not to be treated as quite self-evident; it ought rather to be introduced as a new axiom upon whose acceptance or rejection the admissibility of the proof depends.

4. The opposite view, however, is more frequently met with, that this theorem is not sufficiently trustworthy to serve as a basis of demonstration, or even that it is incorrect.

With reference hereto, I must first explain Rankine's manner of treating the subject. In a memoir which appeared almost at the same time as mine†, Rankine developed the theory of a

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* I have treated this subject, which in other respects is interesting, in a separate paper read before the Scientific Society of Zurich last June, and which will appear in a forthcoming Number of these Annals. [It forms the Eighth Memoir of this collection.]

† It was communicated to the Royal Society of Edinburgh in the same month (February 1850) in which my paper was read to the Academy of Berlin. Rankine states in a communication to Poggendorff that his paper was sent in in October 1849. Its publication, however, took place somewhat later than mine did. It appeared in the 'Transactions of the Royal Society of Edinburgh,' vol. xx. p. 147, and was republished, with some changes, in the Phil. Mag. S. 4. vol. vii. 1854.

peculiar molecular motion assumed by him and termed molecular vortices, and from it he deduced conclusions concerning the deportment of bodies, particularly of gases and vapours, which agree in some measure with those at which I arrived in the *first part* of my memoir by means of the law of the equivalence of heat and work. The subject of the *second part* of my memoir, Carnot's theorem, as modified by me, and its consequences, is, however, not contained in Rankine's memoir.

In a subsequent paper communicated to the Royal Society of Edinburgh in April 1851, and appended as Section 5 to his former memoir*, Rankine occupies himself with that second fundamental theorem. He there remarks with reference to my modified theorem, that he "*had at first doubts as to the reasoning*" by which I maintained it†, but that he was induced by W. Thomson, to whom he had communicated his doubts, to examine the subject more closely. He arrived thereby at the conclusion that this theorem ought not to be treated as an independent principle in the theory of heat; but that it might be deduced as a consequence of the equations established by him in the first section of his memoir.

I must, however, confess that I cannot regard as satisfactory the demonstration of the theorem thereupon given by Rankine.

5. In the heat which must be communicated to a body in order to raise its temperature, Rankine distinguishes, as I also have done, two different portions; one of which serves to increase the heat actually present in a body, and the other is consumed by work. The latter portion includes the heat consumed by interior as well as by exterior work.

For the heat consumed by work Rankine employs an expression deduced by him in the first section of his paper from the hypothesis of molecular vortices. I need not here enter more closely into this mode of deduction, since the circumstance that it depends on a peculiar hypothesis concerning the constitution of molecules, and on their mode of motion, is sufficient to produce the conviction that complicated considerations must necessarily arise of a nature to raise doubts as to the degree of its trustworthiness. In my memoirs I have taken especial care

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* Phil. Mag. S. 4. vol. vii. p. 249.

† Ibid. p. 251.

to base the development of the equations which enter into the mechanical theory of heat upon certain general axioms, and not upon particular views regarding the molecular constitution of bodies, and accordingly I should be inclined to regard my treatment of the subject as the more appropriate one, even were the above-mentioned circumstance the only one which could be adduced against Rankine's demonstration. But the determination of the first portion of the heat communicated to a body, *i. e.* of the portion which serves to increase the heat actually present therein, is still more uncertain.

Rankine represents, by the product $\mathfrak{t}dt$ simply, the increment of heat present in the body when its temperature $t$ is increased by $dt$, no matter whether the volume of the body does or does not change at the same time; and in his demonstration he treats the magnitude $\mathfrak{t}$, which he terms "*the real specific heat*"[*], as a magnitude *independent of the volume.* We seek in vain, however, in his memoir for a sufficient reason for this procedure, in fact, statements appear therein which are in direct contradiction thereto.

In the introduction to his memoir he gives in equation (XIII) an expression for the real thermal capacity, which contains a factor $k$, of which he says[†], "The coefficient $k$ (which enters into the value of specific heat) being the ratio of the *vis viva* of the entire motion impressed on the atomic atmospheres by the action of their nuclei, to the *vis viva* of a peculiar kind of motion, may be conjectured to have a specific value for each substance, depending in a manner yet unknown on some circumstance in the constitution of its atoms. Although it varies in some cases for the same substance in the solid, liquid, and gaseous states, there is no experimental evidence that it varies for the same substance in the same condition." According to this, Rankine is of opinion that the real thermal capacity of one and the same substance may be different in different states of aggregation; and for the assumption that it is

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[*] [In a note to the Sixth Memoir, p. 229, I have proposed to employ the term *real capacity for heat,* instead of *real specific heat,* since the former, or the equivalent expression *real thermal capacity,* literally signifies that the heat under consideration is really contained in the body.—1864.]

[†] Phil. Mag. S. 4. vol. vii. p. 10.

invariable in the same state of aggregation, the only reason he gives is, that no known experiment contradicts it.

At page 307 of a more recent work by Rankine, entitled "A Manual of the Steam-engine and other Prime Movers," London and Glasgow, 1859, occurs a still more definite statement on this subject, already cited by me on a former occasion, to the following effect, "*a change of real specific heat, sometimes considerable, often accompanies the change between any two of those conditions,*" i. e. the three states of aggregation. The magnitude of the differences between the real thermal capacities of one and the same substance in different states of aggregation, held by Rankine to be possible, is manifest from a statement on the same page to the effect that in liquid-water the specific heat determined by observation, termed by him the apparent specific heat, is nearly equal to the real specific heat. Now as Rankine knows very well that the observed specific heat of water is twice as great as that of ice, and more than twice as great as that of vapour, and since the real specific heat (thermal capacity) of ice and of vapour can certainly not be greater than the observed one, it follows that Rankine must assume that the real thermal capacity of water exceeds twice that of ice and of vapour.

If we now inquire how, in accordance with this assumption, for a body whose temperature $t$ is increased by $dt$, and whose volume $v$ is increased by $dv$, the corresponding increment of heat actually present in the body is to be expressed, we must proceed as follows.

In the case where the body, during its change of volume, suffers no change of condition, the increment of actually present heat would no doubt be expressible, as Rankine states, by a simple product of the form $\mathfrak{k}\,dt$; but different values would have to be ascribed to the factor $\mathfrak{k}$ for different states of aggregation. Where the body, however, changes its state of aggregation as well as its volume; for instance, in the case often considered, where a quantity of matter is given partly in a liquid and partly in a vaporous condition, and where during a change of volume the magnitude of both these parts is altered, either by the partial evaporation of the liquid, or by the partial condensation of the vapour, we should not be able to represent by a simple product $dt$ the increase of heat which accompanies a change both of temperature and volume; we should, on the contrary, have to employ for the latter an expression of the form

$$\mathfrak{t}dt + \mathfrak{t}_1 dv ;$$

in fact, if the real thermal capacity of a substance were different in different states of aggregation, we should necessarily conclude that the quantity of heat present therein depended upon its state of aggregation, so that equal quantities of the substance in the solid, liquid, and gaseous states would contain different quantities of heat; accordingly, whenever the state of aggregation of a part of the substance changes without any change of temperature, the total quantity of heat present therein must also change.

From this it follows that Rankine, according to his own admission, can only regard the manner in which he expresses the increment of heat present in the body, and in which he treats this expression in his demonstration, as trustworthy in cases where no changes of the state of aggregation present themselves; and consequently it is only in these cases that he can claim accuracy for his proof. In all cases, therefore, where changes of the state of aggregation present themselves, the theorem remains unproved; and notwithstanding this, these cases are particularly important, inasmuch as it is precisely to them that the theorem has hitherto been most frequently applied.

We must indeed go further, and assert that the demonstration loses hereby all trustworthiness, even in those cases where no changes of the state of aggregation present themselves. For if Rankine assumes that the real thermal capacity can be different in different states of aggregation, we do not at all see on what grounds it is to be regarded as unchangeable, when the state of aggregation is the same. We know that in solid and liquid bodies changes in the condition of cohesion may occur without any change in the state of aggregation, and that in gaseous bodies, besides the great differences in volume, the circumstance also presents itself that they follow the laws of Mariotte and Gay-Lussac with more or less accuracy, according as they are more or less distant from their point of condensation. Why, therefore, if changes in the state of aggregation have an influence on the real thermal capacity, may not to these changes of cohesion an influence, the same in kind though less in degree, be with equal justice ascribed? The assumption that the real thermal capacity is invariable in the same state of aggregation, is consequently not merely left unestablished by Rankine, but would be rendered in the highest degree improbable if the other assumptions made by him were accurate.

6. The method which I have proposed for the treatment of the second fundamental theorem in the mechanical theory of heat, and which, notwithstanding Rankine's objection, I still hold to be the most convenient, is essentially the following.

By means of the axiom *that heat cannot of itself pass from a colder to a warmer body,* I have first proved the theorem in question for *cyclical processes,* that is to say, for processes wherein all the *interior* work that may possibly be performed is subsequently cancelled, so that *exterior* work alone remains. After having brought the theorem to such a form that from its simplicity we may almost conclude with certainty that it cannot be limited to a special class of phenomena, but must be generally true, I have then applied it also to the *interior* work. I have been thereby led to the establishment of a general law for the dependence of the active force of heat upon the temperature, according to which *the effective force of heat is proportional to the absolute temperature.* By combining the equation which expresses this law with the equation which I had proved from the above axiom in the case of a cyclical process, I was led to the conclusion, *that the quantity of heat actually present in a body must depend on its temperature solely, and not upon the arrangement of its molecules.* If this conclusion be correct, the real thermal capacity of a body must not only be independent of its volume when its state of aggregation remains unaltered, but, contrary to Rankine's expressed opinion, it must also be independent of the state of aggregation.

The last result being obtained, the course of reasoning might perhaps be reversed. For if we assume, from the commencement, the truth both of the theorem, that the quantity of heat actually present in a body is independent of the arrangement of its molecules, and of the before mentioned law relative to the dependence of the effective force of heat on the temperature, we can prove therefrom the correctness of the equation which expresses for cyclical processes the second fundamental theorem of the mechanical theory of heat*. I cannot but think, however, that little encouragement would have been given to the physicist who should have proposed to start from the improved theorem relative to the heat actually present, which involves the con-

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* [It will, I think, be useful here to collect together the equations which express the above mentioned theorems in order to render perfectly clear the relation which exists between them.

Let $dL$ be the total work, or, in other words, the sum of the interior and exterior work done by the heat during the time that the body undergoes, in a reversible manner, an infinitesimal change of condition, and let T be the absolute temperature of the body at the moment this change of condition occurs, then the law that *the effective force of heat is proportional to the absolute temperature* is expressed by saying that the equation

$$\int\frac{dL}{T}=0$$

must hold for every reversible cyclical process.

The heat which must be imparted to the body during the above-mentioned infinitesimal change of condition, and whose quantity has always been denoted by $dQ$, consists of two parts, (1) the quantity $dH$, which serves to increase the heat H actually present in the body, and (2) the quantity $AdL$ consumed in the production of the work $dL$. We have, therefore, the equation

$$dQ=dH+AdL,$$

whence we deduce

$$dL=\frac{dQ-dH}{A}.$$

By the substitution of this value of $dL$, the above equation expressing the law relative to the effective force of heat assumes the form

$$\int\frac{dQ-dH}{T}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

The theorem that *the heat actually present in a body depends solely upon the temperature of the latter and not upon the arrangement of its molecules*, and therefore that the magnitude H, which denotes this heat, is a function of T solely, may be expressed by saying that the equation

$$\int\frac{dH}{T}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

holds for every cyclical process.

Lastly, *the second fundamental theorem of the mechanical theory of heat* is, for every cyclical process, expressed by the equation

$$\int\frac{dQ}{T}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

A glance at the three equations (a), (b), (c) is sufficient to show that each is a necessary consequence of the other two.—1866.]

sequence, that the real thermal capacity of a body may differ so far from the specific heat determined by observation, as to amount to less than half of the latter. A theorem which differs so much as this does from hitherto received notions, could only have a prospect of recognition on being supported by reasons which other considerations have rendered extremely probable. It appears to me, therefore, that this reversed mode of reasoning, although useful as elucidating the subject from another side, is not suitable for the purpose of demonstration.

Another circumstance which gives a preference to my mode of treating the subject is, that the fundamental theorem under consideration is proved thereby, so far as it refers to cyclical processes, without the assistance of any assumption whatever concerning the interior condition of a body, and that it is only on applying the theorem to interior work that the interior condition of the body, and in particular the quantity of heat present in the body, enters into consideration. Thence arises the advantage that the fundamental theorem, so far as it refers to cyclical processes, can be maintained unchanged, even by one who entertains doubts concerning the accuracy of the conclusion concerning the quantity of heat contained in the body*.

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* [Now that the theorem that the heat actually present in a body is independent of the arrangement of its molecules, and hence that its real thermal capacity is the same in all conditions, has gained a certain scientific foundation from the developments contained in the Sixth Memoir, we may possibly soon come to regard this theorem from the commencement no longer as improbable, but rather as theoretically probable. The theorem, too, may receive additional verification if the attention of many physicists be directed thereto. In this case it may hereafter appear more justifiable to deduce the equation

$$\int\frac{dQ}{T}=0,$$

which expresses for a reversible cyclical process the second fundamental theorem in the mechanical theory of heat, from the theorem mentioned in the text relative to the dependence of the effective force of heat upon the temperature, together with the theorem just alluded to concerning the heat actually present in a body; and this mode of deduction will possibly be not unfrequently employed, since it is both convenient and easily intelligible.

In doing so, however, it must not be forgotten that the two theorems upon which this mode of deduction is based, first acquired their credibility from the circumstance that they lead to an equation whose truth has been proved in another manner. The reduction of the equation, therefore, to such

7. A more definite objection to my axiom has recently been raised by Hirn, and it is from this that the present memoir principally originated, since the same objection appears to other authors to be valid.

In a former work, entitled *Recherches sur l'équivalent mécanique de la Chaleur,* Hirn opposed the theorem of the equivalence of heat and work. In his new work, *Exposition analytique et expérimentale de la théorie mécanique de la Chaleur,* he withdraws his former assertions relative to the equivalence, but opposes the axiom that heat cannot of itself pass from a colder to a warmer body. After the appearance of this work, he extended his views on the same subject, in two articles published in *Cosmos**. I replied in the same journal†; and he thereupon‡ explained that in bringing forward his objection, he only intended to direct attention to an *apparent* contradiction, for that essentially he agreed with me. I cannot but think, however, that his objection arises from an incorrect interpretation of my axiom, a misconception which certainly might easily be formed, and which on that account renders a thorough correction more necessary.

Hirn describes a peculiar operation invented by himself, the result of which he believes to be in contradiction to my axiom.

Let A and B, in fig. 9, represent two cylinders of equal cross section, connected at the bottom by a comparatively narrow tube, and in which move air-tight pistons; let the piston-rods be provided with teeth which fit on both sides into the teeth of a wheel situated between them, so that when one of the pistons descends the other must ascend to an equal extent. The total space consisting of the spaces underneath the pistons, and of the space enclosed by the tube connecting the

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theorems cannot exactly be regarded as a *proof* of the equation, but rather as a means of rendering its physical meaning clear. It will certainly be granted that at a time when those theorems were in nowise accepted, and when one of them indeed was at variance with views which were very widely entertained, this mode of deduction could not even have served to raise the probability of the truth of the equation in the minds of the scientific public.—1864.]

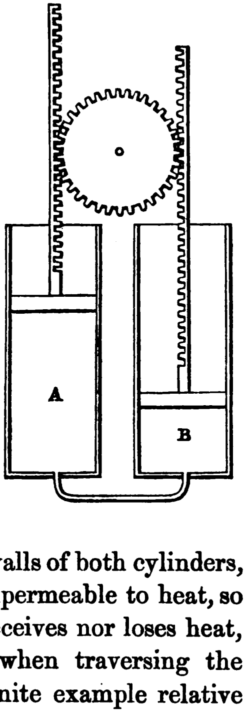
* Tome xxii. (Premier semestre, 1863) pp. 283 & 413.

† Ibid. p. 560.

‡ Ibid. p. 734.

two cylinders, must consequently remain invariable during the motion of the pistons; since every diminution of space in the one cylinder is accompanied by just as great an augmentation in the other.

Fig. 9.



Let us suppose that at the commencement one piston is quite at the bottom of the cylinder B, and consequently the other at the top of the cylinder A; and let us assume that the latter is filled with a perfect gas of a given density, whose temperature is $t_0$. Now let the piston in A gradually descend and consequently that in B ascend, so that the gas shall be gradually driven from the cylinder A to the cylinder B. Let us conceive, moreover, that the connecting tube through which the gas must pass is maintained constantly at a temperature $t_1$ higher than $t_0$, so that each quantity of gas which traverses the tube shall be thereby raised to the temperature $t_1$, and shall pass at this temperature into the cylinder B. The walls of both cylinders, on the contrary, shall be supposed to be impermeable to heat, so that the gas within the cylinder neither receives nor loses heat, but merely receives heat from without when traversing the connecting tube. In order to have a definite example relative to temperatures, we will suppose that the initial temperature of the gas in the cylinder A is that of the freezing-point 0°; the temperature of the connecting tube being 100°, as it would be, if, for instance, it were surrounded by the vapour of boiling water.

The result of this operation may now be understood without difficulty.

The first small quantity of gas which passes through the connecting tube has its temperature raised from 0° to 100°, and consequently expands proportionally, that is to say, by about the $\frac{100}{273}$th part of its original volume. The gas which is still in the cylinder A will thereby be somewhat compressed, and consequently the pressure in both cylinders will be increased. The next small quantity of gas which passes through the tube will likewise expand, and thereby compress the gas in both cylinders. In a similar manner every succeeding quantity of gas which passes through the tube contributes by its expansion not only to the still further compression of the gas remaining in A, but also to that of the gas already in B, which had previously expanded, so that the density of the latter gradually approaches to what it was before. The compression causes a heating of the gas in both cylinders; and since the quantities of gas which successively pass into the cylinder B have all the temperature 100° at their entrance, they must subsequently acquire temperatures above 100°; and, moreover, this excess of temperature must be greater the more the quantity in question is afterwards again compressed.

If we consider, therefore, the condition at the close of the operation, when all the gas has been forced from A into B, it is evident that the highest stratum of gas immediately under the piston, which first passed over and consequently suffered the greatest subsequent compression, must be the hottest. The underlying strata, taken in order down to the lowest, which possesses exactly the temperature 100° which it assumed on passing over, will be less and less heated.

For our present purpose it is not necessary to know the temperatures of the several strata individually, it will suffice to determine the *mean temperature*, which is also that temperature which would ensue if the temperatures existing in the several strata became equalized by conduction or by a mixture of the quantities of gas. This mean temperature amounts to about 120°.

In an article which subsequently appeared in *Cosmos*, Hirn completed this operation by supposing the gas in B, after being heated, to be brought into contact with quicksilver at 0°, and thereby cooled again to 0°; and then he supposed the gas to be driven back from B to A under the same circumstances under which it had arrived from A to B, and thus that it became heated in the same manner; then he again supposes it to be cooled by quicksilver, subsequently again driven from A to B, and so on, so that a periodical process is obtained by which the gas continually returns to its initial state, and all the heat given up by the source of heat ultimately passes to the quicksilver used in cooling. We will not, however, here enter into the extension of this procedure, but will limit ourselves to the consideration of the previously described simple operation through which the gas is heated from 0° to a mean temperature of 120°; for this operation already contains the essential parts whereon the objection of Hirn is based.

8. In this operation external work is neither gained nor lost; for since the pressure in both cylinders is always the same, both pistons are pressed upwards at each instant with equal force, and these forces destroy one another on the toothed wheel upon which the teeth of the piston rods work; so that, disregarding friction, the smallest force would be sufficient to cause a rotation of the toothed wheel in one sense, or in the other, and thereby a descent of the one piston and ascent of the other. The excess of heat in the gas, therefore, cannot be generated by exterior work, and there can of course be no question of interior work, since the latter is altogether excluded by the hypothesis of a perfect gas.

The process is manifestly the following. When a quantity of gas, very small in proportion to the whole quantity under consideration, becomes heated in the connecting tube and thereby expanded, it must receive from the source as much heat as is requisite to elevate its temperature *under constant pressure.* Of this quantity one portion serves to increase the heat actually present in the gas, and another portion is consumed by the work of expansion. But since the expansion of the gas in the tube necessitates a compression of that in the cylinder, just as much heat must here be generated as was there consumed. This second portion of the heat given up by the source, and which has become transformed to work in the tube, appears again in the cylinders, therefore, as heat, and serves to heat the gas still in A above its initial temperature 0°, and to heat the gas already in B, which at its entrance had the temperature 100°, above this temperature, and thus to bring about the above-mentioned excess of temperature.

Consequently, without taking the intermediate processes into consideration, we may say that the entire quantity of heat which the gas contains at the end of the operation above that which it had at first, proceeds from the source of heat surrounding the connecting tube. We thereby arrive at the peculiar result, that the enclosed gas is heated above 100°, viz. to a mean temperature of 120°, by means of a body at 100°, that is to say, by the aqueous vapour surrounding the connecting tube. Hirn finds in this a contradiction of the axiom, that heat cannot of itself pass from a colder to a warmer body, since, according to his representation, the heat given by the vapour to the gas has passed from a body at 100° to another at 120°.

9. In so doing, however, he has overlooked one circumstance. If the gas had had at the commencement a temperature of 100°, or more, and had then been raised to a still higher temperature by vapour which had only a temperature of 100°, then a contradiction to my axiom would certainly have presented itself. The state of the case, however, is different. In order that at the end of the operation the gas may be warmer than 100°, it must necessarily be colder than 100° at the commencement, and in our example, where at the conclusion it has a temperature of 120°, it had at the commencement a temperature 0°. The heat imparted by the vapour to the gas, therefore, has served partly to raise the gas from 0° to 100°, and partly to bring it from 100° to 120°.

Now since the temperatures alluded to in my axiom are those which the bodies between which the transfer of heat takes place, possess at the moment when they receive or lose heat, and are not those which the bodies subsequently possess, we must form the following conception of the transfer of heat which takes place in this operation. One part of the heat given up by the vapour has passed into the gas during the time that its temperature was still below 100°, has passed therefore from the vapour into a colder body; it is only the other portion of the heat, viz., that which serves to raise the gas above 100°, which has passed from the vapour to a warmer body.

If we compare this with the principle according to which, whenever heat is to pass from a colder to a warmer body without either a transformation from work into heat, or a change in the molecular condition of a body, other heat must necessarily pass in the same operation from a warmer to a colder body, it will be at once manifest that a complete accordance exists. The peculiarity presented by the operation which Hirn has conceived, consists solely in the fact, that there are not two different bodies of which one is colder and the other warmer than the source of heat, but that one and the same body, the gas, plays in one portion of the operation the part of a colder, and in the other portion of the operation the part of a warmer body. This involves, however, no departure from my axiom, it is merely a special case of the many possible cases. Hirn's misconception has arisen from his directing his attention to the final temperature solely, instead of taking into account the different temperatures which the gas possesses successively during the course of the operation.

10. The subject may be further represented in a somewhat different manner, and by so doing a conception will come under discussion, which I have introduced in my last memoir*, and which in my opinion is of great importance in the theory of heat; I refer to the *transformation-value* of the heat contained in a body. I wish in conclusion to consider this subject, since an explanation of this conception will perhaps powerfully contribute to prevent misconceptions of the before mentioned kind.

In my memoirs I have given the term transformation to the passage of heat from a body of one temperature to a body at another temperature, since it may be said that heat of a certain temperature is transformed to heat of another temperature. This process is thereby brought into parallelism with two other processes, which may also be termed transformations, that is to say, with the transformations of heat into work, and *vice versâ*, and with the transformation which I have designated as a change of "disgregation." In order to be able to distinguish in a suitable mathematical manner the direction of the passage of heat, I have called the passage from a warmer to a colder body a positive transformation, and the passage from a colder to a warmer body a negative one; accordingly the above axiom may be expressed by saying that a negative transformation cannot occur of itself, that is to say, without being accompanied in the same operation by a positive transformation, whilst a

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* [Sixth Memoir of this collection.]

positive transformation, on the contrary, can very well take place without being accompanied by a negative one.

On applying this to the above described operation, in which a quantity of gas is heated to 120° by means of heat proceeding from vapour at 100°, the question arises how the heat contained in a body must be considered when we wish to determine its temperature. Can we, in fact, consider all the heat contained in a body of the temperature $t$, simply as heat of the temperature $t$, or must we ascribe other temperatures to this heat?

If the first were the case, that is to say, if the heat contained in a body of the temperature $t$ were to be considered throughout as heat of the temperature $t$, we should, through the above described operation conceived by Hirn, arrive at a result in contradiction to my axiom, for we should have to reason thus. The heat contained in the aqueous vapour is heat of 100°. If by means of a portion of this heat the gas is raised to 120°, this portion is present in the gas as heat of 120°, and consequently whatever the intermediate temperatures may have been, a certain quantity of heat becomes ultimately transformed from heat of 100° to heat of 120°.

This is not the conception, however, from which I started when formulizing the theorem of the equivalence of transformations.

When a body is heated, a portion of the heat which must be imparted to it for this purpose, is in general consumed in exterior and interior work (provided the body by being heated changes its volume and the arrangement of its molecules), and the other portion serves to increase the heat actually present in the body. We may here neglect the first portion, and limit ourselves solely to the consideration of the second. If we now conceive the body to be raised from any initial temperature $t_0$ to any other temperature $t$, it will not receive all the heat which is necessary thereto at the temperature $t$, but it will receive the different elements of this heat at different and gradually increasing temperatures, so that to each element of heat a definite temperature will correspond. If, on the other hand, the body be cooled, it will not give off all the heat which is necessary thereto at one and the same temperature, but it will part with different elements at different and gradually sinking temperatures.

Now, when we speak of the temperature of the heat contained in a body, we must not, according to my view, ascribe one and the same temperature to the whole quantity of heat; we must rather conceive this whole quantity to be divided into an infinite number of elements, and to each element we must consider that temperature to correspond which the body on cooling would have at the moment when it parted with this element, or that which on being heated it would have at the moment when it received this element of heat.

11. In the memoir above alluded to I gave a simple mathematical magnitude in which the temperatures of the several elements of heat were taken into account in the manner required by the theorem of the equivalence of transformations, and I termed this magnitude the *transformation-value* of the body's heat.

In fact, if we conceive that the heat which serves to raise the temperature of a given body (and of which, as before said, we only consider the portion which is finally present as heat in the body, and not the portion which may have been consumed in work consequent upon the change of condition caused by heating) has proceeded, in some manner or other, from the transformation of work into heat, we may determine the *equivalence-value* of the transformation of each element of heat thus generated. Let T denote the temperature of the body counted from the *absolute zero*, and let us suppose this temperature to be increased by $dT$, the increase which thereby takes place in the heat actually present in the body will then be represented by the product $mcdT$; wherein $m$ denotes the mass of the body, and $c$ its real thermal capacity. The equivalence-value of the transformation from work to heat, from which this element of heat has proceeded, will be expressed by the fraction

$$\frac{mcdT}{T}.$$

If we apply this to the determination of the quantity of heat which must be added to that present in the body, in order to raise it from the given inital temperature $T_0$ to another temperature T, the equivalence-value of the transformation from which this quantity of heat, with its temperatures rising from element to element has proceeded, will be represented by the integral

$$\int_{T_0}^{T} \frac{mcdT}{T},$$

which I have called the *transformation-value* of the body's heat estimated from a given initial temperature.

If it were required to determine the transformation-value of the entire quantity of heat present in the body, we should have to conceive the body to be heated from the *absolute zero* up to the absolute temperature T under consideration, and consequently to put 0 as the lower limit of the above integral. The value of the integral would thereby become infinitely great, since the product *mc*, which appears in the numerator, cannot vanish. In order, therefore, to obtain a finite value for the integral, it is necessary to start from a *finite* absolute temperature as a lower limit, and consequently not to determine the transformation-value of the entire heat present in the body, but only that of the additional quantity of heat which the body at its present temperature possesses above what it had at the temperature chosen as the starting-point for heating.

The actual integration is rendered very simple by the help of a deduction previously drawn by me. In fact, for reasons into which I will not here enter, I concluded that the real thermal capacity of a body is not only independent of its molecular arrangement, but also of its temperature. We may consequently place the real thermal capacity *c*, together with the mass *m*, as factors before the sign of integration, whereby the integral becomes

$$mc\int_{T_0}^{T} \frac{dT}{T} = mc \log \frac{T}{T_0}.$$

Should this last simplification, however, not be deemed a sufficiently well grounded one, should it, in fact, be deemed desirable to regard *c* as a still unknown function of the temperature, it would merely be necessary to change, somewhat, the form of the expression for the tranformation-value of the body's heat, the conception of a transformation-value would thereby suffer no essential alteration.

By the introduction of this new conception, we can very easily and with perfect accuracy characterize the changes which may spontaneously occur in the distribution of heat. If we conceive any process whatever such that ultimately no other transformations remain except passages of heat between bodies of different temperatures, all other transformations which may possibly occur in the course of the process being again cancelled by opposite transformations which likewise occur therein, we may enunciate the following general theorem relative to passages of heat, and the changes in the distribution of heat consequent thereon. The change which occurs by such a process in the distribution of heat can only be such *that the sum of the transformation-values of the heat in the several bodies is thereby increased or in the limit remains unchanged*; it can never be such *that the sum of the transformation-values diminishes thereby.*

If we test in this manner the result of the operation above considered, by which a quantity of gas has its temperature raised from 0° to 120° by means of the heat arising from vapour at 100°, we shall find that here also the sum of the transformation-values of the heat contained in the vapour and in the gas increases, and that accordingly the theorem of the equivalence of transformations, and the axiom from which it is deduced, is simply verified by this operation*.

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* [I regret very much that I have here been compelled to dissent from Hirn's expositions of the second fundamental theorem in a manner similar to that in which, on a former occasion, I found it necessary to declare myself opposed to his view of the first fundamental theorem of the mechanical theory of heat. I feel convinced, however, that no one will think of reproaching him for having raised the objection which has been discussed in the present memoir.

The second fundamental theorem of the mechanical theory of heat, and all that depends thereupon, is much more difficult to understand than the first fundamental theorem, and the way in which Hirn has interpreted the former is, in fact, as has already been mentioned, not an unnatural one, so that in all probability others may also have encountered the same difficulty. Under these circumstances the objection raised by Hirn was fully justified from a scientific point of view; and when, as in the present case, an objection of this kind is made with such clearness and precision, and accompanied by so ingenious an illustration as the operation conceived by Hirn, science can only derive profit therefrom; such a procedure, in fact, deserves to be regarded as a meritorious one. The exposition of the subject is very much facilitated by the definite and clear elucidation of the apparent contradiction, and in this manner the advantage is gained of at once and for ever settling a difficulty which, otherwise perhaps, might have given rise to many misconceptions and rendered necessary frequent and long discussions.—1864.]

# EIGHTH MEMOIR.

## ON THE CONCENTRATION OF RAYS OF HEAT AND LIGHT, AND ON THE LIMITS OF ITS ACTION*.

THE starting-point of my treatment of the second fundamental theorem in the mechanical theory of heat, was the difference which exists between the transfer of heat from a warmer to a colder body, and that from a colder to a warmer one; the former may, but the latter cannot, take place of itself. This difference between the two kinds of transmission being assumed from the commencement, it can be proved that an exactly corresponding difference must exist between the conversion of work into heat, and the transformation of heat into work; that heat, in fact, cannot simply transform itself into work (another simultaneous change, serving as a compensation, being always necessary thereto), whereas the opposite transformation of work into heat may occur without compensation.

A general and prevailing tendency in nature to changes of a certain character is indicated by these principles, and the latter may be extended in a similar manner to a third action, affecting the changes of the condition of bodies; into this, however, I do not propose to inquire here. On applying the above considerations to the universe as a whole, we arrive at the remarkable conclusion to which W. Thomson first drew attention†, he having then admitted the truth of the modification applied by me to Carnot's theorem, and adopted my conception of the second fundamental theorem in the mechanical theory of heat. For if in the universe cases continually occur, through friction or other similar impediments to motion, of the conversion into heat, that is to say, into molecular motions, of the motions with which large masses are animated, and which are due, either

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* Communicated June 22, 1863, to the Natural Science Association of Zurich, and published in Poggendorff's *Annalen* for January 1864, vol. cxxi. p. 1.

† Phil. Mag. S. 4. vol. iv. p. 304.

actually or conceivably, to work done by natural forces; and if, further, heat always strives to alter its distribution, so that existing differences of temperature may be cancelled, then the universe must gradually be approaching more and more to the condition in which forces can produce no further motion, and differences of temperature can no longer exist.

This conclusion suggested to Rankine his paper "On the Reconcentration of the Mechanical Energy of the Universe"*, wherein the question is examined whether, to counterbalance the above processes whereby mechanical energy becomes more and more dissipated, another of an opposite effect is not conceivable, whereby mechanical energy may be again concentrated and stored up in individual masses.

After having spoken of the manifold ways in which heat may be produced by the work of natural forces, and of the incessant tendency of heat to distribute itself amongst bodies so as to annul existing differences of temperature, and after adding that the heat present in bodies has also a tendency to become converted into radiant heat, so that all the bodies in the universe continually give off more and more heat to the æther which pervades space, Rankine continues†:—

"Let it now be supposed that, in all directions round the visible world, the interstellar medium has bounds beyond which there is empty space.

"If this conjecture be true, then on reaching those bounds the radiant heat of the world will be totally reflected, and will ultimately be reconstituted into foci. At each of these foci, the intensity of heat may be expected to be such that, should a star (being at that period an extinct mass of inert compounds) in the course of its motions arrive at that part of space, it will be vaporized and resolved into its elements, a store of chemical power being thus reproduced at the expense of a corresponding amount of radiant heat.

"Thus it appears that, although, from what we can see of the known world, its condition seems to tend continually towards the equable diffusion, in the form of radiant heat, of all physical energy, the extinction of the stars, and the cessation of all phenomena, yet the world, as now created, may possibly be pro-

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* Phil. Mag. S. 4. vol. iv. p. 358.

† Ibid. p. 360.

vided within itself with the means of reconcentrating its physical energies, and renewing its activity and life."

According to this, Rankine appears to think it possible so to concentrate rays of heat by reflexion, that in the foci thereby produced, a body may be heated to a temperature higher than that of the bodies which emitted the rays. If this view were correct, the principle assumed by me as an axiom, that heat cannot of itself pass from a colder to a warmer body, would be false, and as a consequence the proof, founded on this axiom, of the second fundamental theorem in the mechanical theory of heat would have to be rejected.

The wish to put the truth of the axiom beyond all doubt of this kind, and the fact that, apart from this special question, the concentration of rays of heat, with which that of luminous rays is closely connected, is a subject offering many points of interest, have induced me to submit to closer mathematical investigation the laws which govern the concentration of rays, and the influence which the latter may have on the interchange of rays between bodies. The results of this investigation I propose here to communicate.

### I. *Insufficiency of the previous determination of the mutual radiation between two surfaces for the case now under consideration.*

1. When two bodies are placed in a medium penetrable by rays of heat, they transmit heat to each other by radiation. In general, one portion of the rays which fall on a body is absorbed, whilst another portion is partly reflected and partly transmitted; and it is well known that the powers of absorption and emission have a simple relation to each other. As it forms no part of our present object to examine the variations and regularities involved in this relation, we will take the simple case where the bodies under consideration have the property of at once completely absorbing all incident rays, either at their surfaces, or within a stratum so thin that its thickness may be neglected. Such bodies have been denominated *perfectly black* by Kirchhoff in his well-known and remarkable memoir on the relation between emission and absorption*.

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* Poggendorff's *Annalen*, vol. cix. p. 275, and Phil. Mag. S. 4. vol. xx. p. 1.

Bodies of this kind have also the greatest possible emissive power, and it has long been assumed as certain that the intensity of their emission depends solely upon their temperature; so that at the same temperature all perfectly black bodies radiate the same amount of heat from equally large portions of their surfaces; now, since the rays which a body emits are not homogeneous, but of different colours, the emission must be considered specially with respect to the different colours: Kirchhoff accordingly has completed the above theorem by showing that perfectly black bodies at the same temperature not only radiate the same total amount of heat, but also equal quantities of every particular kind of heat; moreover, since, in our investigation, these particularities are likewise to be excluded from consideration, we shall always assume in future that we are solely concerned with rays of a particular kind, or more strictly, with rays whose wave-lengths vary only within infinitely small limits. For whatever holds for one kind of rays being, in a corresponding manner, true for every other kind, the results found for homogeneous heat may without difficulty be extended to heat consisting of different kinds of rays.

To avoid unnecessary complications, we will likewise disregard all phenomena of polarization, and assume that we have to deal with unpolarized rays solely. Helmholtz and Kirchhoff have explained how polarization will have to be taken into account in considerations of this kind.

2. Let $s_1$ and $s_2$ be given surfaces of any two perfectly black bodies of the same temperature, and upon them let any two elements, $ds_1$ and $ds_2$, be selected with a view of determining and comparing the quantities of heat which they mutually transmit to each other by radiation. When the medium which surrounds the bodies and fills the intervening space is homogeneous, so that the rays proceed in right lines from one surface to the other, it is easy to see that the quantity of heat which the element $ds_1$ sends to $ds_2$ must be just as great as that which $ds_2$ sends to $ds_1$. If, however, the medium which surrounds the bodies is not homogeneous, but of such a character as to cause refractions and reflexions, the procedure is less simple, and a more careful consideration is necessary in order to convince ourselves that here also the above perfect reciprocity still exists. Kirchhoff has examined this question in a very elegant manner,

and I will here briefly give his results so far as they have reference to the case, where the rays suffer no diminution of intensity on their way from one element to the other, that is to say, where the refractions and reflexions occur without loss, and the propagation is not accompanied by absorption. In doing so I shall merely change, to some extent, his notation and his system of coordinates in order to secure a closer agreement with what will follow.

Of the infinite number of rays which one of two given points emits, only one can in general attain the other; or should more do so in consequence of refractions and reflexions, their number will at all events be limited, and each can be considered individually*. The path pursued by a ray which, starting from one of the two points, arrives at the other, is determined on the principle that the time required to traverse it is less than that which any other adjacent path would have demanded. This *minimum* time, which, with Kirchhoff, we will denote by T, is determined by the positions of the two points, a single ray being, of course, selected for consideration in the case where many separate rays present themselves.

Returning now to the two elements $ds_1$ and $ds_2$, we will conceive tangent planes to each surface drawn at a point of each element, and consider $ds_1$, $ds_2$ as elements of these planes. In each of the latter we will introduce an arbitrary system of rectangular coordinates, $x_1, y_1$ and $x_2, y_2$†. If in each plane we now take a point, the time T, which the ray requires to travel

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* That a *point* can emit an infinite number of rays may perhaps be regarded, from a strictly mathematical point of view, as an incorrect mode of expression; since a *surface* only, not a mathematical point, can radiate heat or light. It would accordingly be more correct to refer the radiation of light and heat to a surface-element in the vicinity of the point, instead of to the point itself. Nevertheless, since the notion of a ray is itself a pure mathematical abstraction, the conception of an infinity of rays proceeding from each point of a surface may be retained without fear of any misunderstanding arising therefrom. When the *quantity* of heat or light which a surface radiates has to be determined, the magnitude of the surface will of course enter into consideration, and when the surface is divided into elements, these elements will not be points but infinitesimal surfaces, whose magnitudes will enter as factors into the formulæ which represent the quantities of heat or light radiated from these surface-elements.

† Kirchhoff placed his coordinate systems in two planes perpendicular to the directions of the ray in the vicinity of the two surface-elements, and upon these planes he likewise projected the elements.

from one to the other, is, as above remarked, determined by the positions of the two points, and accordingly is to be regarded as a function of the four coordinates of the two points.

This granted, the following is, according to Kirchhoff*, the expression for the quantity of heat which the element $ds_1$ sends to the element $ds_2$ during the unit of time,

$$\frac{e_1}{\pi}\left(\frac{d^2\mathrm{T}}{dx_1\,dx_2}\cdot\frac{d^2\mathrm{T}}{dy_1\,dy_2}-\frac{d^2\mathrm{T}}{dx_1\,dy_2}\cdot\frac{d^2\mathrm{T}}{dy_1\,dx_2}\right)ds_1\,ds_2,$$

wherein $\pi$ denotes the ratio of the circumference to the diameter of a circle, and $e_1$ is the intensity of the emission of the surface $s_1$ at the element $ds_1$, so that $e_1\,ds_1$ represents the total quantity of heat which the element $ds_1$ radiates during the unit of time.

In order to obtain the expression for the quantity of heat which $ds_2$ sends to $ds_1$, we have only to replace $e_1$ in the preceding expression by the intensity of emission $e_2$ of the surface $s_2$ at the element $ds_2$. Everything else remains unchanged; for the expression is symmetrical with respect to the two elements; since the time T which a ray requires in order to traverse the path between two points of the two elements is the same in whichever direction the ray moves. If, now, we assume that the two surfaces, when at the same temperature, radiate equal quantities of heat (that, in short, $e_1=e_2$), it will follow that the element $ds_1$ must send just as much heat to $ds_2$ as $ds_2$ sends to $ds_1$.

3. It was stated above that between two given points only one ray, or a limited number of rays, was in general possible. In particular cases, however, it may happen that an *infinite number* of the rays, which proceed from one point, may converge to the other, and these may either fill a part of the surface of a cone, or of the solid angle formed by a cone. The same applies obviously to rays of light as well as to rays of heat, and in optics it is customary to call the point to which the rays proceeding from a given point and filling a conical space converge, the *image* of the latter point, or since the first point may also be the image of the second, the two are called *conjugate foci*. When what has here been said of two isolated points applies

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* Pogg. *Ann.* vol. cix, p. 286; Phil. Mag. S. 4. vol. xx. p. 9.

to all the points of two surfaces, so that every point of the one surface has its conjugate focus at a point on the other, one surface is said to be the optical image of the other.

The question now arises, how does the ray-interchange take place between the elements of two such surfaces? Is the above reciprocity still maintained; in other words, the temperatures being equal, does each element of the one surface send to an element of the other surface exactly as much heat as it receives therefrom? If so, one body could not raise another to a higher temperature than its own; if otherwise, then by the concentration of rays it would be possible for one body to raise another to a higher temperature than it possesses itself.

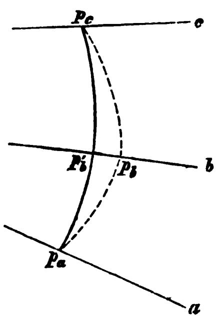
Kirchhoff's expression is not directly applicable to the case under consideration. For if the surface $s_2$ were the optical image of $s_1$, then the rays proceeding from a point $p_1$ of the surface $s_1$, and filling a certain cone, would converge to a determinate point $p_2$ of the surface $s_2$, and none of the points of $s_2$ adjacent to $p_2$ would receive rays from $p_1$, consequently the coordinates $x_1$, $y_1$ of the point $p_1$ being given, the coordinates $x_2$, $y_2$ of the point $p_2$ will no longer be arbitrary, but perfectly determined; and similarly, when $x_2$, $y_2$ are given, the coordinates $x_1$, $y_1$ will be determined. Accordingly no real magnitude of a finite value can be represented by a differential coefficient of the form $\frac{d^2T}{dx_1\,dx_2}$, wherein, when differentiating according to $x_1$, the coordinate $x_1$ is to be regarded as variable, whilst the second coordinate $y_1$ of the same point, as well as the coordinates $x_2$, $y_2$ of the other point, are to be considered as having constant values, and similarly, when differentiating according to $x_2$ the coordinate $x_2$ is to be considered variable, whilst $y_2$, $x_1$, $y_1$ remain constant.

In this case, therefore, an expression of a form somewhat different from that of Kirchhoff's must be found, and to this end the following considerations, similar in kind to those which led Kirchhoff to his own expression, will be of service.

## II. *Determination of corresponding points and of corresponding surface-elements in three planes intersected by rays.*

4. Let three planes *a, b, c* be given, of which *b* lies between *a* and *c* (fig 10). In each plane let a system of coordinates be established, and let the latter be denoted respectively by $x_a, y_a$; $x_b, y_b$; and $x_c, y_c$. If a point $p_a$ be given in the plane *a,* and a point $p_b$ in the plane *b,* and we consider a ray passing from one to the other, we shall have for the determination of its path the condition, that the time required for its passage thereon will be a *minimum* when compared with the times of passage along all neighbouring paths. Let $T_{ab}$ denote this *minimum* time, which will be a function of the coordinates $x_a, y_a$, and $x_b, y_b$ of the points $p_a$ and $p_b$. In a similar manner let $T_{ac}$ be the time of passage of the ray between the two points $p_a$ and $p_c$ in the planes *a* and *c,* and $T_{bc}$ the time required for a ray to pass from one to the other of the points $p_b$ and $p_c$ in the planes *b* and *c.* We must consider $T_{ac}$ as a function of the four quantities $x_a, y_a, x_c, y_c$, and $T_{bc}$ as a function of $x_b, y_b, x_c, y_c$.

Fig. 10.



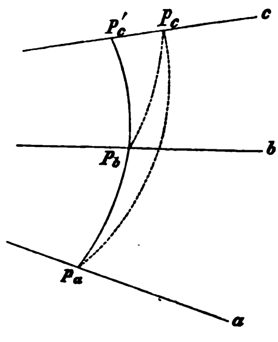
Now since a ray, which passes through two planes, also cuts in general the third, we have for each ray three intersections which are so related to one another, that in general any one is determined by the other two. Suitable equations for this determination may be easily established by help of the above condition.

We will first assume the points $p_a$ and $p_c$ in the planes *a* and *c* (fig. 10) to be immediately given; the point where the ray cuts the intermediate plane *b* being still unknown, shall be represented by $p'_b$ in order to distinguish it from other points in that plane. We will now select any point $p_b$ whatever in the plane *b,* and consider two *auxiliary* rays, of which one passes from $p_a$ to $p_b$, and the other from $p_b$ to $p_c$. In fig. 10 the auxiliary rays are denoted by broken lines, and the principal ray, proceeding directly from $p_a$ to $p_c$, with which we are really concerned, is shown by a full line*. If in accordance with the preceding we call $T_{ab}$, $T_{bc}$ the times corresponding to the two auxiliary rays, and form the sum $T_{ab}+T_{bc}$, the value of the latter will depend upon the position of the selected point $p_b$, and must accordingly be considered as a function of the coordinates $x_b$, $y_b$ of $p_b$; since the points $p_a$ and $p_c$ are supposed to be given. Now of all the values which this sum can acquire by giving to the point $p_b$ different positions in the vicinity of the point $p'_b$, the one obtained on allowing $p_b$ to coincide with $p'_b$, and thus causing the two auxiliary rays to coincide with portions of the direct one proceeding from $p_a$ to $p_c$, must be a *minimum*. Hence to determine the coordinates of the point $p'_b$, we have the following two equations of condition,

$$\frac{d(T_{ab}+T_{bc})}{dx_b}=0; \quad \frac{d(T_{ab}+T_{bc})}{dy_b}=0. \quad . \quad . \quad (1)$$

Since the quantities $T_{ab}$ and $T_{bc}$, besides the coordinates $x_b$, $y_b$ of the previously unknown point, likewise contain the coordinates $x_a$, $y_a$ and $x_c$, $y_c$ of the points previously supposed to be given, the two preceding equations, once established, may be regarded simply as two equations between the six coordinates of the three points in which the three planes are intersected by one and the same ray.

Fig. 11.



We will now regard as previously given, the two points $p_a$ and $p_b$, in which the ray intersects the planes $a$ and $b$ (fig. 11), and as unknown the point $p'_c$, in which it cuts the plane $c$. We will then select any point $p_c$ whatever in the plane $c$, and consider the two auxiliary rays passing, respectively, from $p_a$ to $p_c$, and from $p_b$ to $p_c$. In the figure, the latter are again indicated by broken lines, and the principal ray by a full line. Calling the times of passage along

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* The paths of the rays are drawn somewhat curved in the figure, merely

the auxiliary rays $T_{ac}$ and $T_{bc}$, the difference, $T_{ac}-T_{bc}$, will be dependent upon the position in the plane $c$ of the selected point $p_c$. Of all the values acquired by this difference when the point $p_c$ is placed near the point $p'_c$, none will be so great as that which results from making $p_c$ coincide with $p'_c$. For in this case the ray proceeding from $p_a$ to $p_c$ cuts the plane $b$ in the given point $p_b$, and consequently it consists of the rays passing from $p_a$ to $p_b$, and from $p_b$ to $p_c$. We may therefore put

$$T_{ac}=T_{ab}+T_{bc},$$

and hence deduce the equation

$$T_{ac}-T_{bc}=T_{ab}$$

for the difference under consideration. But should the point $p_c$ not coincide with $p'_c$, the ray proceeding from $p_a$ to $p_c$ would not coincide with the two rays from $p_a$ to $p_b$, and from $p_b$ to $p_c$, and the direct ray between $p_a$ and $p_c$ being the one which corresponds to the least time of passage, we should have the inequality

$$T_{ac}<T_{ab}+T_{bc},$$

whence we should deduce for the difference under consideration the inequality

$$T_{ac}-T_{bc}<T_{ab},$$

that is to say, the difference $T_{ac}-T_{bc}$ could in general be smaller than in the foregoing special case, where the point $p_c$ lay in the production of the ray proceeding from $p_a$ to $p_b$; that particular value of the difference, therefore, is a *maximum**. Hence we

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to indicate that the path pursued by a ray between two given points is not necessarily the right line which connects these points, but that, in consequence of refractions and reflexions, another route may be imposed upon it which may consist either of a broken line composed of several straight ones, or of a curved line, according as the medium traversed by the ray changes suddenly or gradually.

* In Kirchhoff's memoir, p. 285 (p. 8 of translation), the quantity is stated to be a *minimum*, which corresponds essentially to the difference last considered,—the only modification being that Kirchhoff's quantity has reference

again deduce two equations of condition; namely,

$$\frac{d(\mathrm{T}_{ac}-\mathrm{T}_{bc})}{dx_c}=0\,; \quad \frac{d(\mathrm{T}_{ac}-\mathrm{T}_{bc})}{dy_c}=0. \quad . \quad . \quad . \qquad (2)$$

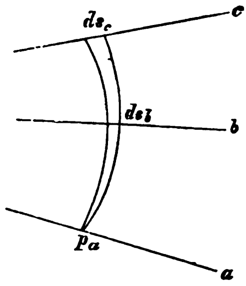
If, lastly, we suppose the points $p_b$ and $p_c$ in the planes *b* and *c* to be given, and regard the point where the ray cuts the plane *a* as unknown, we obtain the following two equations by a process of reasoning which, being precisely similar to the foregoing, may be here omitted:—

$$\frac{d(\mathrm{T}_{ac}-\mathrm{T}_{ab})}{dx_a}=0\,; \quad \frac{d(\mathrm{T}_{ac}-\mathrm{T}_{ab})}{dy_a}=0. \quad . \quad . \quad . \qquad (3)$$

We have thus arrived at three pairs of equations, of which each pair may serve to express the mutual relation which exists between the three points in which a ray intersects the three planes *a*, *b*, *c*, and this in such a manner that, whenever two of the points are given, the third can be found; or still more generally, when of the six coordinates of the three points any four are given, the remaining two may be determined.

5. We will now consider the following problem. Let a point $p_a$ be given in one of the three planes, say *a*, and in a second plane *b*, a surface-element $ds_b$. If we conceive the rays which proceed from the point $p_a$ to the several points of $ds_b$ to be continued until they reach the third plane *c*, they will in general determine on the plane *c* an infinitesimal surface-element $ds_c$ (see fig. 12); required the ratio of the surface-elements $ds_b$ and $ds_c$.

Fig. 12.



In this case two, $x_a$ and $y_a$, of the six coordinates of the three points in which each ray intersects the three planes are given. Hence any values of the coordinates $x_b$, $y_b$ being assumed, the

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to four planes instead of three. This error is probably typographical; whatever its origin, however, a substitution of the term *minimum* for *maximum* at that place involves no further error, since the theorem, that the differential coefficients must vanish, which is employed in the calculations which follow, holds for a maximum as well as for a minimum.

coordinates $x_c$, $y_c$ are thereby in general determined. In this case, therefore, each of the coordinates $x_c$ and $y_c$ may be regarded as a function of the two coordinates $x_b$, $y_b$.

If we suppose the arbitrary form of the surface-element $ds_b$ to be that of a rectangle $dx_b \, . \, dy_b$, and seek the points in $c$ which correspond to the several points of its contour, we shall obtain in the latter plane an infinitesimal parallelogram for the form of the corresponding element $ds_c$. Irrespective of its sign, the magnitude of this parallelogram will be represented, according to simple geometrical principles, by

$$\left(\frac{dx_c}{dx_b} \cdot \frac{dy_c}{dy_b} - \frac{dx_c}{dy_b} \cdot \frac{dy_c}{dx_b}\right) dx_b \, . \, dy_b.$$

The circumstance that in the determination of this surface-element the absolute magnitude alone is considered, shall be indicated by prefixing the letters *v.n.* (*valor numericus*) to the differential expression which may itself have a positive or negative value. We may then write

$$ds_c = v.n. \left(\frac{dx_c}{dx_b} \cdot \frac{dy_c}{dy_b} - \frac{dx_c}{dy_b} \cdot \frac{dy_c}{dx_b}\right) ds_b. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

To determine the relation which exists between the coordinates $x_c$, $y_c$ and the coordinates $x_b$, $y_b$, we must employ one of the three pairs of equations in Art. 4. To this end we will first employ the two equations (1). On differentiating the latter according to $x_b$ and to $y_b$, and remembering that each of the quantities denoted by T contains those two of the three pairs of coordinates $x_a$, $y_a$; $x_b$, $y_b$; $x_c$, $y_c$ which are indicated by its suffixes, and that $x_c$ and $y_c$ have to be treated as functions of $x_b$ and $y_b$, whilst $x_a$ and $y_a$ are to be regarded as constants, we obtain the following four equations:—

$$\left.\begin{aligned}
&\frac{d^2(\mathrm{T}_{ab}+\mathrm{T}_{bc})}{(dx_b)^2}+\frac{d^2\mathrm{T}_{bc}}{dx_b\,dx_c}\cdot\frac{dx_c}{dx_b}+\frac{d^2\mathrm{T}_{bc}}{dx_b\,dy_c}\cdot\frac{dy_c}{dx_b}=0,\\
&\frac{d^2(\mathrm{T}_{ab}+\mathrm{T}_{bc})}{dx_b\,dy_b}+\frac{d^2\mathrm{T}_{bc}}{dx_b\,dx_c}\cdot\frac{dx_c}{dy_b}+\frac{d^2\mathrm{T}_{bc}}{dx_b\,dy_c}\cdot\frac{dy_c}{dy_b}=0,\\
&\frac{d^2(\mathrm{T}_{ab}+\mathrm{T}_{bc})}{dx_b\,dy_b}+\frac{d^2\mathrm{T}_{bc}}{dy_b\,dx_c}\cdot\frac{dx_c}{dx_b}+\frac{d^2\mathrm{T}_{bc}}{dy_b\,dy_c}\cdot\frac{dy_c}{dx_b}=0,\\
&\frac{d^2(\mathrm{T}_{ab}+\mathrm{T}_{bc})}{(dy_b)^2}+\frac{d^2\mathrm{T}_{bc}}{dy_b\,dx_c}\cdot\frac{dx_c}{dy_b}+\frac{d^2\mathrm{T}_{bc}}{dy_b\,dy_c}\cdot\frac{dy_c}{dy_b}=0.
\end{aligned}\right\}\quad\ldots\quad(5)$$

The required relation between the elements $ds_b$ and $ds_c$ is now obtained by substituting the values of $\frac{dx_c}{dx_b}, \frac{dx_c}{dy_b}, \frac{dy_c}{dx_b}, \frac{dy_c}{dy_b}$, as determined by these equations in the equation (4). In order to exhibit the result of this substitution in an abbreviated form, we will introduce the symbols

$$\mathrm{A}=v.n.\left(\frac{d^2\mathrm{T}_{bc}}{dx_b\,dx_c}\cdot\frac{d^2\mathrm{T}_{bc}}{dy_b\,dy_c}-\frac{d^2\mathrm{T}_{bc}}{dx_b\,dy_c}\cdot\frac{d^2\mathrm{T}_{bc}}{dy_b\,dx_c}\right),\quad\ldots\ldots\quad(6)$$

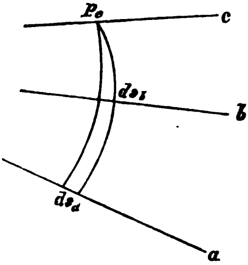
$$\mathrm{E}=v.n.\left\{\frac{d^2(\mathrm{T}_{ab}+\mathrm{T}_{bc})}{(dx_b)^2}\cdot\frac{d^2(\mathrm{T}_{ab}+\mathrm{T}_{bc})}{(dy_b)^2}-\left[\frac{d^2(\mathrm{T}_{ab}+\mathrm{T}_{bc})}{dx_b\,dy_b}\right]^2\right\}.\quad(7)$$

The required relation may then be written thus:

$$\frac{ds_c}{ds_b}=\frac{\mathrm{E}}{\mathrm{A}}.\quad\ldots\ldots\ldots\quad(8)$$

Similarly, on assuming a definite point $p_c$ to be given in the plane $c$ (fig. 13), we may determine the surface-element $ds_a$ in the plane $a$, which corresponds to the given element $ds_b$ in the plane $b$; in fact, the result may be deduced from the foregoing by simply interchanging everywhere the suffixes $a$ and $c$. If, for brevity, we likewise introduce the symbol

Fig. 13.

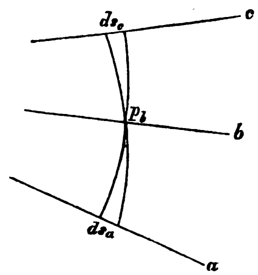


$$\mathrm{C}=v.n.\left(\frac{d^2\mathrm{T}_{ab}}{dx_a\,dx_b}\cdot\frac{d^2\mathrm{T}_{ab}}{dy_a\,dy_b}-\frac{d^2\mathrm{T}_{ab}}{dx_a\,dy_b}\cdot\frac{d^2\mathrm{T}_{ab}}{dy_a\,dx_b}\right),\quad\ldots\quad(9)$$

we shall have

$$\frac{ds_a}{ds_b}=\frac{E}{C}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Fig. 14.



Let us, lastly, suppose a definite point $p_b$ to be given in the plane $b$ (fig. 14), and in the plane $a$ let us select any surface-element $ds_a$. Conceive rays to proceed from the several points of the latter element, and passing through the point $p_b$ to be continued to the plane $c$. If we seek the magnitude of the surface-element $ds_c$, which all these rays determine on the plane $c$, we shall find on employing the symbols already introduced,

$$\frac{ds_c}{ds_a}=\frac{C}{A}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From this we see that the two surface-elements which here correspond are related to one another in precisely the same manner as are the two surface-elements which we obtain when, a definite element $ds_b$ being given in the plane $b$, we first assume a point on the plane $a$, and afterwards a point in the plane $c$, as the starting-point, and determine each time the surface-element in the third plane, $c$ or $a$, which corresponds to $ds_b$.

6. In the calculations of the foregoing article we have employed only the first of the three pairs of available equations, given in Art. 4. The calculations, however, may be performed in the same manner on employing either of the other two pairs (2) or (3). By means of each pair we are led to three quantities, analogous to A, C, and E, which serve to express the ratio of the surface-elements. Of the nine quantities which, on the whole, present themselves in this manner, it occurs three times that two are equal to one another, so that the nine quantities are reduced to six. Although the expressions for three of these six quantities have already been given, I will here for the sake of completeness give the whole series.

$$\left.\begin{aligned}
A&=v.n.\left(\frac{d^2T_{bc}}{dx_b\,dx_c}\cdot\frac{d^2T_{bc}}{dy_b\,dy_c}-\frac{d^2T_{bc}}{dx_b\,dy_c}\cdot\frac{d^2T_{bc}}{dy_b\,dy_c}\right),\\
B&=v.n.\left(\frac{d^2T_{ac}}{dx_a\,dx_c}\cdot\frac{d^2T_{ac}}{dy_a\,dy_c}-\frac{d^2T_{ac}}{dx_a\,dy_c}\cdot\frac{d^2T_{ac}}{dy_a\,dy_c}\right),\\
C&=v.n.\left(\frac{d^2T_{ab}}{dx_a\,dx_b}\cdot\frac{d^2T_{ab}}{dy_a\,dy_b}-\frac{d^2T_{ab}}{dx_a\,dy_b}\cdot\frac{d^2T_{ab}}{dy_a\,dx_b}\right),\\
D&=v.n.\left\{\frac{d^2(T_{ac}-T_{ab})}{(dx_a)^2}\cdot\frac{d^2(T_{ac}-T_{ab})}{(dy_a)^2}-\left[\frac{d^2(T_{ac}-T_{ab})}{dx_a\,dy_a}\right]^2\right\},\\
E&=v.n.\left\{\frac{d^2(T_{ab}+T_{bc})}{(dx_b)^2}\cdot\frac{d^2(T_{ab}+T_{bc})}{(dy_b)^2}-\left[\frac{d^2(T_{ab}+T_{bc})}{dx_b\,dy_b}\right]^2\right\},\\
F&=v.n.\left\{\frac{d^2(T_{ac}-T_{bc})}{(dx_c)^2}\cdot\frac{d^2(T_{ac}-T_{bc})}{(dy_c)^2}-\left[\frac{d^2(T_{ac}-T_{bc})}{dx_c\,dy_c}\right]^2\right\}.
\end{aligned}\right\}\qquad\text{(I)}$$

By means of these six quantities each ratio of two surface-elements may be represented by three different fractions, in the following manner:—

$$\left.\begin{aligned}
\frac{ds_c}{ds_b}&=\frac{E}{A}=\frac{A}{F}=\frac{C}{B},\\
\frac{ds_b}{ds_a}&=\frac{C}{E}=\frac{B}{A}=\frac{D}{C},\\
\frac{ds_a}{ds_c}&=\frac{A}{C}=\frac{F}{B}=\frac{B}{D}.
\end{aligned}\right\}\quad\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\quad\text{(II)}$$

As is easily seen, the three equations have reference, respectively, to the three cases where the definite point through which the rays must pass is taken in the plane $a$, in $c$, or in $b$. Of the three vertical rows of fractions representing the ratios of the surface-elements, the first is deduced from the equations (1), the second from the equations (2), and the third from the equations (3) of Art. 4.

Since the three fractions which represent a definite ratio of two surface-elements must be equal to one another, we obtain the following equations between the six quantities from which the fractions are formed:—

$$D=\frac{BC}{A};\quad E=\frac{CA}{B};\quad F=\frac{AB}{C}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

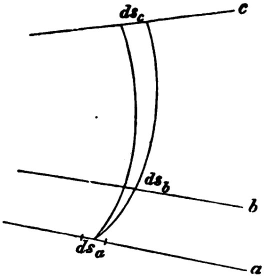
$$A^2=EF;\quad B^2=FD;\quad C^2=DE. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

Now our subsequent calculations are to be made with these six quantities; and since each ratio of two surface-elements is represented by three different fractions, we may select from the latter, in each special case, the fraction which proves to be most convenient.

## III. *Determination of the mutual radiation in the case where no concentration of rays takes place.*

7. We will in the first place consider the case to which Kirchhoff's expression refers, by seeking to determine how much heat two surface-elements transmit to each other, on the hypothesis that each point of either element receives from each point of the other but one ray, or at most but a limited number of single rays, each of which admits of separate consideration.

Fig. 15.



Two elements, $ds_a$ and $ds_c$, in the planes *a* and *c* (fig. 15) being given, we will first determine the heat which the element $ds_a$ sends to the element $ds_c$.

To this end let us conceive an intermediate plane *b* to be drawn parallel to *a*, and at so small a distance $\rho$ from the latter that the portion of each ray proceeding from $ds_a$ to $ds_c$ which lies between the two planes *a* and *b* may be regarded as rectilinear, and the medium between the two plan as homogeneous. Let any point be now taken in the element $ds_a$, and let us consider the pencil of rays which proceed therefrom to the element $ds_c$; this pencil intersects the plane *b* in an element $ds_b$, whose magnitude may be expressed by one of the three fractions standing in the uppermost of the horizontal rows of (II). Selecting the last of these fractions, we have the equation

$$ds_b=\frac{B}{C}ds_c. \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

This quantity C may in the present case be reduced to a particularly simple form in consequence of the peculiar position of the plane $b$.

We will, with Kirchhoff, choose the coordinate system in $b$ so that it shall correspond perfectly with the coordinate system in the parallel plane $a$. That is to say, the origins of the two coordinate systems shall lie in a line perpendicular to both planes, and the coordinates of one system shall be parallel to the corresponding coordinates of the other system. The distance $r$ from a point $x_a$, $y_a$ in the one plane to a point $x_b$, $y_b$ in the other will then be determined by the equation

$$r = \sqrt{\rho^2 + (x_b - x_a)^2 + (y_b - y_a)^2}. \quad . \quad . \quad . \quad (15)$$

Now the propagation of rays between the two planes being by hypothesis rectilinear, the length of the path described by a ray proceeding from one to the other of these points will be simply the distance $r$ between the points themselves; and if we represent by $v_a$ the velocity of propagation in the neighbourhood of the plane $a$, the time required for the description of the distance $r$ will be determined by the equation

$$T_{ab} = \frac{r}{v_a},$$

since the velocity $v_a$, according to our hypothesis, does not sensibly change in the interval between the planes $a$ and $b$. Accordingly the expression for C may be thus written :—

$$C = v.n. \frac{1}{v_a^2} \left( \frac{d^2 r}{dx_a\, dx_b} \cdot \frac{d^2 r}{dy_a\, dy_b} - \frac{d^2 r}{dx_a\, dy_b} \cdot \frac{d^2 r}{dy_a\, dx_b} \right).$$

Substituting here the value of $r$ as given by (15), we have

$$C = \frac{1}{v_a^2} \cdot \frac{\rho^2}{r^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The equation (14), therefore, becomes

$$ds_b = v_a^2 \frac{r^4}{\rho^2} \mathrm{B}\, ds_c. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If, further, we denote by $\vartheta$ the angle between the infinitely small pencil of rays proceeding from a point of the element

$ds_a$, and the normal to that element, we may put

$$\cos\vartheta = \frac{\rho}{r},$$

and the foregoing equation will thereby assume the form

$$ds_b = \frac{v_a r^2}{\cos^2\vartheta} \mathrm{B} ds_c. \quad \ldots \ldots \quad (18)$$

8. The magnitude of the surface-element $ds_b$ being thus found, the quantity of heat which the element $ds_a$ transmits to the element $ds_c$ may be also easily expressed. For an infinitely small pencil of rays proceeds to $ds_c$ from each point of the element $ds_a$, and the conical apertures of the pencils proceeding from the several points may be regarded as equal to one another. The magnitude of the conical aperture of each such pencil of rays is determined by the magnitude and position of the surface-element $ds_b$ which the cone determines on the plane *b*. To express this conical aperture geometrically, conceive a spherical surface of radius $\rho$ described around the vertex of the cone as centre. All rays being propagated in right lines within this sphere, the aperture of the cone will be represented by the fraction $\frac{d\sigma}{\rho^2}$, if $d\sigma$ be the surface-element in which the spherical surface is intersected by the cone of rays. Now the element $ds_b$ being at the distance *r* from the vertex of the cone and the normal to $ds_b$, like its parallel the normal to $ds_a$, making with the infinitely small cone the angle $\vartheta$, we have the equation

$$\frac{d\sigma}{\rho^2} = \frac{\cos\vartheta \,.\, ds_b}{r^2}, \quad \ldots \ldots \quad (19)$$

from which, by substituting the value of $ds_b$ as given in (18), we deduce

$$\frac{d\sigma}{\rho^2} = \frac{v_a^2}{\cos\vartheta} \mathrm{B} ds_c. \quad \ldots \ldots \quad (20)$$

We have now to determine how much of the heat emitted by the element $ds_a$ corresponds to this infinitely small aperture; in other words, how much heat the element $ds_a$ transmits through that particular element $d\sigma$ of the spherical surface. In the first place this quantity of heat must be proportional to the magnitude of the radiating element $ds_a$; it must further be proportional to the magnitude of the aperture of the cone, that is to say, to the fraction $\frac{d\sigma}{\rho^2}$; and lastly, according to the known law of radiation, it must be also proportional to the cosine of the angle $\vartheta$ which the infinitely small cone of rays forms with the normal. It may therefore be expressed by the product

$$\epsilon \cos \vartheta \frac{d\sigma}{\rho^2} ds_a,$$

where $\epsilon$ is a factor dependent on the temperature of the surface-element. To determine this factor, we have the condition that the total quantity of heat radiated by the element $ds_a$, in other words, the quantity transmitted by it to the whole hemispherical surface above the plane $a$, must be equal to the product $e_a \, ds_a$, where $e_a$ denotes the intensity of the emission of the plane $a$ at the position of the element $ds_a$. We have, consequently, the equation

$$\frac{\epsilon}{\rho^2} \int \cos \vartheta d\sigma = e_a,$$

where the integration is to be extended over the whole hemisphere. From this it follows that

$$\epsilon \pi = e_a.$$

On introducing the value of $\epsilon$, thus determined, into the above expression, we obtain the following formula for the quantity of heat transmitted by the element $ds_a$ through $d\sigma$:

$$\frac{e_a}{\pi} \cos \vartheta \frac{d\sigma}{\rho^2} ds_a.$$

In order to obtain the required expression for *the quantity of heat transmitted by the element* $ds_a$ *to the element* $ds_c$, we have merely to substitute in this formula the value of the fraction $\frac{d\sigma}{\rho^2}$ already found and given in the equation (20). The result is

$$e_a v_a^2 \frac{B}{\pi} ds_a \, ds_c.$$

If, in exactly the same manner, we seek *the quantity of heat* *which, on the contrary, the element $ds_c$ sends to $ds_a$,* and in doing so denote by $e_c$ the intensity of the emission from the plane $c$ in proximity to the element $ds_c$, and by $v_c$ the velocity with which the rays are propagated in the neighbourhood of this element, we shall find the expression

$$e_c v_c^2 \frac{B}{\pi} ds_a \, ds_c.$$

9. The expressions obtained in the preceding article are essentially the same as Kirchhoff's expression given in Art. 2, the only difference being that the former still contain the square of the velocity of propagation as a factor, which factor does not appear in Kirchhoff's expression on account of his having, for the object in view, considered solely the velocity of propagation *in empty space* and considered that as unity. Since the bodies, however, whose mutual radiation is under consideration may possibly be situate in different media, in which latter the velocities of propagation differ, this factor is not unessential in such cases, and its appearance leads at once to a peculiar and theoretically interesting conclusion.

As mentioned in Art. 1, it has been hitherto assumed that, for perfectly black bodies, the intensity of emission depends upon the temperature solely; so that, at the same temperature, equal portions of the surfaces of two such bodies radiate equal quantities of heat. So far as I know, it has nowhere been stated that the nature of the surrounding medium can have any influence on the intensity of the radiation. Since in both the above expressions for the mutual radiation of two elements, however, a factor is involved, which depends on the nature of the medium, the necessity of considering the medium is forced upon us, and at the same time the possibility presents itself of determining its influence.

On forming the ratio of those two expressions, and cancelling the factor $\frac{B}{\pi} ds_a \, ds_c$, which is common to both terms, we find that the quantity of heat which the element $ds_a$ transmits to the element $ds_c$, bears to that which the element $ds_c$ transmits to the element $ds_a$ the ratio

$$e_a v_a^2 : e_c v_c^2.$$

Now if we were to assume that the radiation is necessarily the same at the same temperature, even when the media adjacent to the two elements differ, we should have to put $e_a = e_c$ for equal temperatures, and the quantities of heat which the two elements transmit to each other would then have the ratio of $v_a^2 : v_c^2$, instead of being equal to each other. Hence it would follow that two bodies placed in different media, *e. g.* the one in water and the other in air, do not seek to equalize their temperatures by mutual radiation, but that the one could by radiation raise the other to a temperature higher than its own.

If, on the contrary, the theorem stated by me as an axiom be admitted in all its generality, namely that heat cannot of itself pass from a colder to a warmer body, then the mutual radiations of two perfectly black surface-elements of the same temperature must be considered as equal to one another, and we must put

$$e_a v_a^2 = e_c v_c^2. \qquad (21)$$

Hence follows the proportion

$$e_a : e_c = v_c^2 : v_a^2 ; \qquad (22)$$

or, since the ratio of the velocities of propagation is the inverse of that of the coefficients of refraction of the two media, say $n_a$ and $n_c$, the proportion

$$e_a : e_c = n_a^2 : n_c^2. \qquad (23)$$

According to this, therefore, *the radiations of perfectly black bodies of the same temperature are different in different media; they are inversely proportional to the squares of the velocities of propagation in those media, and therefore directly proportional to the squares of their coefficients of refraction.* The radiation in water, for instance, must have to that in air the ratio of $\left(\frac{4}{3}\right)^2 : 1 = 16 : 9$ nearly.

If we take into consideration the circumstance that in the heat radiated from a perfectly black body there are rays of very different colours, and if we admit that the equality of the mutual radiation must hold not only for the total heat, but likewise for that of each particular colour, we shall obtain proportions like (22) and (23) for each colour; in these proportions, however, the ratios on the right, to which the ratios of radiation are equated, will have somewhat different values.

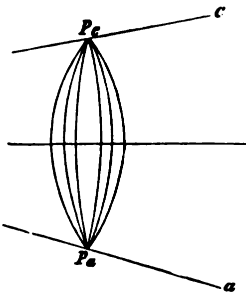
If we wish to consider, instead of perfectly black bodies, bodies which absorb incident rays partially instead of completely, we must introduce into the formulæ, instead of emission, a fraction having emission for its numerator and the coefficient of absorption for its denominator, and thus obtain for this fraction relations corresponding to those which previously had reference to emission alone. Into this generalization of our result, which would involve a discussion of the influence of ray-direction on emission and absorption, I need not here enter, since it follows at once from an appropriate consideration of the subject.

## IV. *Determination of the mutual radiation between two elements which are optical images of each other.*

10. We will now proceed to the case where it is no longer true, as before assumed, that the planes $a$ and $c$, so far as they enter into consideration, interchange rays in such a manner, that from each point of the one plane proceeds but one ray, or at most a limited number of distinct rays, to each point of the other plane. The rays which diverge from each point of one plane may, in consequence of refractions or reflexions, become convergent and meet again in the other plane; so that corresponding to a point $p_a$, selected for consideration in the plane $a$, there may be in the plane $c$ one or more points or lines in which an infinite number of the rays which issued from $p_a$ intersect, whilst other parts of the plane $c$ may receive no rays whatever from that point. In such a case, of course, similar properties are also possessed by the rays which, issuing from the plane $c$, arrive at the plane $a$, since the same paths are pursued by the rays which pass to and fro between the two planes.

From the infinity of different cases of this kind, we will for the sake of greater clearness, first treat the extreme one where all the rays which issue from the point $p_a$ in the plane $a$, and fall within a certain finite conical space, meet again at a definite

Fig. 16.



point $p_c$ of the plane $c$, as shown in fig. 16. This case would occur, for instance, if the directions of the rays were changed by a spherical mirror or by a lens, or by any system of centred mirrors or lenses, and we were to disregard the accompanying spherical and chromatic aberrations; it may be remarked, indeed, that chromatic aberration is in every case to be excluded, since, from the commencement, we have limited our considerations to homogeneous rays. As already stated, the name *conjugate foci* will be given to two points so related, that the rays which issue from the other converge in each.

In such a case, with the coordinates $x_a$, $y_a$ of the point $p_a$ from which each of the rays in question has issued, are simultaneously determined the coordinates $x_c$, $y_c$ of the point $p_c$, where the ray strikes the plane $c$. The other points of the plane $c$, which are in the neighbourhood of $p_c$, receive no rays from the point $p_a$, since there is no path leading to them which possesses the property of being describable by a ray in a time which is a mathematical minimum when compared with the times of description of every other adjacent path. Accordingly the quantity $T_{ac}$, which represents this minimum of time, can have no real value for points adjacent to $p_c$, but solely for the point $p_c$ itself. As a consequence of this it follows, that the differential coefficients of $T_{ac}$ cannot be real and finite magnitudes if formed on the assumption that the coordinates $x_a$, $y_a$ are constant, whilst one of the coordinates $x_c$, $y_c$ varies; or, on the contrary, that $x_c$, $y_c$ are constant during the variation of $x_a$ or $y_a$. Hence we conclude, that of the six quantities A, B, C, D, E, F determined by the six formulæ (I), the three, B, D, F, which contain differential coefficients of $T_{ac}$ are not applicable to our present inquiry.

The three other quantities, A, C, E, contain, however, differential coefficients of $T_{ab}$ and $T_{bc}$ solely. Consequently, if we assume the plane $b$ to be so chosen, that between it and the planes $a$ and $c$, so far at least as the latter enter into consideration, the ray-interchange takes place in the manner previously described, that is to say, from each point of $b$ proceeds one, but only one ray to each point of the planes $a$ and $c$, or at most a limited number of distinct rays, the quantities $T_{ab}$ and $T_{bc}$ will have real and not infinitely great values for all points which have to be considered. The quantities A, C, and E, therefore, are just as applicable in the present as in the former case.

In the present case, one of these magnitudes, E, takes a special value, which may be at once deduced. The two equations (1), or

$$\frac{d(T_{ab}+T_{bc})}{dx_b}=0; \quad \frac{d(T_{ab}+T_{bc})}{dy_b}=0,$$

must hold with respect to the three points in which a ray intersects the three planes $a$, $b$, $c$. Now since in our present case the positions of the points $p_a$ and $p_c$ in the planes $a$ and $c$ do not suffice to determine the position of the intersection of a ray with the plane $b$, inasmuch as the latter plane may be intersected in any point within a certain finite area, the two foregoing equations must hold for all such points, whence it follows that, by the differentiation of these equations according to $x_b$ and $y_b$, new and equally true equations must be obtained. We have therefore

$$\frac{d^2(T_{ab}+T_{bc})}{dx_b^2}=0; \quad \frac{d^2(T_{ab}+T_{bc})}{dx_b\, dy_b}=0; \quad \frac{d^2(T_{ab}+T_{bc})}{dy_b^2}=0. \qquad (24)$$

On applying these equations to the one by which, in the system (I), E is defined, we have

$$E=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

The two other quantities, A and C, have, in general, finite values dependent upon the circumstances of each individual case; these values must be employed in the following determinations.

11. Let it be granted that the element $ds_a$ of the plane $a$ has $ds_c$ for its optical image in the plane $c$, so that each point of the element $ds_a$ forms, with a point of the element $ds_c$, a pair of conjugate foci, and *vice versâ*. We will inquire whether the quan-

tities of heat are equal which these two elements, considered as belonging to the surfaces of two perfectly black bodies of the same temperature, transmit to each other.

In order, first, to determine the position and magnitude of the image $ds_c$ of the given element $ds_a$, let us select any point $p_b$ in the intermediate plane $b$, and conceive rays passing through it from every point of the element $ds_a$. Each of these rays strikes the plane $c$ in the conjugate focus of the point whence the ray issued, hence the surface-element in which this pencil of rays cuts the plane $c$ is precisely the optical image of the element $ds_a$; in other words it is $ds_c$. To express the magnitude of the image $ds_c$ relative to $ds_a$, therefore, we may employ one of the three fractions, in the lowest horizontal row of (II.), which represent the ratio of the two surface-elements which an infinitesimal pencil of rays, with vertex $p_b$ in the intermediate plane $b$, determines upon the planes $a$ and $c$. Of the three fractions in question, however, one only is suitable, the two others being indeterminate, so that we have the equation

$$\frac{ds_a}{ds_c}=\frac{\text{A}}{\text{C}}. \quad \ldots \ldots \ldots \quad (26)$$

This equation is of interest in optics, since it is the most general equation for determining the relative magnitudes of an object and its optical image; it may be remarked with respect to it, that the intermediate plane $b$, to which the quantities A and C have reference, being arbitrary, may in each particular case be chosen so as most to facilitate the calculation.

12. The surface-element $ds_c$, image of $ds_a$, having been determined, let us take a surface-element $ds_b$ instead of a point in the plane $b$, and consider the rays which the two elements $ds_a$ and $ds_c$ transmit through it. All rays which, issuing from a point of the element $ds_a$, pass through the element $ds_b$ unite again in a point of the element $ds_c$; accordingly, all rays transmitted by the element $ds_a$ through $ds_b$ precisely reach $ds_c$, and *vice versâ*, the rays which $ds_c$ sends through $ds_b$ all strike the element $ds_a$. The two quantities of heat which the elements $ds_a$ and $ds_c$ transmit to the element $ds_b$ are, therefore, also the

quantities of heat which the elements $ds_a$ and $ds_c$ transmit to each other through the intermediate element $ds_b$. Now these quantities of heat may be at once found, according to previously established principles.

In fact, for the quantity of heat which the element $ds_a$ sends to the element $ds_b$, the same expression holds which in Art. 8 was developed for the quantity of heat which the element $ds_a$ sends to the element $ds_c$; provided we therein replace $ds_c$ and B by $ds_b$ and C respectively. The required expression is, therefore,

$$e_a v^2 \frac{C}{\pi} ds_a ds_b.$$

Similarly the expression already found for the quantity of heat which the element $ds_c$ transmits to the element $ds_a$ furnishes the quantity of heat which the element $ds_c$ sends to the element $ds_b$, on changing in the former $ds_a$ to $ds_b$, and replacing the quantity B by the quantity A. Hence the expression required is

$$e_c v_c^2 \frac{A}{\pi} ds_c ds_b.$$

On remembering now that, according to equation (26),

$$C ds_a = A ds_c,$$

we conclude that the two quantities here expressed are to each other in the ratio of $e_a v_a^2 : e_c v_c^2$.

We arrive at precisely the same result when, in the intermediate plane $b$, we take any other surface-element $ds_b$ and consider the quantities of heat which the elements $ds_a$ and $ds_c$ transmit to each other through it. The two quantities of heat always bear to each other the ratio of $e_a v_a^2 : e_c v_c^2$. Now, since the total quantities of heat which the elements $ds_a$ and $ds_c$ transmit to each other consist of those which they transmit through the several elements of the intermediate plane, we conclude, as the final result, that the total quantities of heat which the surface-elements $ds_a$ and $ds_c$ transmit to each other have the ratio $e_a v_a^2 : e_c v_c^2$.

This is the same ratio as that which was found in Arts. 8 and 9 for the case where no concentration took place. It follows, therefore, that however much the concentration of rays may change the *absolute magnitudes* of the quantities of heat which two surface-elements interchange by radiation, the *ratio* of these quantities is not altered thereby.

In Art. 9 it was shown that if for ordinary unconcentrated inter-radiation the theorem is to hold, in virtue of which heat cannot be thereby transferred from a colder to a warmer body, the radiation must necessarily vary in different media, and that in such a manner that for perfectly black bodies of the same temperature we have always

$$e_a v_a^2 = e_c v_c^2.$$

If this equation be fulfilled, then in the present case also, where of the two surface-elements $ds_a$ and $ds_c$ one is the image of the other, the quantities of heat must be equal which they transmit to each other, and hence, notwithstanding the concentration, neither element can raise the other to a temperature higher than its own.

## V. *Relation between the enlargement and the ratio of the apertures of an elementary pencil of rays.*

13. As a secondary result of the preceding investigation, I may be allowed here to develope a proportion which appears to me to possess general interest, inasmuch as it renders manifest a peculiar difference in the constitution of the pencil of rays at the object and at its image, which difference must always present itself in a definite manner whenever object and image are of unequal magnitude.

If we consider the infinitesimal pencil of rays which, issuing from a point of the element $ds_a$, pass through the element $ds_b$ of the intermediate plane and then combine in a point of the element $ds_c$, we may compare the divergence which these rays present at the point of issue with their convergence at the point of combination. This divergence and convergence, in other words, the *apertures of the infinitesimal cones,* which the rays form at the points of issue and combination, may be immediately found by the same method as that which we employed in Art. 8.

Around each of the points in question we conceive a spherical surface to be described with a radius so small, that the rays within the sphere may be regarded as rectilinear, and we consider the element which the pencil intercepts on the spherical surface. Let this surface-element be denoted by $d\sigma$, and let $\rho$ be the radius of the sphere; then the aperture of the infinitesimal cone formed by the rays, considered as rectilinear, will be represented by the fraction $\frac{d\sigma}{\rho^2}$.

In the similar case treated in Art. 8 we determined this fraction by the equation (20); and to obtain the expression applicable to our present case, it will suffice to change slightly the letters involved in the expression there found. To express the aperture of the cone, whose vertex is at the point of the plane $a$ whence the rays issue, we have to put in place of the element $ds_c$, and the quantity B of our former expression, the element $ds_b$ and the quantity C. In order, moreover, to indicate more distinctly that we are considering the cone whose vertex is in the plane $a$, we will use the symbol $\vartheta_a$ instead of $\vartheta$ to denote the angle between the elementary pencil and the normal to the surface-element $ds_a$; and for a similar reason we will provide the fraction $\frac{d\sigma}{\rho^2}$, which represents the required aperture with the suffix $a$. We have then

$$\left(\frac{d\sigma}{\rho^2}\right)_a = \frac{v_a^2}{\cos\vartheta_a} C ds_b. \quad . \quad . \quad . \quad . \quad . \quad (27)$$

In order to obtain the corresponding formula for the aperture of the cone, whose vertex is at the point in the plane $c$ where the rays unite, we have merely to replace every suffix $a$ in the preceding formula by $c$, and likewise the quantity C by A. The result is

$$\left(\frac{d\sigma}{\rho^2}\right)_c = \frac{v_c^2}{\cos\vartheta_c} A ds_b. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

From these two equations we obtain the proportion

$$\frac{\cos\vartheta_a}{v_a^2}\left(\frac{d\sigma}{\rho^2}\right)_a : \frac{\cos\vartheta_c}{v_c^2}\left(\frac{d\sigma}{\rho^2}\right)_c = C : A;$$

and if to this we apply the equation (26), we find

$$\frac{\cos\vartheta_a}{v_a^2}\left(\frac{d\sigma}{\rho^2}\right)_a : \frac{\cos\vartheta_c}{v_c^2}\left(\frac{d\sigma}{\rho^2}\right)_c = ds_c : ds_a. \quad . \quad . \qquad (29)$$

On introducing coefficients of refraction in place of velocities of propagation, this proportion becomes

$$n_a^2 \cos\vartheta_a \left(\frac{d\sigma}{\rho^2}\right)_a : n_c^2 \cos\vartheta_c \left(\frac{d\sigma}{\rho^2}\right)_c = ds_c : ds_a. \quad . \qquad (30)$$

On the right of this proportion stands the ratio of the magnitudes of a surface-element of the image, and the corresponding surface-element of the object; in short, the superficial enlargement; it furnishes, therefore, a simple relation between the enlargement and the ratio of the apertures of an elementary conical pencil of rays. It is moreover obvious that for the truth of the proportions it is not absolutely necessary that the rays should be ultimately *convergent* and actually intersect in a point; on the contrary, they may be *divergent*, so that their rectilinear backward productions meet in a point and form a so-called virtual image.

If, as a special case, we assume the medium to be the same at the point whence the rays issue and where they combine; if, for example, the rays proceed from an object in air and, after suffering any refractions and reflexions whatever, give an image in air, really or virtually, then $v_a = v_c$ and $n_a = n_c$, and we have

$$\cos\vartheta_a \left(\frac{d\sigma}{\rho^2}\right)_a : \cos\vartheta_c \left(\frac{d\sigma}{\rho^2}\right)_c = ds_c : ds_a.$$

If we further introduce the condition that the elementary pencil of rays is to make equal angles with both surface-elements, for instance, to be normal to each, the cosines will disappear, and we shall have

$$\left(\frac{d\sigma}{\rho^2}\right)_a : \left(\frac{d\sigma}{\rho^2}\right)_c = ds_c : ds_a.$$

In this case, therefore, the apertures of the elementary conical pencils of rays at the object and at the image are simply inversely proportional to the magnitudes of the corresponding surface-elements of object and image.

In the clear and elaborate exposition of the laws of refraction in systems of spheric surfaces, which Helmholtz has given in his 'Physiological Optics'* preparatory to examining the refractions which take place in the eye, I find on p. 50, and expanded on p. 54, an equation which expresses the relation between the magnitude of the image and the convergence of the rays for the case where the directions of rays are changed by refraction, or even by reflexion in centred spheric surfaces, and where the rays strike the planes containing object and image normally or approximately so. So far as I know, the relation has never before been given with the generality which appertains to the proportions (29) and (30).

## VI. *General determination of the mutual radiation between two surfaces in which any concentrations whatever occur.*

14. The investigation must now be generalized so as to embrace every imaginable case of ray-concentration, and not merely the extreme case where all the rays, issuing from a point of the plane $a$ within a certain finite conical angle, are again collected in a point of the plane $c$, so that a conjugate focus there ensues. To define more accurately the conception of concentration, we will introduce the following definition. If rays, issuing from any point $p_a$, fall on the plane $c$, and have in the neighbourhood of this plane directions such that at any point thereon the density of the incident rays is infinite compared with the mean density, we shall say that at that point occurs a concentration of the rays issuing from $p_a$.

According to this definition we may easily make the concentration of rays mathematically intelligible. Between the point $p_a$ and the plane $c$ we take any intermediate plane $b$, so situated that in it no concentration of the rays issuing from $p_a$ occurs, and also so related to the plane $c$ that, as far as our considerations extend, the pencils of rays which proceed from points in the one suffer no concentration in the other. We then conceive an infinitesimal pencil of rays proceeding from $p_a$, and compare the magnitudes of the surface-elements $ds_b$ and $ds_c$ which it intercepts on the planes $b$ and $c$. If on doing so we find $ds_c$ to be infinitely small in comparison with $ds_b$, so that we

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* *Allgemeine Encyklopädie der Physik*, edited by G. Karsten.

may put

$$\frac{ds_c}{ds_b}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (31)$$

the fact will indicate that a concentration of rays, in the above sense, takes place in the plane *c*.

Returning now to the equations (II) of Art. 6, of which equations those in the first horizontal row have reference to the present case, we find that of the three fractions in that row, each of which represents the ratio of the surface-elements, the first is applicable to the case under consideration; since, according to the hypothesis now made relative to the position of the intermediate plane, the magnitudes A and E are determinable in the ordinary way. We have, accordingly, the equation

$$\frac{ds_c}{ds_b}=\frac{E}{A}.$$

In order that this fraction representing the ratio of the two elements may vanish, the numerator E must do so, since the denominator A, in virtue of our hypothesis relative to the position of the plane *b*, cannot be infinitely great. Hence the equation of condition,

$$E=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (32)$$

is the mathematical criterion for deciding whether the rays issuing from the point $p_a$ do or do not suffer a concentration at the particular point of the plane *c*; in the case of a concentration this equation must be fulfilled.

If, on the contrary, we now suppose a point $p_c$ to be given in the plane *c*, and we inquire whether or not the rays issuing from this point suffer a concentration at any place on the plane *a*, we find in an exactly similar manner the condition

$$\frac{ds_a}{ds_b}=0;$$

and since, according to (II), we may put

$$\frac{ds_a}{ds_b}=\frac{E}{C},$$

we obtain the same condition,

$$E=0.$$

It is, in fact, manifest that when rays proceeding from a point of the plane $a$ suffer concentration in a point of the plane $c$, the rays which issue from the latter point must likewise undergo concentration in the first plane.

Having in the equations (12) and (13) expressed the relations which exist between the six magnitudes A, B, C, D, E, F, we may employ these equations to find what B, D, and F become when E=0, and A and C have values different from zero. According to those equations, we have

$$B=\frac{AC}{E}, \quad D=\frac{C^2}{E}, \quad F=\frac{A^2}{E}, \quad . \quad . \quad . \quad (33)$$

so that all three magnitudes become infinitely great in the case under consideration.

15. We will now seek to determine the ratio of the quantities of heat which two surfaces interchange by radiation, in such a manner that the result shall always hold, no matter whether a concentration of rays takes place or not.

For the sake of greater generality, let any two surfaces, $s_a$ and $s_c$, be given in place of the two planes $a$ and $c$. Between these two surfaces we take a third, $s_b$, subject only to the condition that the rays which proceed from $s_a$ to $s_c$, or in the contrary direction, suffer no concentration in $s_b$. In $s_a$ let any element $ds_a$ be now chosen, and let $ds_b$ be an element in $s_b$ so situated that the rays from $ds_a$ which pass through $ds_b$ reach, when prolonged, the surface $s_c$. This done, we will next determine *how much heat the element $ds_a$ sends to and receives from the surface $s_c$ through the element $ds_b$ of the intermediate surface.*

To find the first of these two quantities of heat, we have merely to determine how much heat the element $ds_a$ sends to the element $ds_b$; for according to the hypothesis relative to the position of the element $ds_b$, the whole of this heat, after passing through the element $ds_b$, reaches the surface $s_c$. The required quantity of heat may be at once expressed by means of the formulæ previously developed. To do so, we conceive the tangent plane to the surface $s_a$ drawn at a point of the element $ds_a$, and likewise the tangent plane to $s_b$ at a point of the element $ds_b$, and consider the given surface-elements as coincident with elements of these planes. On introducing coordinate systems $x_a$, $y_a$ and $x_b$, $y_b$ into these tangent planes and forming the magnitude C, as defined by the third of the equations (I), the required quantity of heat transmitted by the element $ds_a$ to the element $ds_b$, and thence to the surface $s_c$, will be represented by the expression

$$e_a v_a^2 \frac{C}{\pi} ds_a \, ds_b.$$

Passing next to the quantity of heat which the element $ds_a$ receives from the surface $s_c$ through the element $ds_b$, it must be observed, with reference to the points of the surface $s_c$ from which the several rays proceed, that in general the simple relation no longer holds here, as in the special case, where the element $ds_a$ had an optical image $ds_c$ in the surface $s_c$, and was consequently itself the optical image of $ds_c$. If we select any definite point $p_b$ of the intermediate element $ds_b$, and conceive rays passing through this point from all points of the element $ds_a$, we obtain an infinitely small pencil of rays which intersect $s_c$ in a certain surface-element. It is from this surface-element that rays proceed to the element $ds_a$ through the selected point $p_b$. If, however, we were to choose any other point in $ds_b$ as the vertex of a pencil of rays, we should obtain a somewhat differently situated element in the surface $s_c$. Consequently the rays which the element $ds_a$ receives from the surface $s_c$ through the several points of the intermediate element, do not all proceed from one and the same element of the surface $s_c$.

Nevertheless, the magnitude of the intermediate element $ds_b$ being arbitrary, there is nothing to prevent us from making it as small as we please,—in fact an infinitesimal of a higher order than the given element $ds_a$. This granted, the element of the surface $s_c$, which corresponds to the element $ds_a$, will change its position so little when the vertex of the pencil of rays moves within the element $ds_b$, that the differences will be infinitesimal when compared with the dimensions of the element itself, and may accordingly be neglected. On this hypothesis, therefore, we may consider the portion of the surface $s_c$, which interchanges rays with the element $ds_a$ through the element $ds_b$, to be identical with the element $ds_c$, which we obtain on selecting any point $p_b$ of the element $ds_b$ as the vertex of a pencil of rays proceeding from $ds_a$.

The magnitude of this element $ds_c$ can be easily expressed by foregoing principles. We conceive, as before, the tangent plane to the surface $s_b$ at the point $p_b$ to be drawn, as well as the tangent plane to the surface $s_a$, at a point of the element $ds_a$, and the tangent plane to $s_c$ at a point of $ds_c$; and we regard the two last surface-elements as elements of the respective tangent planes. On introducing systems of coordinates into the three tangent planes and forming the magnitudes A and C, as defined by the first and third of the equations (I), we have, by (II),

$$ds_c = \frac{C}{A}\, ds_a.$$

The quantity of heat which this element $ds_c$ transmits to the element $ds_b$, and which, as above explained, may be regarded as equal to the quantity received by the element $ds_a$ from the surface $s_c$ through the element $ds_b$, is represented by

$$e_c\, v_c^2 \frac{A}{\pi}\, ds_c\, ds_b,$$

or, on substituting for $ds_c$ the value just given, by

$$e_c\, v_c^2 \frac{C}{\pi}\, ds_a\, ds_b.$$

On comparing this expression with the one previously found for the quantity of heat, which the element $ds_a$ transmits through $ds_b$ to the surface $s_c$, it will be seen that the two quantities have to each other the ratio

$$e_a\, v_a^2 : e_c\, v_c^2.$$

Now if we suppose $s_a$ and $s_c$ to be surfaces of two perfectly black bodies of the same temperature, and assume that for such surfaces the two products $e_a v_a^2$ and $e_c v_c^2$ are equal—an assumption which was shown to be necessary in the case of radiation without concentration—the quantities of heat represented by the two expressions under consideration will likewise be equal to one another.

16. If we take a different element in the intermediate surface $s_b$, again considered as an infinitesimal of higher order, the element of the surface $s_c$, which interchanges rays, through it, with the element $ds_a$, will have a different position; but the two interchanged quantities of heat will again be equal to one another, and the same will be true for all other elements of the intermediate surface.

To obtain the total quantity of heat which the element $ds_a$ transmits to the surface $s_c$, and likewise the total quantity which it receives in return, the two expressions above found must be integrated relative to the intermediate surface $s_b$, and the integral extended to that portion of this surface which is encountered by the rays which proceed from the element $ds_a$ to the surface $s_c$, and *vice versâ*. It is manifest that the two integrals will be equal to one another, since for each element $ds_b$ the two differential expressions are equal.

Lastly, the quantity of heat which the entire surface $s_a$ interchanges with the surface $s_c$ will be obtained by the further integration of the two expressions relative to the surface $s_a$, and here again the equality which exists for the several elements $ds_a$ will not be disturbed.

The theorem above established for more special cases, in virtue of which two perfectly black bodies of the same temperature interchange equal quantities of heat, provided the equation $e_a v_a^2 = e_c v_c^2$ is applicable to them, also presents itself as the result of considerations altogether independent of the circumstance whether or not the rays proceeding from $s_a$ to $s_c$, or from $s_c$ to $s_a$ suffer concentration. The only condition imposed was, that the rays proceeding from $s_a$ and $s_c$ suffer no concentration in the intermediate surface $s_b$, and this condition may always be fulfilled, inasmuch as the intermediate surface may be arbitrarily chosen.

From this result it further follows, of course, that when reciprocal action takes place between a given black body and any number of other black bodies of the same temperature, the former receives from all the latter, put together, exactly as much heat as it transmits to them.

17. The preceding developments were made on the supposition that the reflections and refractions therein involved occur without loss, and that no absorption takes place. It may easily be shown, however, that the final result remains unchanged, even when this condition is relinquished. To this end let us consider for a moment the different ways in which a ray may become weakened during its passage from one body to another. On reaching the dividing surface of two media, one portion may suffer reflection, and the other, after refraction, pursue its course in the adjacent medium. Whichever of these two portions, however, we consider as the prolongation of the original ray, we shall have a weaker ray. Again, a ray on passing through a medium may suffer absorption. Now in each of these cases the law holds that the weakening effect is proportionally the same for two rays propagated in opposite directions along the same path. The effect of such processes will be, therefore, to diminish to the same degree both the quantities of heat which two bodies mutually transmit to each other, so that if these quantities were equal before the weakening occurred, they will remain equal afterwards.

Another circumstance to be mentioned in connexion with the above-named processes is, that a body may receive like-directed rays proceeding from different bodies. For instance, from a point situated in the dividing surface of two media, a body, A, may receive two rays coincident in direction, but proceeding from two different bodies, B and C; and of these rays one may have come from the adjacent medium, after having suffered refraction at the point, whilst the other may have remained in the same medium, and have suffered reflection merely. In this case, however, the two rays must have been weakened by refraction and reflection in such a manner that, if originally equal in intensity, the sum of their intensities must afterwards be equal to the original intensity of each. If we now conceive an equally intense ray to proceed in an opposite direction from the body A, it will, at the same point, be divided into two parts, one of which will enter the adjacent medium and proceed to the body B, whilst the other will be reflected to the body C. The two parts which in this manner reach B and C from A will be just as great as the parts of rays which A receives from B and C. Under the hypothesis of equal temperatures, therefore, the relation between the body A and the bodies B and C is such, that it exchanges equal quantities of heat with each. In consequence of the equality of the actions on two rays which pursue, in opposite directions, any path whatever, the above relations must hold in all other cases, however complicated.

Further, if, instead of perfectly black bodies, we also consider bodies which only partially absorb incident rays, or if, instead of homogenous heat, we consider heat due to waves of different lengths, or lastly, if, instead of regarding all rays as unpolarized, we have regard to the phenomena of polarization, we shall in all cases be concerned solely with circumstances which affect, to the same extent, the heat emitted by a body, and the heat which it receives from other bodies.

It is not necessary to consider here all these circumstances, for they occur also in ordinary radiation without concentration, and the sole object of the present memoir was to investigate the effects which may possibly arise from the concentration of rays.

18. The following is a brief summary of the principal results of the foregoing considerations :—

1. To harmonize the effects of ordinary radiation, without concentration, with the principle that heat cannot of itself pass from a colder to a warmer body, it is necessary to assume that the intensity of emission from any body depends not only upon its own constitution and its temperature, but also upon the nature of the surrounding medium; in fact the intensities of emission of one and the same body in different media must be inversely proportional to the squares of the velocities with which rays are therein propagated, or, in other words, directly proportional to the squares of the coefficients of refraction for these media.

2. If this assumption as to the influence of the surrounding medium be correct, the above principle must obtain, not only for ordinary radiation, but also when the rays become concentrated in any manner whatever through reflections and refractions; for although concentration may change the absolute magnitudes of the quantities of heat which two bodies radiate to each other, it cannot alter the ratio of these magnitudes.

# NINTH MEMOIR.

## ON SEVERAL CONVENIENT FORMS OF THE FUNDAMENTAL EQUATIONS OF THE MECHANICAL THEORY OF HEAT*.

In my former Memoirs on the Mechanical Theory of Heat, my chief object was to secure a firm basis for the theory, and I especially endeavoured to bring the second fundamental theorem, which is much more difficult to understand than the first, to its simplest and at the same time most general form, and to prove the necessary truth thereof. I have pursued special applications so far only as they appeared to me to be either appropriate as examples elucidating the exposition, or to be of some particular interest in practice.

The more the mechanical theory of heat is acknowledged to be correct in its principles, the more frequently endeavours are made in physical and mechanical circles to apply it to different kinds of phenomena, and as the corresponding differential equations must be somewhat differently treated from the ordinarily occurring differential equations of similar forms, difficulties of calculation are frequently encountered which retard progress and occasion errors. Under these circumstances I believe I shall render a service to physicists and mechanicians by bringing the fundamental equations of the mechanical theory of heat from their most general forms to others which, corresponding to special suppositions and being susceptible of direct application to different particular cases, are accordingly more convenient for use.

1. The whole mechanical theory of heat rests on two fundamental theorems,—that of the equivalence of heat and work, and that of the equivalence of transformations.

In order to express the first theorem analytically, let us

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* Read at the Philosophical Society of Zürich on the 24th of April, 1865, published in the Vierteljahrsschrift of this Society, Bd. x. S. 1.; Pogg. *Ann.* July, 1865, Bd. cxxv. S. 353; Journ. de Liouville, 2e sér. t. x. p. 361.

contemplate any body which changes its condition, and consider the quantity of heat which must be imparted to it during the change. If we denote this quantity of heat by Q, a quantity of heat given off by the body being reckoned as a negative quantity of heat absorbed, then the following equation holds for the element $dQ$ of heat absorbed during an infinitesimal change of condition,

$$dQ = dU + A dW. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Here U denotes the magnitude which I first introduced into the theory of heat in my memoir of 1850, and defined as the sum of the free heat present in the body, and of that consumed by interior work*. Since then, however, W. Thomson has proposed the term *energy* of the body for this magnitude†, which mode of designation I have adopted as one very appropriately chosen; nevertheless, in all cases where the two elements comprised in U require to be separately indicated, we may also retain the phrase *thermal and ergonal content*, which, as already explained on p. 255, expresses my original definition of U in a rather simpler manner. W denotes the exterior work done during the change of condition of the body, and A the quantity of heat equivalent to the unit of work, or more briefly, the *thermal equivalent of work*. According to this AW is the exterior work expressed in thermal units, or according to a more convenient terminology recently proposed by me, the *exterior ergon*. (See Appendix A. to Sixth Memoir.)

If, for the sake of brevity, we denote the exterior ergon by a simple letter,

$$w = AW,$$

we can write the foregoing equation as follows,

$$dQ = dU + dw. \quad . \quad . \quad . \quad . \quad . \quad . \quad (I\,a)$$

In order to express analytically the second fundamental theorem in the simplest manner, let us assume that the changes which the body suffers constitute a *cyclical process*, whereby the body returns finally to its initial condition. By $dQ$ we will again understand an element of heat absorbed, and T shall

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* Pogg. *Ann.* Bd. lxxix. S. 385, and p. 29 of this collection.

† Phil. Mag. S. 4. vol. ix. p. 523.

denote the temperature, counted from the absolute zero, which the body has at the moment of absorption, or, if different parts of the body have different temperatures, the temperature of the part which absorbs the heat element $dQ$. If we divide the thermal element by the corresponding absolute temperature and integrate the resulting differential expression over the whole cyclical process, then for the integral so formed the relation

$$\int \frac{dQ}{T} \leqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

holds, in which the sign of equality is to be used in cases where all changes of which the cyclical process consists are *reversible*, whilst the sign $<$ applies to cases where the changes occur in a *non-reversible* manner*.

2. We will first consider more closely the magnitudes occurring in equation (I $a$) in reference to different kinds of changes of the body.

The exterior ergon $w$, which is produced whilst the body passes from a given initial condition to another definite one, depends not merely on the initial and final conditions, but also on the nature of the transition.

In the first place, we have to consider the exterior forces which act on the body, and which are either overcome by, or overcome the forces of the body itself;—the exterior ergon being positive in the former, and negative in the latter case. The question

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* In my memoir "On a Modified Form of the Second Fundamental Theorem of the Mechanical Theory of Heat" (Fourth Memoir of this collection), in which I first gave the most general expression of the Second Fundamental Theorem for a Cyclical Process, the signs of the differentials $dQ$ were differently chosen; there a thermal element given up by a changing body to a reservoir of heat is reckoned positive, an element withdrawn from a reservoir of heat is reckoned negative. With this choice of signs, which in certain general theoretical considerations is convenient, we have to write instead of (II),

$$\int \frac{dQ}{T} \geqq 0.$$

In the present memoir, however, the choice mentioned in the text is everywhere retained, according to which a quantity of heat absorbed by a changing body is positive, and a quantity given off by it is negative.

then arises, are these exterior forces, at each moment, the same as, or different from the forces of the body? Now although we may assert that for one force to overcome another, the former must necessarily be the greater; yet since the difference between them may be as small as we please, we may consider the case where absolute equality exists as the limiting case, which, although never reached in reality, must be theoretically considered as possible. When force and counter-force are different, the mode in which the change occurs is not a reversible one.

In the second place, the change taking place in a reversible manner, the exterior ergon likewise depends upon the intermediate conditions through which the body passes when changing from the initial to the final condition, or, as it may be figuratively expressed, upon the *path* which the body pursues when passing from its initial to its final condition.

With the *energy* U of the body whose element, as well as that of the exterior ergon, enters into the equation (I *a*), it is quite different. If the initial and final conditions of the body are given, the variation in energy is completely determined, without any knowledge of the way in which the transition from the one condition to the other took place—in fact neither the nature of the passage nor the circumstance of its being made in a reversible or non-reversible manner, has any influence on the contemporaneous change of energy. If, therefore, the initial condition and the corresponding value of the energy be supposed to be given, we may say that the energy is fully defined by the actually existing condition of the body.

Finally, since the *heat* Q which is absorbed by the body during the change of condition is the sum of the change of energy and of the exterior ergon produced, it must like the latter depend upon the way in which the transition of the body from one condition to another takes place.

Now in order to limit the field of our immediate investigation, we shall always assume, unless the contrary is expressly stated, *that we have to do with reversible changes solely.*

The equation (I *a*) which expresses the first fundamental theorem, holds for reversible as well as for non-reversible changes; hence, in order to apply it specially to reversible changes, we have not to modify it externally in any manner, but merely to understand that by $w$ and Q are meant the exterior ergon and quantity of heat which correspond to reversible changes.

On applying to reversible changes the relation (II) which expresses the second fundamental theorem, we have not only to understand by Q the quantity of heat which relates to reversible changes, but also, instead of the double sign $\leqq$, we have simply to employ the sign of equality. We obtain for all reversible cyclical processes, therefore, the equation

$$\int\frac{dQ}{T}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\text{II } a)$$

3. In order to be able to calculate with the equations (I $a$) and (II $a$), we will assume that the condition of the body under consideration is defined by any appropriate magnitudes whatever; the cases which most frequently occur are those where the condition of the body is either defined by its temperature and volume, or by its temperature and the pressure to which it is exposed, or finally by its volume and pressure. We will not at present, however, confine ourselves to any particular magnitudes, but assume that the condition of the body is defined by any two magnitudes, say $x$ and $y$; these magnitudes will be considered in the calculations as independent variables. In special applications, we are of course always at liberty to identify one or both of these variables with any one or two of the above-named magnitudes, temperature, volume, and pressure.

If the magnitudes $x$ and $y$ define the condition of the body, then its energy U, which depends only on the instantaneous condition of the body, must admit of being represented as a function of these two variables. It is otherwise with the magnitudes $w$ and Q. The differential coefficients of these magnitudes, which we will denote in the following manner,

$$\frac{dw}{dx}=m, \qquad \frac{dw}{dy}=n, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

$$\frac{dQ}{dx}=M, \qquad \frac{dQ}{dy}=N, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

are definite functions of $x$ and $y$. For if we assume that the variable $x$ becomes $x+dx$, whilst $y$ remains unchanged, and that this change of condition of the body takes place in a reversible manner, a perfectly definite process is assumed, and hence the exterior work thereby done is defined, whence it follows, further, that the function $\frac{dw}{dx}$ must likewise have a definite value. The same holds good if we assume that $y$ changes to $y+dy$, whilst $x$ remains constant. But if the differential coefficients of the exterior ergon $w$ are definite functions of $x$ and $y$, it follows from equation (I $a$) that the differential coefficients of the heat Q which is absorbed by the body, must likewise be definite functions of $x$ and $y$.

If we now form for $dw$ and $d$Q their expressions in $dx$ and $dy$ and, neglecting terms of a higher order than the first in $dx$ and $dy$, write

$$dw = mdx + ndy, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$dQ = Mdx + Ndy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

we obtain two complete differential equations, which cannot be integrated so long as the variables $x$ and $y$ are independent of one another, since the magnitudes $m$, $n$, and M, N do not satisfy the conditions of integrability:—

$$\frac{dm}{dy} = \frac{dn}{dx} \text{ and } \frac{dM}{dy} = \frac{dN}{dx}.$$

The magnitudes $w$ and Q thus belong to those which were discussed in the mathematical introduction to this collection of Memoirs, whose peculiarity consists in the fact that, although their differential coefficients are definite functions of both independent variables, they themselves cannot be represented by such functions, but only become defined when a further relation is given between the variables, and by that means the sequence of, or path pursued during the changes is prescribed.

4. If we return to equation (I $a$), and put therein for $dw$ and $d$Q the expressions (3) and (4), and also separate $d$U into the two parts which have reference to $dx$ and $dy$, we obtain the equation

$$Mdx + Ndy = \left(\frac{dU}{dx} + m\right)dx + \left(\frac{dU}{dy} + n\right)dy.$$

Since this equation must hold for all values of $dx$ and $dy$, it may be resolved into the following two :—

$$M=\frac{dU}{dx}+m,$$

$$N=\frac{dU}{dy}+n.$$

If we differentiate the first of these equations with respect to $y$, and the second with respect to $x$, we obtain

$$\frac{dM}{dy}=\frac{d^2U}{dx\,dy}+\frac{dm}{dy},$$

$$\frac{dN}{dx}=\frac{d^2U}{dy\,dx}+\frac{dn}{dx}.$$

Now to U may be applied the well-known theorem, according to which when any function whatever is differentiated successively according to each of two variables, the order in which the differentiations are made has no influence on the result; accordingly

$$\frac{d^2U}{dx\,dy}=\frac{d^2U}{dy\,dx}.$$

If, having regard to this last equation, we subtract the second of the two former equations from the first, we get

$$\frac{dM}{dy}-\frac{dN}{dx}=\frac{dm}{dy}-\frac{dn}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

In order to treat equation (II $a$) in a similar manner, let us substitute in it for $dQ$ its value given in (4), we thus obtain

$$\int\left(\frac{M}{T}dx+\frac{N}{T}dy\right)=0.$$

If the integral standing on the left-hand side vanish as often as $x$ and $y$ resume their original values, the expression under the integral sign must be a perfect differential of a function of $x$ and $y$, and hence the above-named condition of integrability must be fulfilled; in the present case this condition is

$$\frac{d}{dy}\left(\frac{M}{T}\right)=\frac{d}{dx}\left(\frac{N}{T}\right).$$

On performing the differentiations, and remembering that the temperature T of the body is also to be considered as a function of $x$ and $y$, we obtain

$$\frac{1}{\mathrm{T}}\cdot\frac{d\mathrm{M}}{dy}-\frac{\mathrm{M}}{\mathrm{T}^2}\cdot\frac{d\mathrm{T}}{dy}=\frac{1}{\mathrm{T}}\cdot\frac{d\mathrm{N}}{dx}-\frac{\mathrm{N}}{\mathrm{T}^2}\cdot\frac{d\mathrm{T}}{dx};$$

or differently arranged,

$$\frac{d\mathrm{M}}{dy}-\frac{d\mathrm{N}}{dx}=\frac{1}{\mathrm{T}}\left(\mathrm{M}\frac{d\mathrm{T}}{dy}-\mathrm{N}\frac{d\mathrm{T}}{dx}\right). \quad . \quad . \quad . \quad . \quad (6)$$

We will give to the equations (5) and (6) thus obtained, a somewhat different form. In order not to have too many different letters in the formulæ, we will in future replace M and N, which were introduced as symbols for the differential coefficient $\frac{d\mathrm{Q}}{dx}$ and $\frac{d\mathrm{Q}}{dy}$, by the differential coefficients themselves. We further observe that the difference on the right-hand side of (5), which on replacing $m$ and $n$ by the differential coefficients $\frac{dw}{dx}$ and $\frac{dw}{dy}$ becomes

$$\frac{d}{dy}\left(\frac{dw}{dx}\right)-\frac{d}{dx}\left(\frac{dw}{dy}\right),$$

is a function of $x$ and $y$, which may usually be regarded as known, inasmuch as the forces operating on the body externally being susceptible of direct observation, the exterior ergon can be determined. We shall call this difference, which frequently occurs in the following pages, the *ergonal difference corresponding to $xy$*, and introduce for it a particular symbol by putting

$$\mathrm{E}_{xy}=\frac{d}{dy}\left(\frac{dw}{dx}\right)-\frac{d}{dx}\left(\frac{dw}{dy}\right). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In consequence of this change in the notation, the equations (5) and (6) become

$$\frac{d}{dy}\left(\frac{d\mathrm{Q}}{dx}\right)-\frac{d}{dx}\left(\frac{d\mathrm{Q}}{dy}\right)=\mathrm{E}_{xy}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\frac{d}{dy}\left(\frac{d\mathrm{Q}}{dx}\right)-\frac{d}{dx}\left(\frac{d\mathrm{Q}}{dy}\right)=\frac{1}{\mathrm{T}}\left(\frac{d\mathrm{T}}{dy}\cdot\frac{d\mathrm{Q}}{dx}-\frac{d\mathrm{T}}{dx}\cdot\frac{d\mathrm{Q}}{dy}\right). \quad . \quad . \quad (9)$$

These two equations form, for reversible changes, the analytical expressions of the two fundamental theorems in the case where the condition of the body is defined by any two variables. From them a third, and simpler equation at once results, inasmuch as it contains only the differential coefficients of Q of the first order, namely,

$$\frac{dT}{dy}\cdot\frac{dQ}{dx}-\frac{dT}{dx}\cdot\frac{dQ}{dy}=TE_{xy}. \quad . \quad . \quad . \quad . \quad (10)$$

5. The three foregoing equations are particularly simple, when we select the temperature of the body as one of the independent variables. To this end we will put $y=T$, so that now the undetermined magnitude $x$ and the temperature T are the two independent variables. When $y=T$, it follows that

$$\frac{dT}{dy}=1.$$

Moreover, with respect to the differential coefficient $\frac{dT}{dx}$, we supposed on forming it that, whilst $x$ changes to $x+dx$, the other variable, hitherto called $y$, remains constant. Since at present T itself is the other variable, which is supposed to be constant in the differential coefficient, we have to put

$$\frac{dT}{dx}=0.$$

The ergonal-difference corresponding to $x$T is now

$$E_{xT}=\frac{d}{dT}\left(\frac{dw}{dx}\right)-\frac{d}{dx}\left(\frac{dw}{dT}\right); \quad . \quad . \quad . \quad . \quad (11)$$

and on introducing this value the equations (8), (9) and (10) become

$$\frac{d}{dT}\left(\frac{dQ}{dx}\right)-\frac{d}{dx}\left(\frac{dQ}{dT}\right)=E_{xT}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\frac{d}{dT}\left(\frac{dQ}{dx}\right)-\frac{d}{dx}\left(\frac{dQ}{dT}\right)=\frac{1}{T}\cdot\frac{dQ}{dx}, \quad . \quad . \quad . \quad . \quad (13)$$

$$\frac{dQ}{dx}=TE_{xT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If we introduce the product $TE_{xT}$, given in (14), in place of the differential coefficient $\frac{dQ}{dx}$ in equation (12), and differentiate it, as there prescribed, according to T, we obtain the following simple equation,

$$\frac{d}{dx}\left(\frac{dQ}{dT}\right)=T\frac{dE_{xT}}{dT}. \qquad (15)$$

6. We have hitherto made no special assumptions concerning the exterior forces to which the body is subjected, and to which the exterior ergon produced during a change of condition refers. We will now consider more closely a case which is of very frequent occurrence, namely, that where the only external force, or at least the only one which is important enough to merit notice in the calculations, is a pressure acting on the surface of the body with equal intensity at all points, and which is everywhere directed perpendicularly to that surface.

In this case exterior ergon is produced solely in consequence of changes of volume in the body. If we call $p$ the pressure on a unit of surface, the exterior *work* which is done, when the volume $v$ increases by $dv$, is

$$dW=pdv,$$

and accordingly the exterior *ergon*, that is to say, the exterior work measured by thermal units, is

$$dw=Apdv \qquad (16)$$

If we conceive the condition of the body to be defined by any two variables $x$ and $y$, the pressure $p$ and the volume $v$ must be considered as functions of $x$ and $y$. We can consequently write the foregoing equation in the following form,

$$dw=Ap\left(\frac{dv}{dx}dx+\frac{dv}{dy}dy\right);$$

from which it follows that

$$\left.\begin{aligned}\frac{dw}{dx}&=Ap\frac{dv}{dx},\\ \frac{dw}{dy}&=Ap\frac{dv}{dy}.\end{aligned}\right\} \qquad (17)$$

Introducing these values of $\frac{dw}{dx}$ and $\frac{dw}{dy}$ into the expression for $E_{xy}$ given in (7), performing the two differentiations therein indicated, and remembering at the same time that $\frac{d^2v}{dx\,dy}=\frac{d^2v}{dy\,dx}$, we obtain

$$E_{xy}=A\left(\frac{dp}{dy}\cdot\frac{dv}{dx}-\frac{dp}{dx}\cdot\frac{dv}{dy}\right).\quad .\quad .\quad .\quad (18)$$

We have to employ this value of $E_{xy}$ in the equations (8) and (10).

If $x$ and T be the two independent variables, we obtain

$$E_{xT}=A\left(\frac{dp}{dT}\cdot\frac{dv}{dx}-\frac{dp}{dx}\cdot\frac{dv}{dT}\right),\quad .\quad .\quad .\quad (19)$$

which quite corresponds to the preceding equation. This value has to be employed in the equations (12), (14), and (15).

The expression (18) acquires very simple forms when we choose either the volume or the pressure as one of the independent variables, and when we make the volume and the pressure the two independent variables. In these cases, as may be easily seen, the equation (18) becomes transformed, respectively, into

$$E_{vy}=A\frac{dp}{dy},\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (20)$$

$$E_{py}=-A\frac{dv}{dy},\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (21)$$

$$E_{vp}=A.\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (22)$$

If, finally, in those cases where either the volume or the pressure is taken as one of the independent variables, we wish to make the temperature the other independent variable, we need only replace $y$ by T in equations (20) and (21).

7. Under the circumstances before alluded to, when the only existing exterior force is a uniform and normal surface-pressure, the independent variables most frequently used for defining the condition of the body, are the magnitudes just mentioned, that is to say, volume and temperature, or pressure and temperature, or finally, volume and pressure. Although the systems of differential equations answering to these three cases could easily be deduced from the above general systems, yet on account of their frequent application I will here place them side by side.

The first system is the one which I have always employed in my memoirs when special cases were under consideration.

When $v$ and T are chosen as independent variables,

$$\left.\begin{aligned}
&\frac{d}{d\mathrm{T}}\left(\frac{d\mathrm{Q}}{dv}\right)-\frac{d}{dv}\left(\frac{d\mathrm{Q}}{d\mathrm{T}}\right)=\mathrm{A}\frac{dp}{d\mathrm{T}},\\
&\frac{d}{d\mathrm{T}}\left(\frac{d\mathrm{Q}}{dv}\right)-\frac{d}{dv}\left(\frac{d\mathrm{Q}}{d\mathrm{T}}\right)=\frac{1}{\mathrm{T}}\cdot\frac{d\mathrm{Q}}{dv},\\
&\frac{d\mathrm{Q}}{dv}=\mathrm{AT}\frac{dp}{d\mathrm{T}},\\
&\frac{d}{dv}\left(\frac{d\mathrm{Q}}{d\mathrm{T}}\right)=\mathrm{AT}\frac{d^2p}{d\mathrm{T}^2}.
\end{aligned}\right\}\quad\ldots\ldots\quad(23)$$

When $p$ and T are chosen as independent variables,

$$\left.\begin{aligned}
&\frac{d}{d\mathrm{T}}\left(\frac{d\mathrm{Q}}{dp}\right)-\frac{d}{dp}\left(\frac{d\mathrm{Q}}{d\mathrm{T}}\right)=-\mathrm{A}\frac{dv}{d\mathrm{T}},\\
&\frac{d}{d\mathrm{T}}\left(\frac{d\mathrm{Q}}{dp}\right)-\frac{d}{dp}\left(\frac{d\mathrm{Q}}{d\mathrm{T}}\right)=\frac{1}{\mathrm{T}}\frac{d\mathrm{Q}}{dp},\\
&\frac{d\mathrm{Q}}{dp}=-\mathrm{AT}\frac{dv}{d\mathrm{T}},\\
&\frac{d}{dp}\left(\frac{d\mathrm{Q}}{d\mathrm{T}}\right)=-\mathrm{AT}\frac{d^2v}{d\mathrm{T}^2}.
\end{aligned}\right\}\quad\ldots\ldots\quad(24)$$

When $v$ and $p$ are taken as the independent variables,

$$\left.\begin{aligned}
&\frac{d}{dp}\left(\frac{d\mathrm{Q}}{dv}\right)-\frac{d}{dv}\left(\frac{d\mathrm{Q}}{dp}\right)=\mathrm{A},\\
&\frac{d}{dp}\left(\frac{d\mathrm{Q}}{dv}\right)-\frac{d}{dv}\left(\frac{d\mathrm{Q}}{dp}\right)=\frac{1}{\mathrm{T}}\left(\frac{d\mathrm{T}}{dp}\cdot\frac{d\mathrm{Q}}{dv}-\frac{d\mathrm{T}}{dv}\cdot\frac{d\mathrm{Q}}{dp}\right),\\
&\frac{d\mathrm{T}}{dp}\cdot\frac{d\mathrm{Q}}{dv}-\frac{d\mathrm{T}}{dv}\cdot\frac{d\mathrm{Q}}{dp}=\mathrm{AT}.
\end{aligned}\right\}\quad.\quad(25)$$

8. The simplest of the cases to which the equations of the preceding Article are applicable, is that where a homogeneous body is given of absolutely uniform temperature, which is exposed to a uniform and normal surface-pressure, and can, by a change of temperature and of pressure, change its volume without at the same time changing its state of aggregation.

In this case the differential coefficient $\frac{d\mathrm{Q}}{d\mathrm{T}}$ has a simple physical meaning. For if we suppose the weight of the body to be equal to unity, this differential coefficient denotes the specific heat at constant volume, or the specific heat at constant pressure, according as, when forming it, the volume or the pressure was supposed to be constant.

In cases where the nature of the subject requires that the independent variables should often be changed, and hence where differential coefficients occur which only differ from one another in that the magnitude which was supposed to be constant during differentiation is not the same in all, it is convenient to denote this difference by an outward mark, in order to avoid the necessity of repeated verbal explanations. I shall do this by enclosing the differential coefficients in brackets, and adding, in the form of a suffix with a bar over it, the magnitude which is supposed to be constant during differentiation. Accordingly, we will write the two differential coefficients which denote the specific heat at constant volume, and the specific heat at constant pressure, in the following manner:—

$$\left(\frac{dQ}{dT}\right)_{\bar{v}}, \quad \text{and} \quad \left(\frac{dQ}{dT}\right)_{\bar{p}}.$$

Further, of the three magnitudes, temperature, volume, and pressure, which in our present case come under consideration when determining the condition of the body, each is to be regarded as a function of the other two, hence the following six differential coefficients may be formed:—

$$\left(\frac{dp}{dT}\right)_{\bar{v}}, \left(\frac{dp}{dv}\right)_{\bar{T}}; \quad \left(\frac{dv}{dT}\right)_{\bar{p}}, \left(\frac{dv}{dp}\right)_{\bar{T}}; \quad \left(\frac{dT}{dv}\right)_{\bar{p}}, \left(\frac{dT}{dp}\right)_{\bar{v}}.$$

The suffixes, which here indicate the magnitude which in each differentiation is supposed constant, might be omitted provided we agreed, once for all, that of the three magnitudes $T$, $v$, and $p$, the one which does not occur in the differential coefficients is to be considered as constant. Nevertheless, for the sake of clearness, and because differential coefficients of the same magnitudes occur in which the quantity supposed to be constant is not the same as at present, we will, at least in the following equations, retain the suffixes.

It will facilitate the calculations to be made with these six differential coefficients, if we first determine the relations existing between them.

In the first place, it is clear that amongst the six differential coefficients there are three pairs of reciprocals. For example, if we assume the magnitude $v$ to be constant, the dependence between the two other magnitudes T and $p$ is such that each of them may be regarded simply as a function of the other. It is the same with T and $v$ if $p$ be assumed to be constant, and with $v$ and $p$ when T is supposed to be invariable. Consequently we must put

$$\frac{1}{\left(\frac{dT}{dp}\right)_{\bar{v}}}=\left(\frac{dp}{dT}\right)_{\bar{v}};\quad \frac{1}{\left(\frac{dT}{dv}\right)_{\bar{p}}}=\left(\frac{dv}{dT}\right)_{\bar{p}};\quad \frac{1}{\left(\frac{dp}{dv}\right)_{\bar{T}}}=\left(\frac{dv}{dp}\right)_{\bar{T}}\quad . \quad . \quad . \quad (26)$$

In order to obtain the relation between the three pairs of differential coefficients, we will by way of example consider $p$ as a function of T and $v$. Then we have the complete differential equation

$$dp=\left(\frac{dp}{dT}\right)_{\bar{v}}dT+\left(\frac{dp}{dv}\right)_{\bar{T}}dv.$$

If, now, we apply this equation to the case where $p$ is constant, we have to put

$$dp=0 \text{ and } dv=\left(\frac{dv}{dT}\right)_{\bar{p}}dT,$$

whereby it is transformed into

$$0=\left(\frac{dp}{dT}\right)_{\bar{v}}dT+\left(\frac{dp}{dv}\right)_{\bar{T}}\cdot\left(\frac{dv}{dT}\right)_{\bar{p}}dT.$$

If we remove $dT$ and then divide by $\left(\frac{dp}{dT}\right)_{\bar{v}}$, we obtain

$$\left(\frac{dp}{dv}\right)_{\bar{T}}\cdot\left(\frac{dv}{dT}\right)_{\bar{p}}\cdot\left(\frac{dT}{dp}\right)_{\bar{v}}=-1.\quad . \quad . \quad . \quad . \quad (27)$$

With the help of this equation, in conjunction with the equations (26), we can represent each of the six differential coefficients as a product or quotient of two other differential coefficients.

9. To return to the consideration of the absorption and production of heat by the given body, let us denote the specific heat at constant volume by $c$, and the specific heat at constant pressure by C; then, if we assume the weight of the body to be unity, we must put

$$\left(\frac{dQ}{dT}\right)_{\bar{v}}=c;\quad \left(\frac{dQ}{dT}\right)_{\bar{p}}=C.$$

Further, according to equations (23) and (24),

$$\left(\frac{dQ}{dv}\right)_T = AT\left(\frac{dp}{dT}\right)_v; \quad \left(\frac{dQ}{dp}\right)_T = -AT\left(\frac{dv}{dT}\right)_p;$$

so that we can form the following complete differential equations,

$$dQ = c\,dT + AT\left(\frac{dp}{dT}\right)_v dv, \quad \ldots\ldots \tag{28}$$

$$dQ = C\,dT - AT\left(\frac{dv}{dT}\right)_p dp. \quad \ldots\ldots \tag{29}$$

By comparing these two expressions of $dQ$, we may at once deduce the relation which exists between the two specific heats $c$ and $C$. In fact, from the last equation, which has reference to $T$ and $p$ as independent variables, we can deduce an equation wherein the independent variables are $T$ and $v$. To do this, we need only consider $p$ as a function of $T$ and $v$, and accordingly write

$$dp = \left(\frac{dp}{dT}\right)_v dT + \left(\frac{dp}{dv}\right)_T dv.$$

By the introduction of this value of $dp$ in equation (29) it is transformed into

$$dQ = \left[C - AT\left(\frac{dv}{dT}\right)_p \cdot \left(\frac{dp}{dT}\right)_v\right] dT - AT\left(\frac{dv}{dT}\right)_p \cdot \left(\frac{dp}{dv}\right)_T dv.$$

If in place of the product of two differential coefficients in the last term of the above, we put by help of equation (27) a simple differential coefficient, we get

$$dQ = \left[C - AT\left(\frac{dv}{dT}\right)_p \cdot \left(\frac{dp}{dT}\right)_v\right] dT + AT\left(\frac{dp}{dT}\right)_v dv.$$

On comparing this expression for $dQ$ with that given in (28), and considering that the coefficients of $dT$ in both expressions must be equal, we obtain the following equation expressing the relation between the two specific heats,

$$c = C - AT\left(\frac{dv}{dT}\right)_p \cdot \left(\frac{dp}{dT}\right)_v. \quad \ldots\ldots \tag{30}$$

The differential coefficient $\left(\frac{dv}{dT}\right)_p$ which here occurs represents the expansion of the body caused by an increase in its temperature, and is to be considered as known. The other differential coefficient, $\left(\frac{dp}{d\mathrm{T}}\right)_v$, is not, it is true, usually given directly by observation in the case of solid and liquid bodies, but according to (27) we may put

$$\left(\frac{dp}{d\mathrm{T}}\right)_v = -\frac{\left(\frac{dv}{d\mathrm{T}}\right)_p}{\left(\frac{dv}{dp}\right)_\mathrm{T}},$$

and the differential coefficient in the numerator of this fraction is again the one before referred to, whilst the differential coefficient in the denominator represents, when taken with a negative sign, the diminution of volume through increase of pressure or the compressibility; for a number of liquids this has been measured, and for solid bodies it can be approximately estimated from the coefficients of elasticity. By the introduction of this fraction equation (30) becomes

$$c = \mathrm{C} + \mathrm{AT}\frac{\left(\frac{dv}{d\mathrm{T}}\right)_p^2}{\left(\frac{dv}{dp}\right)_\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

On using this equation for numerical calculations, it must be remembered that the unit of volume in the differential coefficients is the cube of that unit of length which was employed in the determination of the magnitude A; and the unit of pressure is the pressure which a unit of weight exerts when spread over a unit of surface. Hence we have to reduce to these units the coefficients of expansion and the coefficients of compressibility whenever the latter have been referred to other units, as is usually the case.

Since the differential coefficient $\left(\frac{dv}{dp}\right)_\mathrm{T}$ is always negative, it follows that the specific heat at constant volume must always be less than that at constant pressure. The other differential coefficient $\left(\frac{dv}{d\mathrm{T}}\right)_p$ is generally a positive magnitude. For water, however, at the temperature of maximum of density it vanishes, and accordingly the two specific heats at this temperature are equal. At all other temperatures, under or over the temperature of maximum density, the specific heat at constant volume is less than that at constant pressure; for even if the differential coefficient $\left(\frac{dv}{dT}\right)_{\bar{p}}$ have a negative value below this temperature, the signs in the formula are not affected thereby, since the square of this differential coefficient is alone involved therein*.

From the equations (28) and (29) we can easily deduce a complete differential equation for Q, having reference to $p$ and $v$ as independent variables. To do this, we need only consider

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* To give an example of the application of equation (31), we will consider water at a few definite temperatures, and calculate the difference between the two specific heats.

According to the observations of Kopp, whose results are tabulated in the *Lehrbuch der Phys. und Theor. Chemie*, S. 204, we have for water, if its volume at 4° be taken as unit, the following coefficients of expansion

at $\overset{\circ}{0}$ .... −0·000061,
at 25 .... +0·00025,
at 50 .... +0·00045.

According to the observations of Grassi (*Ann. de Chim. et de Phys.* 3 sér. t. xxxi. p. 437, and Krönig's *Journ. für Physik des Auslandes*, Bd. ii. S. 129), we have for the compressibility of water the following numbers, which give the diminution of volume, caused by an increase of pressure equal to an atmosphere, expressed as a fraction of the volume corresponding to the original pressure:—

at $\overset{\circ}{0}$ .... 0·000050,
at 25 .... 0·000046,
at 50 .... 0·000044.

We will now by way of example go through the calculation for the temperature of 25°.

As unit of length we will choose the metre, and as unit of weight the kilogramme. We then have to assume a cubic metre as the unit of volume, and since the volume of a kilogramme of water at 4° is 0·001 cubic metre, we must, in order to obtain $\left(\frac{dv}{dT}\right)_{\bar{p}}$, multiply the above-given coefficient of expansion with 0·001, hence

$$\left(\frac{dv}{dT}\right)_{\bar{p}}=0{\cdot}00000025=25\,.\,10^{-8}.$$

In accordance with the foregoing, the unit of volume, in the case of compressibility, is that which water occupies at the temperature under consideration and at the original pressure, which we may assume to be the ordinary pressure of one atmosphere. This volume is, at 25°, equal to 0·001003 cubic metre. Moreover, one atmosphere is taken as the unit of pressure, whilst we must take for our unit the pressure of a kilogramme upon a square

T as a function of $p$ and $v$, and accordingly put

$$d\mathrm{T}=\left(\frac{d\mathrm{T}}{dp}\right)_{\bar{v}}dp+\left(\frac{d\mathrm{T}}{dv}\right)_{\bar{p}}dv.$$

If we substitute this value in equation (29) for $d\mathrm{T}$, we have

$$d\mathrm{Q}=\left[\mathrm{C}\left(\frac{d\mathrm{T}}{dp}\right)_{\bar{v}}-\mathrm{AT}\left(\frac{dv}{d\mathrm{T}}\right)_{\bar{p}}\right]dp+\mathrm{C}\left(\frac{d\mathrm{T}}{dv}\right)_{\bar{p}}dv$$
$$=\left(\frac{d\mathrm{T}}{dp}\right)_{\bar{v}}\left[\mathrm{C}-\mathrm{AT}\left(\frac{dv}{d\mathrm{T}}\right)_{\bar{p}}\cdot\left(\frac{dp}{d\mathrm{T}}\right)_{\bar{v}}\right]dp+\mathrm{C}\left(\frac{d\mathrm{T}}{dv}\right)_{\bar{p}}dv.$$

The difference, standing between square brackets in the last expression, is by (30) equal to $c$, hence we can write the equation thus:

$$d\mathrm{Q}=c\left(\frac{d\mathrm{T}}{dp}\right)_{\bar{v}}dp+\mathrm{C}\left(\frac{d\mathrm{T}}{dv}\right)_{\bar{p}}dv. \quad \ldots\ldots\ldots \quad (32)$$

10. The three complete differential equations (28), (29), and

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metre, whereby one atmosphere of pressure will be represented by 10333. Accordingly we have

$$\left(\frac{dv}{dp}\right)_{\bar{\mathrm{T}}}=-\frac{0{\cdot}000046\,.\,0{\cdot}001003}{10333}=-45\,.\,10^{-13}.$$

Besides this we have, at 25°, to put

$$\mathrm{T}=273+25=298,$$

and, with Joule, we will assume

$$\mathrm{A}=\frac{1}{424}.$$

These numerical values introduced into equation (31) give

$$\mathrm{C}-c=\frac{298}{424}\cdot\frac{25^2\,.\,10^{-16}}{45\;.\,10^{-13}}=0{\cdot}0098.$$

In the same manner the following numbers result from the above values of the coefficients of expansion and of compressibility at 0° and 50°;

at 0° .... $\mathrm{C}-c=0{\cdot}0005$,
at 50 .... $\mathrm{C}-c=0{\cdot}0358$.

If for the specific heat C at constant pressure we use the values found experimentally by Regnault, we obtain for the two specific heats the following pairs of numbers:—

at 0° $\left\{\begin{array}{l}\mathrm{C}=1,\\ c=0{\cdot}9995;\end{array}\right.$

at 25° $\left\{\begin{array}{l}\mathrm{C}=1{\cdot}0016,\\ c=0{\cdot}9918;\end{array}\right.$

at 50° $\left\{\begin{array}{l}\mathrm{C}=1{\cdot}0042,\\ c=0{\cdot}9684.\end{array}\right.$

(32) do not fulfil the condition of immediate integrability; this is at once manifest, as far as the two first are concerned, from the equations already given. In fact, if we introduce into the equations, which in the systems (23) and (24) stand lowest, the letters $c$ and C, they become

$$\left.\begin{aligned}\left(\frac{dc}{dv}\right)_{\bar{T}}&=AT\left(\frac{d^2p}{dT^2}\right)_{\bar{v}},\\ \left(\frac{dC}{dp}\right)_{\bar{T}}&=-AT\left(\frac{d^2v}{dT^2}\right)_{\bar{p}};\end{aligned}\right\}\quad\ldots\ldots\quad(33)$$

whilst the equations which must be fulfilled if (28) and (29) are integrable, are

$$\left(\frac{dc}{dv}\right)_{\bar{T}}=A\left[T\left(\frac{d^2p}{dT^2}\right)_{\bar{v}}+\left(\frac{dp}{dT}\right)_{\bar{v}}\right],$$
$$\left(\frac{dC}{dp}\right)_{\bar{T}}=-A\left[T\left(\frac{d^2v}{dT^2}\right)_{\bar{p}}+\left(\frac{dv}{dT}\right)_{\bar{p}}\right].$$

In a similar, though somewhat more tedious manner, it may be proved that the equation (32) is not integrable; this, however, is manifest from the circumstance that (32) is deduced from (28) and (29). The three equations belong, therefore, to those complete differential equations which are described in the Introduction to the present collection of Memoirs, and which can only be integrated when another relation between the variables is given, and by that means the sequence of the changes is prescribed.

Among the manifold applications which can be made of the equations (28), (29), and (32), I will here only adduce one by way of example. Let us assume that the body changes its volume in a reversible manner through a change of pressure, without thereby losing or acquiring heat. We will determine the change of volume which, under these circumstances, is caused by a given change of pressure, and in what manner the temperature simultaneously changes, or more generally, what relations, under these circumstances, exist between temperature, volume, and pressure.

We obtain these relations immediately by putting $dQ=0$ in the three above-named equations. Equation (28) gives

$$c\,dT+AT\left(\frac{dp}{dT}\right)_{\bar{v}}dv=0.$$

If we divide the terms of this equation by $dv$, the fraction $\frac{dT}{dv}$ thereby resulting is, for this particular case, the differential coefficient of T according to $v$, which we will distinguish from other differential coefficients of T according to $v$ by giving to it the suffix $\overline{Q}$. Hence we obtain

$$\left(\frac{dT}{dv}\right)_{\overline{Q}}=-\frac{AT}{c}\left(\frac{dp}{dT}\right)_{\overline{v}}. \qquad (34)$$

In a similar manner we obtain from equation (29)

$$\left(\frac{dT}{dp}\right)_{\overline{Q}}=\frac{AT}{C}\left(\frac{dv}{dT}\right)_{\overline{p}}. \qquad (35)$$

From the equation (32) we obtain, in the first place,

$$\left(\frac{dv}{dp}\right)_{\overline{Q}}=-\frac{c}{C}\frac{\left(\frac{dT}{dp}\right)_{\overline{v}}}{\left(\frac{dT}{dv}\right)_{\overline{p}}},$$

for which, according to (27), we may write

$$\left(\frac{dv}{dp}\right)_{\overline{Q}}=\frac{c}{C}\left(\frac{dv}{dp}\right)_{\overline{T}}. \qquad (36)$$

On introducing into this equation the value of $c$ as given in (31), it becomes

$$\left(\frac{dv}{dp}\right)_{\overline{Q}}=\left(\frac{dv}{dp}\right)_{\overline{T}}+\frac{AT}{C}\left(\frac{dv}{dT}\right)_{\overline{p}}^{2}. \qquad (37)$$

11. When the equations of the two foregoing Articles are applied to a perfect gas, they assume still more definite, and at the same time very simple forms.

In this case the laws of Mariotte and Gay-Lussac give the following relation between T, $v$, and $p$,

$$pv=RT, \qquad (38)$$

wherein R is a constant. From this it follows that

$$\left.\begin{array}{ll}\left(\frac{dp}{dT}\right)_{\overline{v}}=\frac{R}{v}; & \left(\frac{dv}{dT}\right)_{\overline{p}}=\frac{R}{p}, \\ \left(\frac{d^2p}{dT^2}\right)_{\overline{v}}=0; & \left(\frac{d^2v}{dT^2}\right)_{\overline{p}}=0.\end{array}\right\} \qquad (39)$$

On combining the two last equations with the equations (33), we obtain

$$\left(\frac{dc}{dv}\right)_{\mathrm{T}}=0; \quad \left(\frac{d\mathrm{C}}{dp}\right)_{\mathrm{T}}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

From this it follows that for a perfect gas the two specific heats $c$ and C can only be functions of the temperature. On other grounds, which depend on special considerations into which I will not now enter, it may be shown that the two specific heats are independent of the temperature, and consequently are constant; results which, with respect to specific heat at constant pressure, have been corroborated by the experimental researches of Regnault on permanent gases.

If we apply the two first of equations (39) to equation (30), which gives the relation between the two specific heats, we obtain the expression

$$c=\mathrm{C}-\mathrm{A}\frac{\mathrm{R}}{p}\cdot\frac{\mathrm{R}}{v},$$

which by (38) becomes

$$c=\mathrm{C}-\mathrm{AR}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

On applying the first two of equations (39), the equations (28), (29), and (32) assume the following forms :

$$\left.\begin{aligned} d\mathrm{Q}&=cd\mathrm{T}+\mathrm{AR}\frac{\mathrm{T}}{v}\,dv,\\ d\mathrm{Q}&=\mathrm{C}d\mathrm{T}-\mathrm{AR}\frac{\mathrm{T}}{p}\,dp,\\ d\mathrm{Q}&=\frac{c}{\mathrm{R}}\,vdp+\frac{\mathrm{C}}{\mathrm{R}}\,pdv,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

wherein, moreover, the product AR can, in virtue of (41), be replaced by the difference $\mathrm{C}-c$. As in the First Memoir of this collection, and in the Appendix B to the Sixth Memoir, several examples have already been given of the applications of these equations, I will not here enter into further details.

12. Another case, which on account of its frequent applications is of particular interest, is that where with the changes of condition of the body *a partial change of the state of aggregation* is associated.

We will assume that a body is given, of which one part is in one, and the remaining part in another state of aggregation. For instance, one portion of the body may be conceived to be in a liquid, and the rest in a vaporous state (the density of the latter being that which the vapour naturally assumes when in contact with the liquid), or one part of the body may be in a solid and the other in a liquid state, or one part in a solid and the other in a vaporous state. Accordingly we will, for the sake of generality, abstain from explicitly defining the two states of aggregation with which we are to be concerned, and simply refer to them as the *first* and *second* states of aggregation.

Conceive then a certain quantity of matter to be enclosed in a vessel of a given volume, and one portion of it to be in the first and the other in the second state of aggregation. If the specific volumes (volumes referred to the unit of weight) which the substance occupies at a given temperature in the two states of aggregation be unequal, the two portions existing in different states of aggregation in a given space must necessarily have quite definite magnitudes. For when the portion which is in the state of aggregation of greater specific volume increases in magnitude, the pressure which the enclosed substance exerts on the containing walls, and with it the reaction of the latter on the substance, must likewise increase, so that a point will ultimately be reached when the pressure is so great as to prevent all further passage into this state of aggregation. When this point is reached, the magnitudes of the portions present in the two states of aggregation cannot change further, so long as the temperature of the mass and its volume (*i. e.* the volume of the vessel) remain constant. But if, whilst the temperature remains constant, the volume of the vessel increase, the portion which is in the state of aggregation corresponding to the greater specific volume may increase still further at the expense of the other, until the same pressure as before is again reached, and all further change again prevented.

Hence follows a peculiarity which distinguishes this case from all others. For if we take the temperature and the volume of the mass as the two independent variables by which its condition is defined, then the pressure is not a function of both these variables, but of the temperature solely. The same thing also occurs when, instead of the volume, another magnitude is taken for the second independent variable, which can likewise change independently of the temperature and, together with the temperature, define the whole condition of the body;—the pressure cannot depend on such a variable. The two magnitudes, temperature and pressure, cannot in this case be chosen as the two variables which serve to define the condition of the body.

In conjunction with the temperature T, we will now, in order to define the condition of the body, take any undetermined magnitude $x$ as our second independent variable. Accordingly, in the expression

$$E_{xT}=A\left(\frac{dp}{dT}\cdot\frac{dv}{dx}-\frac{dp}{dx}\cdot\frac{dv}{dT}\right),$$

which by (19) gives the ergonal difference corresponding to $xT$, and which we will next consider, we must put $\frac{dp}{dx}=0$, whereby it will become

$$E_{xT}=A\frac{dp}{dT}\cdot\frac{dv}{dx}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

By means of this the three equations (12), (13), and (14) take the following forms :—

$$\frac{d}{dT}\left(\frac{dQ}{dx}\right)-\frac{d}{dx}\left(\frac{dQ}{dT}\right)=A\frac{dp}{dT}\cdot\frac{dv}{dx}, \quad . \quad . \quad . \quad (44)$$

$$\frac{d}{dT}\left(\frac{dQ}{dx}\right)-\frac{d}{dx}\left(\frac{dQ}{dT}\right)=\frac{1}{T}\cdot\frac{dQ}{dx}, \quad . \quad . \quad . \quad . \quad (45)$$

$$\frac{dQ}{dx}=AT\frac{dp}{dT}\cdot\frac{dv}{dx}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

13. In order to give these equations more definite forms, we will call the whole weight of the substance M, and the portion of it which is in the second state of aggregation $m$, so that $M-m$ is the weight of the portion which is in the first state of aggregation. We will, further, consider the magnitude $m$ as the independent variable which, together with T, defines the condition of the body.

Let the specific volume of the substance in the first state of aggregation be denoted by $\sigma$, and the specific volume in the second state of aggregation by $s$. Both magnitudes have reference to the temperature T, and to the pressure corresponding to this temperature, and, like the pressure, are to be regarded as functions of the temperature solely. If we denote, further, the volume which the whole mass possesses by $v$, we have to put

$$\begin{aligned} v &= (M-m)\sigma + ms \\ &= m(s-\sigma) + M\sigma, \end{aligned}$$

or, introducing the symbol $u$ for the difference $s-\sigma$,

$$v = mu + M\sigma, \quad \text{(47)}$$

whence follows

$$\frac{dv}{dm} = u. \quad \text{(48)}$$

Let $r$ be the quantity of heat which must be imparted to the mass in order that a unit of weight of it at the temperature T, and under the corresponding pressure, may pass from the first state of aggregation into the second, so that

$$\frac{dQ}{dm} = r. \quad \text{(49)}$$

We will next introduce the specific heats of the substance in the two states of aggregation into the equations. The specific heat treated of here is neither the specific heat at constant volume nor that at constant pressure, but has reference to that quantity of heat which is necessary to heat the substance when simultaneously with the temperature the pressure changes in the manner determined by the circumstances of the case under consideration. This kind of specific heat is denoted in the following formulæ by $c$ for the first state of aggregation and by $h$ for the second*, and we have

$$\frac{dQ}{dT} = (M-m)c + mh,$$

or, arranged differently,

$$\frac{dQ}{dT} = m(h-c) + Mc. \quad \text{(50)}$$

From (49) and (50) it follows immediately that

$$\frac{d}{dT}\left(\frac{dQ}{dm}\right) = \frac{dr}{dT}; \quad \frac{d}{dm}\left(\frac{dQ}{dT}\right) = h - c. \quad \text{(51)}$$

On introducing the values given in the equations (48) to (51) into the equations (44), (45), and (46), after replacing $x$ by $m$

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* The letter $c$, therefore, has in the following formulæ a meaning different from what it had above, when it denoted the specific heat at constant volume.

in the latter, we have

$$\frac{dr}{d\mathrm{T}}+c-h=\mathrm{A}u\frac{dp}{d\mathrm{T}}, \quad \ldots \ldots \quad (52)$$

$$\frac{dr}{d\mathrm{T}}+c-h=\frac{r}{\mathrm{T}}, \quad \ldots \ldots \quad (53)$$

$$r=\mathrm{AT}u\frac{dp}{d\mathrm{T}}. \quad \ldots \ldots \quad (54)$$

These are the fundamental equations, having reference to the formation of vapour, which have already been established in the First Memoir of this collection (pp. 34, 65, and 52).

In the previous numerical calculations, which had special reference to the vaporization of water, I did not distinguish, in the case of the liquid state of aggregation, the specific heat implied in these equations from the specific heat of water at constant pressure. This procedure was in fact perfectly justifiable, since the difference between these two kinds of specific heat is less than the error of observation occurring in the experimental determination of the specific heat*.

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* We can easily deduce from the above equations the relation which exists between the specific heat at constant pressure and that specific heat which corresponds to the assumption that the pressure increases with the temperature in such a manner that it is always equal to the maximum tension of the vapour given off by the liquid.

According to equation (29), the quantity of heat which must be imparted to a unit-weight of the liquid while the temperature increases by $d\mathrm{T}$, and the pressure by $dp$, is determined by the equation

$$d\mathrm{Q}=\mathrm{C}d\mathrm{T}-\mathrm{AT}\left(\frac{dv}{d\mathrm{T}}\right)_{\bar{p}}dp,$$

wherein C denotes the specific heat at constant pressure. Let us now assume that the pressure increases with the temperature in the same manner as the maximum tension of the vapour, and let us denote the increment of pressure which corresponds to the increment of temperature $d\mathrm{T}$ by $\frac{dp}{d\mathrm{T}}d\mathrm{T}$; the quantity of heat which under these circumstances must be imparted to a unit-weight of liquid in order to raise its temperature by $d\mathrm{T}$, will then be represented by

$$d\mathrm{Q}=\mathrm{C}d\mathrm{T}-\mathrm{AT}\left(\frac{dv}{d\mathrm{T}}\right)_{\bar{p}}\cdot\frac{dp}{d\mathrm{T}}d\mathrm{T}.$$

On dividing this equation by $d\mathrm{T}$, the resulting fraction $\frac{d\mathrm{Q}}{d\mathrm{T}}$ will denote the specific heat under consideration; and since the latter is denoted by $c$ in the

If we form the complete differential equation

$$dQ=\frac{dQ}{dm}dm+\frac{dQ}{dT}dT,$$

and put therein the values given in (49) and (50), we deduce

$$dQ=rdm+[m(h-c)+Mc]dT.$$

On substituting for $h-c$ its value resulting from (53), we have

$$dQ=rdm+\left[m\left(\frac{dr}{dT}-\frac{r}{T}\right)+Mc\right]dT,$$

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text, we shall have

$$c=C-AT\left(\frac{dv}{dT}\right)_{\bar{p}}\cdot\frac{dp}{dT}.$$

Let us apply this specially to water, and at the same time, by way of example, adopt the temperature 100°. According to the experiments of Kopp, the coefficient of expansion of water at 100°, the volume of the water at 4° being taken as unit, is 0·00080. We must multiply this magnitude by 0·001, in order to obtain $\left(\frac{dv}{dT}\right)_{\bar{p}}$, for the case where a cubic metre has been taken as the unit of volume and a kilogramme as the unit of weight. Hence

$$\left(\frac{dv}{dT}\right)_{\bar{p}}=0\cdot00000080.$$

Again, according to the tension series of Regnault, the pressure being expressed in kilogrammes to the square metre, we have for the temperature 100°,

$$\frac{dp}{dT}=370.$$

The absolute temperature T at 100° is nearly equal to 373, and for A we will put with Joule $\frac{1}{424}$; we thus obtain

$$AT\left(\frac{dv}{dT}\right)_{\bar{p}}\cdot\frac{dp}{dT}=\frac{373}{424}\cdot0\cdot00000080\cdot370=\cdot00026.$$

Hence follows

$$c=C-0\cdot00026;$$

and if we now assume for the specific heat of water, at 100°, under constant pressure, the value resulting from Regnault's empirical formulæ, we obtain the following values for the two specific heats under comparison:

$$C=1\cdot013,$$
$$c=1\cdot01274.$$

Hence we see that the two magnitudes are so nearly equal that it would have been useless to take the difference between them into account in my former numerical calculations.

The consideration of the influence of pressure on the freezing of liquids leads to a somewhat different result; for a considerable change in the pressure which equation may also be written

$$dQ = d(mr) - \frac{mr}{T}dT + McdT, \quad . \quad . \quad . \quad (55)$$

or still shorter,

$$dQ = Td\left(\frac{mr}{T}\right) + McdT. \quad . \quad . \quad . \quad . \quad . \quad (56)$$

I will not enter here into the applications of these equations, since they have frequently been discussed in the First and Fifth Memoirs of this collection.

14. All the foregoing considerations had reference to changes

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changes the freezing-point very little, and hence the differential coefficient $\frac{dp}{dT}$ has, in this case, a very great value. The procedure which I adopted in my Note on this subject (p. 82 of this collection) is therefore not quite accurate, since I there also employed, in numerical calculations, the known values of $c$ and $h$ which correspond to the specific heats of water and ice at constant pressure. In the Appendix to the Note (p. 89), I have, in fact, already alluded to this circumstance. If we assume, in accordance with the calculations made in that Note, that for an increment of pressure amounting to one atmosphere the freezing-point sinks about 0°·00733, we must put

$$\frac{dp}{dT} = -\frac{10333}{0{\cdot}00733}.$$

On bringing this value into combination with the coefficients of expansion of water and of ice at 0° in the same manner as before, we obtain, instead of the numbers 1 and 0·48 which represent the specific heats of water and ice at constant pressure, the following values :—

$$c = 1 - 0{\cdot}05 = 0{\cdot}95,$$
$$h = 0{\cdot}48 + 0{\cdot}14 = 0{\cdot}62.$$

Applying these values to the equation

$$\frac{dr}{dT} = c - h + \frac{r}{T},$$

we have, instead of the result,

$$\frac{dr}{dT} = 0{\cdot}52 + 0{\cdot}29 = 0{\cdot}81,$$

given at p. 82, the following somewhat different one :—

$$\frac{dr}{dT} = 0{\cdot}33 + 0{\cdot}29 = 0{\cdot}62.$$

It may, however, be remarked, with reference to the small correction which we have here taken occasion to introduce, that it relates only to an isolated calculation,—in fact to the numerical calculation of an equation, which, as I have stated in the Note, is practically unimportant, and only merits mention for theoretical considerations; the equation itself and the theoretical considerations referring thereto are not affected by this correction.

which occurred in a reversible manner. We will now also take *non-reversible* changes into consideration in order briefly to indicate at least the most important features of their treatment.

In mathematical investigations on non-reversible changes two circumstances, especially, give rise to peculiar determinations of magnitudes. In the first place, the quantities of heat which must be imparted to, or withdrawn from a changeable body are not the same, when these changes occur in a non-reversible manner, as they are when the same changes occur reversibly. In the second place, with each non-reversible change is associated an uncompensated transformation, a knowledge of which is, for certain considerations, of importance.

In order to be able to exhibit the analytical expressions corresponding to these two circumstances, I must in the first place recall a few magnitudes contained in the equations which I have previously established.

One of these is connected with the first fundamental theorem, and is the magnitude U, contained in equation (I *a*) and discussed at the beginning of this Memoir; it represents the *thermal and ergonal content,* or the energy of the body. To determine this magnitude, we must apply the equation (I *a*), which may be thus written,

$$dU = dQ - dw\,; \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (57)$$

or, if we conceive it to be integrated, thus:

$$U = U_0 + Q - w. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (58)$$

Herein $U_0$ represents the value of the energy for an arbitrary initial condition of the body, Q denotes the quantity of heat which must be imparted to the body, and $w$ the exterior *ergon* which is produced whilst the body passes in any manner from its initial to its present condition. As was before stated, the body can be conducted in an infinite number of ways from one condition to another, even when the changes are to be reversible, and of all these ways we may select that one which is most convenient for the calculation.

The other magnitude to be here noticed is connected with the second fundamental theorem, and is contained in equation (II *a*). In fact if, as equation (II*a*) asserts, the integral $\int\frac{dQ}{T}$ vanishes whenever the body, starting from any initial condition, returns thereto after its passage through any other conditions, then the expression $\frac{dQ}{T}$ under the sign of integration must be the complete differential of a magnitude which depends only on the present existing condition of the body, and not upon the way by which it reached the latter. Denoting this magnitude by S, we can write

$$dS = \frac{dQ}{T}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

or, if we conceive this equation to be integrated for any reversible process whereby the body can pass from the selected initial condition to its present one, and denote at the same time by $S_0$ the value which the magnitude S has in that initial condition,

$$S = S_0 + \int \frac{dQ}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

This equation is to be used in the same way for determining S as equation (58) was for defining U.

The physical meaning of the magnitude S has been already discussed in the Sixth Memoir. If in the fundamental equation (II) of the present Memoir, which holds for all changes of condition of the body that occur in a reversible manner, we make a small alteration in the notation, so that the heat taken up by the changing body, instead of the heat given off by it, is reckoned as positive, that equation will assume the form

$$\int \frac{dQ}{T} = \int \frac{dH}{T} + \int dZ. \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

The two integrals on the right are the values for the case under consideration, of two magnitudes first introduced in the Sixth Memoir.

In the first integral, H denotes the heat actually present in the body, which, as I have proved, depends solely on the temperature of the body and not on the arrangement of its parts. Hence it follows that the expression $\frac{dH}{T}$ is a complete differential, and consequently that if for the passage of the body from its initial condition to its present one we form the integral $\int \frac{dH}{T}$, we shall thereby obtain a magnitude which is perfectly defined by the present condition of the body, without the necessity of knowing in what manner the transition from one condition to the other took place. For reasons which are stated in the Sixth Memoir, I have called this magnitude the *transformation-value* of the heat present in the body.

It is natural when integrating, to take, for initial condition, that for which $H=0$, in other words, to start from the absolute zero of temperature; for this temperature, however, the integral $\int\frac{dH}{T}$ is infinite, so that to obtain a finite value, we must take an initial condition for which the temperature has a finite value. The integral does not then represent the transformation-value of the entire quantity of heat contained in the body, but only the transformation-value of the excess of heat which the body contains in its present condition over that which it possessed in the initial condition. I have expressed this by calling the integral thus formed *the transformation-value of the body's heat, estimated from a given initial condition* (p. 248). For brevity we will denote this magnitude by Y.

The magnitude Z occurring in the second integral I have called the *disgregation* of the body. It depends on the arrangement of the particles of the body, and the measure of an increment of disgregation is the equivalence-value of that transformation from ergon to heat which must take place in order to cancel the increment of disgregation, and thus serve as a substitute for that increment. Accordingly we may say that the disgregation is the transformation-value of the existing arrangement of the particles of the body. Since in determining the disgregation we must proceed from some initial condition of the body, we will assume that the initial condition selected for this purpose is the same as that which was selected for the determination of the transformation-value of the heat actually present in the body.

The sum of the two magnitudes Y and Z, just discussed, is the before-mentioned magnitude S. To show this, let us return to equation (61), and assuming, for the sake of generality, that the initial condition, to which the integrals in this equation refer, is not necessarily the same as the initial condition which was selected when determining Y and Z, but that the integrals refer to a change which originated in any manner whatever suited to any special investigation, we may then write the integrals on the right of (61) thus:

$$\int\frac{dH}{T}=Y-Y_0 \quad\text{and}\quad \int dZ=Z-Z_0,$$

wherein $Y_0$ and $Z_0$ are the values of Y and Z which correspond to the initial condition. By these means equation (61) becomes

$$\int\frac{dQ}{T}=Y+Z-(Y_0+Z_0). \quad . \quad . \quad . \quad . \quad . \quad (62)$$

Putting herein

$$Y+Z=S, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

and in a corresponding manner

$$Y_0+Z_0=S_0,$$

we obtain the equation

$$\int\frac{dQ}{T}=S-S_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

which is merely a different form of the equation (60), by which S is determined.

We might call S the *transformational content* of the body, just as we termed the magnitude U its *thermal and ergonal content*. But as I hold it to be better to borrow terms for important magnitudes from the ancient languages, so that they may be adopted unchanged in all modern languages, I propose to call the magnitude S the *entropy* of the body, from the Greek word *τροπή*, *transformation*. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable.

Before proceeding further, let us collect together, for the sake of reference, the magnitudes which have been discussed in the course of this Memoir, and which have either been introduced into science by the mechanical theory of heat, or have obtained thereby a different meaning. They are six in number, and possess in common the property of being defined by the present condition of the body, without the necessity of our knowing the mode in which the body came into this condition: (1) the *thermal content,* (2) the *ergonal content,* (3) the sum of the two foregoing, that is to say the thermal and ergonal content, or the *energy,* (4) the *transformation-value of the thermal content,* (5) the *disgregation,* which is to be considered as the transformation-value of the existing arrangement of particles, (6) the sum of the last two, that is to say, the *transformational content,* or the *entropy.*

15. In order to determine the energy and the entropy for particular cases, the several expressions above given for $dQ$ have to be used in conjunction with the equations (57) and (59), or (58) and (60). I will here, by way of example, treat a few simple cases merely.

Let the body under consideration be homogeneous and of the same temperature throughout, upon which the only active foreign force is a uniform and normal surface-pressure, and let us assume that it can change its volume, with a change of temperature and pressure, without at the same time suffering a partial change of its state of aggregation; then if the weight of the body be taken as unit, we can employ for $dQ$ the equations (28), (29), and (32) given in Art. 9. In these equations, the specific heat at constant volume, there denoted by $c$, and the specific heat at constant pressure, denoted by C, occur; now, since the latter specific heat is that which is usually directly determined by observation, we will use the equation (29) in which it occurs, namely,

$$dQ = C dT - AT\frac{dv}{dT}dp\text{*}.$$

With respect to the exterior ergon we have, for an infinitesimal change of condition during which the volume increases by $dv$, the equation

$$dw = Apdv\,;$$

and if T and $p$ are chosen as independent variables, we can give this equation the form

$$dw = Ap\left(\frac{dv}{dT}dT + \frac{dv}{dp}dp\right).$$

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* I write here simply $\frac{dv}{dT}$ instead of the symbol $\left(\frac{dv}{dT}\right)_p$ in (29), because in a case where only T and $p$ occur as independent variables, it is manifest that in the differentiation with respect to T, the other variable $p$ is supposed constant.

Applying these expressions for $dQ$ and $dw$ to equations (57) and (59), we obtain

$$\left.\begin{aligned} dU &= \left(C - Ap\frac{dv}{dT}\right)dT - A\left(T\frac{dv}{dT} + p\frac{dv}{dp}\right)dp, \\ dS &= \frac{C}{T}dT - A\frac{dv}{dT}dp. \end{aligned}\right\} \quad . \quad . \quad . \quad (65)$$

From the equation

$$\frac{dC}{dp} = -AT\frac{d^2v}{dT^2},$$

the last in (33), it is easy to see that these two complete differential equations are integrable, without necessarily assuming a further relation between the variables. By performing the integration, we obtain expressions for U and S, of which each contains but one undetermined constant; this is the value which the magnitude U or S has in the initial condition of the body selected as one of the limits of the integration.

If the body is a perfect gas, the equations assume a simpler form. They may be obtained either by combining equations (65) with the equation $pv = RT$, which expresses the law of Mariotte and Gay-Lussac, or by going back to the equations (57) and (59), putting therein, in place of $dQ$, one of the expressions before deduced for a perfect gas, and contained in the equations (42), and introducing at the same time one of the three expressions $AR\frac{T}{v}dv$, $AR\left(dT - \frac{T}{p}dp\right)$, and $Apdv$ for $dw$. If we choose the first of equations (42), as being the most convenient for the present case, we have

$$\left.\begin{aligned} dU &= cdT, \\ dS &= c\frac{dT}{T} + AR\frac{dv}{v}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

Since $c$ and AR are constant, these equations may be immediately integrated; on doing so and denoting the initial values of U and S, for which $T = T_0$ and $v = v_0$, by $U_0$ and $S_0$, we have

$$\left.\begin{aligned} U &= U_0 + c(T - T_0), \\ S &= S_0 + c\log\frac{T}{T_0} + AR\log\frac{v}{v_0}. \end{aligned}\right\} \quad . \quad . \quad . \quad (67)$$

We will treat, as a last special case, that to which Arts. 12 and

13 refer, where the body under consideration is a mass of the weight M, of which the portion $M-m$ is in one, and the portion $m$ in a different state of aggregation, and where the pressure, to which the whole mass is exposed, depends only on the temperature.

We will assume that at first the whole mass is in the first state of aggregation, that it has the temperature $T_0$, and is also exposed to the pressure corresponding to this temperature. The values of the energy and entropy in this initial condition may be denoted by $U_0$ and $S_0$. We will next conceive the body to be brought from this initial condition to its final one, in the following manner :—Whilst the entire mass continues in the first state of aggregation, the body is first raised from the temperature $T_0$ to the temperature T, and at the same time the pressure changes so as to have at every moment the magnitude which corresponds to the then existing temperature. Thereupon the portion of the mass whose weight is $m$ passes, at the temperature T, from the first into the second state of aggregation. We will consider these two changes separately, and in so doing employ the notation of Art. 13.

For the first-mentioned change of temperature we have to use the equation

$$dQ = McdT.$$

The magnitude $c$ occurring here is the specific heat of the body in the first state of aggregation, on the assumption that the pressure, during the change of temperature, alters in the manner above stated. The foot-note to Art. 13 gives an account of this magnitude, and according to what is there proved we may without hesitation, in the case where the first state of aggregation is liquid or solid and the second gaseous, put for $c$, in all numerical calculations, the specific heat of the liquid or solid body at constant pressure. It is only when we are concerned with high temperatures, for which the vapour tension increases very rapidly with the temperature, that the difference between the specific heat $c$, and the specific heat at constant pressure, becomes sufficiently great to be regarded. On remembering that with an increase in temperature $dT$, an increase in volume $M\frac{d\sigma}{dT}dT$, and consequently the exterior ergon $\mathrm{MA}p\frac{d\sigma}{d\mathrm{T}}d\mathrm{T}$ is associated, it follows from the foregoing equation that

$$d\mathrm{U}=\mathrm{M}\left(c-\mathrm{A}p\frac{d\sigma}{d\mathrm{T}}\right)d\mathrm{T},$$

$$d\mathrm{S}=\mathrm{M}\frac{c}{\mathrm{T}}d\mathrm{T}.$$

For the change of the state of aggregation taking place at the temperature T, we have

$$d\mathrm{Q}=rdm.$$

Since the increment $dm$ of the portion in the second state of aggregation involves an increment of volume equal to $udm$, and consequently an amount of exterior ergon denoted by $\mathrm{A}pudm$, it follows from the above that

$$d\mathrm{U}=(r-\mathrm{A}pu)\,dm.$$

If in order to replace the magnitude $u$ by magnitudes better known experimentally, we apply the equation (54), which may be thus written,

$$\mathrm{A}u=\frac{r}{\mathrm{T}\frac{dp}{d\mathrm{T}}},$$

it follows that

$$d\mathrm{U}=r\left(1-\frac{p}{\mathrm{T}\frac{dp}{d\mathrm{T}}}\right)dm.$$

At the same time from the expression for $d\mathrm{Q}$, we have directly

$$d\mathrm{S}=\frac{r}{\mathrm{T}}dm.$$

The two differential equations referring to the first process must be integrated according to T from $\mathrm{T}_0$ to T, and the two referring to the second process according to $m$ from 0 to $m$; hence we obtain

$$\left.\begin{aligned}\mathrm{U}&=\mathrm{U}_0+\mathrm{M}\int_{\mathrm{T}_0}^{\mathrm{T}}\left(c-\mathrm{A}p\frac{d\sigma}{d\mathrm{T}}\right)d\mathrm{T}+mr\left(1-\frac{p}{\mathrm{T}\frac{dp}{d\mathrm{T}}}\right),\\ \mathrm{S}&=\mathrm{S}_0+\mathrm{M}\int_{\mathrm{T}_0}^{\mathrm{T}}\frac{c}{\mathrm{T}}d\mathrm{T}+\frac{mr}{\mathrm{T}}\text{*}.\end{aligned}\right\}\quad .\ .\ (68)$$

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* A few more complete mathematical developments concerning energy and entropy will be communicated in an Appendix to this Memoir.

16. If we now assume that in one of the ways above indicated the magnitudes U and S have been determined for a body in its different conditions, the equations which hold good for *non-reversible* changes may be at once written down.

The first fundamental equation (I *a*), and the equation (58), resulting from it by integration, which we will arrange thus,

$$Q = U - U_0 + w, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

hold just as well for non-reversible as for reversible changes; the only difference being, that of the magnitudes standing on the right side, the exterior ergon $w$ has a different value, in the case where a change occurs in a non-reversible manner, from that which it has in the case where the same change occurs in a reversible manner. With respect to the difference $U - U_0$ this disparity does not exist. It only depends on the initial and final condition, and not on the nature of the transition. Consequently we need only consider the nature of the transition so far as is necessary in order to determine the exterior ergon thereby performed; and on adding this exterior ergon to the difference $U - U_0$, we obtain the required quantity of heat Q which the body takes up during the transition.

The *uncompensated transformation* involved in any non-reversible change may be thus obtained:—

The expression for the uncompensated transformation which is involved in a *cyclical process*, is given in equation (11) of the Fourth Memoir (p. 127). If we give to the differential $dQ$ in that equation the opposite sign, a quantity of heat given off by the body to a reservoir of heat being there reckoned positive, whilst here we consider the heat taken up by the body to be positive, it becomes

$$N = -\int \frac{dQ}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

If the body has suffered one change or a series of changes, which do not form a cyclical process, but by which it has reached a final condition which is different from the initial condition, we may afterwards supplement this series of changes so as to form a cyclical process, by appending other changes of such a kind as to reconduct the body from its final to its initial condition. We will assume that these newly appended changes, by which the body is brought back to the initial condition, take place in a reversible manner.

On applying equation (70) to the cyclical process thus formed, we may divide the integral occurring therein into two parts, of which the first relates to the originally given passage of the body from the initial to the final condition, and the second to the supplemented return from the final to the initial condition. We will write these parts as two separate integrals, and distinguish the second, which relates to the return, by giving to its sign of integration a suffix *r*. Hence equation (70) becomes

$$N=-\int\frac{dQ}{T}-\int_r\frac{dQ}{T}.$$

Since by hypothesis the return takes place in a reversible manner, we can apply equation (64) to the second integral, taking care, however, to introduce the difference $S_0-S$ instead of $S-S_0$ (where $S_0$ denotes the entropy in the initial condition, and S the entropy in the final condition), since the integral here in question is to be taken backwards from the final to the initial condition. We have therefore to write

$$\int_r\frac{dQ}{T}=S_0-S.$$

By this substitution the former equation is transformed into

$$N=S-S_0-\int\frac{dQ}{T}. \quad . \quad . \quad . \quad . \quad . \quad (71)$$

The magnitude N thus determined denotes the uncompensated transformation occurring in the whole cyclical process. But from the theorem, that the sum of the transformations which occur in a reversible change is null, and hence that no uncompensated transformation can arise therein, it follows that the supposed reversible return has contributed nothing to the augmentation of the uncompensated transformation, and the magnitude N represents accordingly the uncompensated transformation which has occurred in the given passage of the body from the initial to the final condition. In the deduced expression, the difference $S-S_0$ is again perfectly determined when the initial and final conditions are given, and it is only when forming the integral $\int\frac{dQ}{T}$ that the manner in which the passage from one to the other took place must be taken into consideration.

17. In conclusion I wish to allude to a subject whose complete treatment could certainly not take place here, the expositions necessary for that purpose being of too wide a range, but relative to which even a brief statement may not be without interest, inasmuch as it will help to show the general importance of the magnitudes which I have introduced when formulizing the second fundamental theorem of the mechanical theory of heat.

The second fundamental theorem, in the form which I have given to it, asserts that all transformations occurring in nature may take place in a certain direction, which I have assumed as positive, by themselves, that is, without compensation; but that in the opposite, and consequently negative direction, they can only take place in such a manner as to be compensated by simultaneously occurring positive transformations. The application of this theorem to the Universe leads to a conclusion to which W. Thomson first drew attention[*], and of which I have spoken in the Eighth Memoir. In fact, if in all the changes of condition occurring in the universe the transformations in one definite direction exceed in magnitude those in the opposite direction, the entire condition of the universe must always continue to change in that first direction, and the universe must consequently approach incessantly a limiting condition.

The question is, how simply and at the same time definitely to characterize this limiting condition. This can be done by considering, as I have done, transformations as mathematical quantities whose equivalence-values may be calculated, and by algebraical addition united in one sum.

In my former Memoirs I have performed such calculations relative to the heat present in bodies, and to the arrangement of the particles of the body. For every body two magnitudes have thereby presented themselves—the transformation-value of its thermal content, and its disgregation; the sum of which constitutes its entropy. But with this the matter is not exhausted; radiant heat must also be considered, in other words, the heat distributed in space in the form of advancing oscillations of the æther must be studied, and further, our researches must be extended to motions which cannot be included in the term *Heat*.

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[*] Phil. Mag. Ser. 4. vol. iv. p. 304.

The treatment of the last might soon be completed, at least so far as relates to the motions of ponderable masses, since allied considerations lead us to the following conclusion. When a mass which is so great that an atom in comparison with it may be considered as infinitely small, moves as a whole, the transformation-value of its motion must also be regarded as infinitesimal when compared with its *vis viva*; whence it follows that if such a motion by any passive resistance becomes converted into heat, the equivalence-value of the uncompensated transformation thereby occurring will be represented simply by the transformation-value of the heat generated. Radiant heat, on the contrary, cannot be so briefly treated, since it requires certain special considerations in order to be able to state how its transformation-value is to be determined. Although I have already, in the Eighth Memoir above referred to, spoken of radiant heat in connexion with the mechanical theory of heat, I have not alluded to the present question, my sole intention being to prove that no contradiction exists between the laws of radiant heat and an axiom assumed by me in the mechanical theory of heat. I reserve for future consideration the more special application of the mechanical theory of heat, and particularly of the theorem of the equivalence of transformations to radiant heat.

For the present I will confine myself to the statement of one result. If for the entire universe we conceive the same magnitude to be determined, consistently and with due regard to all circumstances, which for a single body I have called *entropy*, and if at the same time we introduce the other and simpler conception of energy, we may express in the following manner the fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat.

1. *The energy of the universe is constant.*
2. *The entropy of the universe tends to a maximum.*

# APPENDIX TO NINTH MEMOIR [1866].

## ON THE DETERMINATION OF THE ENERGY AND ENTROPY OF A BODY*.

It may perhaps not be inappropriate if I communicate, as an Appendix to the foregoing Memoir, a few further developments, in order to show how the equations which serve for the determination of energy and entropy may be derived directly from the fundamental equations of the mechanical theory of heat.

1. The first fundamental equation will be applied in the form which is given in (I *a*) of the foregoing Memoir, and the second in the form equivalent to that given in (59). We have, therefore,

$$dQ = dU + dw, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

$$dQ = TdS. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

The first of these two equations applies to reversible, as well as to non-reversible changes; the second, on the contrary, holds good for reversible changes solely. But in order to be able to bring the two equations into conjunction, we will suppose that they relate to one and the same reversible change of a body. In this case the thermal element $dQ$ is the same in both equations, hence we can eliminate it from the equations, whereby we obtain

$$TdS = dU + dw. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

We will now assume that the condition of the body is defined by any two variables, which we will provisionally denote quite generally by $x$ and $y$. We can afterwards put in the place of these undefined variables definite magnitudes, such as temperature, volume, pressure, or any others appropriate to the particular investigation in view. If the condition of the body is defined by the two variables $x$ and $y$, all magnitudes which are defined by the actually existing condition of the body, independently of the way in which the body came into this con-

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* The substance of this Appendix is taken from a note which was recently published by me, and which may be found in Schlömilch's *Zeitschrift für Mathematik und Physik*, Bd. xi. S. 31, and in an English Translation in the Phil Mag. Series 4. vol. xxxii. p. 1.

dition, must be capable of being expressed by functions of these variables, in which the variables themselves may be regarded as independent of each other. Accordingly the entropy S and the energy U are to be regarded as functions of the independent variables $x$ and $y$. In this respect, however, the external ergon $w$ deports itself very differently, as was repeatedly stated in the foregoing Memoir. Although the differential coefficients of $w$ may be regarded as definite functions of $x$ and $y$, in so far as reversible changes only are concerned, $w$ itself cannot be expressed by such a function, but can only be defined when, besides the initial and final conditions of the body, the way in which the change from the one to the other takes place is likewise given.

If now in equation ($a$) we put

$$dS = \frac{dS}{dx}dx + \frac{dS}{dy}dy,$$

$$dU = \frac{dU}{dx}dx + \frac{dU}{dy}dy,$$

$$dw = \frac{dw}{dx}dx + \frac{dw}{dy}dy,$$

it is transformed into

$$T\frac{dS}{dx}dx + T\frac{dS}{dy}dy = \left(\frac{dU}{dx} + \frac{dw}{dx}\right)dx + \left(\frac{dU}{dy} + \frac{dw}{dy}\right)dy.$$

Since this equation must be true for arbitrary values of the differentials $dx$ and $dy$, and therefore for that case, amongst others, in which one or other of the differentials vanishes, it resolves itself at once into the two following equations:

$$\left.\begin{aligned} T\frac{dS}{dx} &= \frac{dU}{dx} + \frac{dw}{dx}, \\ T\frac{dS}{dy} &= \frac{dU}{dy} + \frac{dw}{dy}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

From these equations one of the magnitudes S and U may be eliminated by means of a second differentiation.

2. We will first eliminate the magnitude U, since the resulting equation is the simpler of the two.

For this purpose we will differentiate the first of the equations ($b$) with respect to $y$, and the second with respect to $x$. In so doing we will write the second differential coefficients of S and U in the usual way. The differential coefficients of $\frac{dw}{dx}$ and $\frac{dw}{dy}$, on the other hand, shall be written, as in the foregoing Memoir, thus:

$$\frac{d}{dy}\left(\frac{dw}{dx}\right) \text{ and } \frac{d}{dx}\left(\frac{dw}{dy}\right),$$

in order to express explicitly that they are not differential coefficients of the second order of any function of $x$ and $y$. Lastly, we shall have to remember that the magnitude T which occurs in these equations, namely the absolute temperature of the body, must also be regarded as a function of $x$ and $y$. On thus differentiating we obtain

$$\frac{dT}{dy}\cdot\frac{dS}{dx}+T\frac{d^2S}{dxdy}=\frac{d^2U}{dxdy}+\frac{d}{dy}\left(\frac{dw}{dx}\right),$$

$$\frac{dT}{dx}\cdot\frac{dS}{dy}+T\frac{d^2S}{dydx}=\frac{d^2U}{dydx}+\frac{d}{dx}\left(\frac{dw}{dy}\right).$$

Subtracting the second of these equations from the first, and remembering that

$$\frac{d^2S}{dxdy}=\frac{d^2S}{dydx} \text{ and } \frac{d^2U}{dxdy}=\frac{d^2U}{dydx},$$

we have

$$\frac{dT}{dy}\cdot\frac{dS}{dx}-\frac{dT}{dx}\cdot\frac{dS}{dy}=\frac{d}{dy}\left(\frac{dw}{dx}\right)-\frac{d}{dx}\left(\frac{dw}{dy}\right).$$

In the foregoing Memoir I have called the difference which stands here on the right-hand side, *the ergonal difference corresponding to xy*, and denoted it by $E_{xy}$; so that we may put

$$E_{xy}=\frac{d}{dy}\left(\frac{dw}{dx}\right)-\frac{d}{dx}\left(\frac{dw}{dy}\right). \quad \ldots\ldots \quad (c)$$

The foregoing equation is thus transformed into

$$\frac{dT}{dy}\cdot\frac{dS}{dx}-\frac{dT}{dx}\cdot\frac{dS}{dy}=E_{xy}. \quad \ldots\ldots \quad (d)$$

This is the differential equation, resulting from equation (*a*), which serves to define S.

In order now to eliminate the magnitude S from the two equations ($b$), we will write them as follows :—

$$\frac{dS}{dx}=\frac{1}{T}\cdot\frac{dU}{dx}+\frac{1}{T}\cdot\frac{dw}{dx},$$

$$\frac{dS}{dy}=\frac{1}{T}\cdot\frac{dU}{dy}+\frac{1}{T}\cdot\frac{dw}{dy}.$$

Of these equations, again, we will differentiate the first with respect to $y$, and the second with respect to $x$, whereby we have

$$\frac{d^2S}{dxdy}=\frac{1}{T}\cdot\frac{d^2U}{dxdy}-\frac{1}{T^2}\cdot\frac{dT}{dy}\cdot\frac{dU}{dx}+\frac{d}{dy}\left(\frac{1}{T}\cdot\frac{dw}{dx}\right),$$

$$\frac{d^2S}{dydx}=\frac{1}{T}\cdot\frac{d^2U}{dydx}-\frac{1}{T^2}\cdot\frac{dT}{dx}\cdot\frac{dU}{dy}+\frac{d}{dx}\left(\frac{1}{T}\cdot\frac{dw}{dy}\right).$$

Subtracting the second of these equations from the first, bringing all the terms of the resulting equation in which U occurs to the left-hand side, and multiplying the whole equation by $T^2$, we have

$$\frac{dT}{dy}\cdot\frac{dU}{dx}-\frac{dT}{dx}\cdot\frac{dU}{dy}=T^2\left[\frac{d}{dy}\left(\frac{1}{T}\cdot\frac{dw}{dx}\right)-\frac{d}{dx}\left(\frac{1}{T}\cdot\frac{dw}{dy}\right)\right].$$

For the magnitude which here stands on the right-hand side we will likewise employ a special symbol, putting

$$E'_{xy}=T^2\left[\frac{d}{dy}\left(\frac{1}{T}\cdot\frac{dw}{dx}\right)-\frac{d}{dx}\left(\frac{1}{T}\cdot\frac{dw}{dy}\right)\right]. \quad . \quad . \quad (e)$$

The last equation then becomes

$$\frac{dT}{dy}\cdot\frac{dU}{dx}-\frac{dT}{dx}\cdot\frac{dU}{dy}=E'_{xy}. \quad . \quad . \quad . \quad . \quad . \quad (f)$$

This is the differential equation, resulting from equation ($a$), which serves to define U.

3. Before pursuing further the treatment of the two differential equations ($d$) and ($f$), it will be advisable to direct attention for a moment to the magnitudes $E_{xy}$ and $E'_{xy}$ which therein occur.

Between these two magnitudes the following relation exists, which can be easily deduced from the expressions given in ($c$) and ($e$),

$$E'_{xy}=TE_{xy}-\frac{dT}{dy}\cdot\frac{dw}{dx}+\frac{dT}{dx}\cdot\frac{dw}{dy}. \quad . \quad . \quad . \quad (g)$$

Both the magnitudes $E_{xy}$ and $E'_{xy}$ are functions of $x$ and $y$. If in order to define the body we select, instead of $x$ and $y$, any other two variables, which we may call $\xi$ and $\eta$, and form with them the corresponding magnitudes $E_{\xi\eta}$ and $E'_{\xi\eta}$, namely,

$$\left.\begin{aligned} E_{\xi\eta} &= \frac{d}{d\eta}\left(\frac{dw}{d\xi}\right) - \frac{d}{d\xi}\left(\frac{dw}{d\eta}\right), \\ E'_{\xi\eta} &= T^2\left[\frac{d}{d\eta}\left(\frac{1}{T}\cdot\frac{dw}{d\xi}\right) - \frac{d}{d\xi}\left(\frac{1}{T}\cdot\frac{dw}{d\eta}\right)\right], \end{aligned}\right\} \quad . \quad . \quad (h)$$

these magnitudes are of course functions of $\xi$ and $\eta$, just as the foregoing magnitudes are functions of $x$ and $y$. But if now one of the last two expressions, *e.g.* the one for $E_{\xi\eta}$, is compared with the expression for the corresponding magnitude $E_{xy}$, we find that they represent, not merely expressions for the same magnitude with reference to different variables, but actually different magnitudes. For this reason I have not called $E_{xy}$ simply the ergonal difference, but the ergonal difference corresponding to $xy$, whereby it is at once distinguished from $E_{\xi\eta}$ or the ergonal difference corresponding to $\xi\eta$. The same holds good of $E'_{xy}$ and $E'_{\xi\eta}$, which are also to be regarded as two different magnitudes.

The relation existing between the magnitudes $E_{xy}$ and $E_{\xi\eta}$ may be found as follows. The differential coefficients occurring in the expression given for $E_{\xi\eta}$ in $(h)$ may be arrived at by first forming the differential coefficients in relation to the variables $x$ and $y$, and then treating each of these two variables as a function of $\xi$ and $\eta$. In this way we obtain

$$\frac{dw}{d\xi} = \frac{dw}{dx}\cdot\frac{dx}{d\xi} + \frac{dw}{dy}\cdot\frac{dy}{d\xi},$$

$$\frac{dw}{d\eta} = \frac{dw}{dx}\cdot\frac{dx}{d\eta} + \frac{dw}{dy}\cdot\frac{dy}{d\eta}.$$

Let the first of these two expressions be differentiated with respect to $\eta$ and the second with respect to $\xi$, and we then obtain, by the application of the same process,

$$\frac{d}{d\eta}\left(\frac{dw}{d\xi}\right) = \left\{\begin{aligned} & \frac{d}{dx}\left(\frac{dw}{dx}\right)\cdot\frac{dx}{d\xi}\cdot\frac{dx}{d\eta} + \frac{d}{dy}\left(\frac{dw}{dx}\right)\cdot\frac{dx}{d\xi}\cdot\frac{dy}{d\eta} + \frac{dw}{dx}\cdot\frac{d^2x}{d\xi d\eta} \\ & + \frac{d}{dx}\left(\frac{dw}{dy}\right)\cdot\frac{dx}{d\eta}\cdot\frac{dy}{d\xi} + \frac{d}{dy}\left(\frac{dw}{dy}\right)\cdot\frac{dy}{d\xi}\cdot\frac{dy}{d\eta} + \frac{dw}{dy}\cdot\frac{d^2y}{d\xi d\eta}, \end{aligned}\right.$$

$$\frac{d}{d\xi}\left(\frac{dw}{d\eta}\right) = \left\{\begin{aligned} & \frac{d}{dx}\left(\frac{dw}{dx}\right)\cdot\frac{dx}{d\xi}\cdot\frac{dx}{d\eta} + \frac{d}{dy}\left(\frac{dw}{dx}\right)\cdot\frac{dx}{d\eta}\cdot\frac{dy}{d\xi} + \frac{dw}{dx}\cdot\frac{d^2x}{d\xi d\eta} \\ & + \frac{d}{dx}\left(\frac{dw}{dy}\right)\cdot\frac{dx}{d\xi}\cdot\frac{dy}{d\eta} + \frac{d}{dy}\left(\frac{dw}{dy}\right)\cdot\frac{dy}{d\xi}\cdot\frac{dy}{d\eta} + \frac{dw}{dy}\cdot\frac{d^2y}{d\xi d\eta}. \end{aligned}\right.$$

If the second of these equations be subtracted from the first, most of the terms on the right-hand side will disappear, and there will remain only four terms, which may be thus expressed as a product of two binomial expressions—

$$\frac{d}{d\eta}\left(\frac{dw}{d\xi}\right)-\frac{d}{d\xi}\left(\frac{dw}{d\eta}\right)=\left(\frac{dx}{d\xi}\cdot\frac{dy}{d\eta}-\frac{dx}{d\eta}\cdot\frac{dy}{d\xi}\right)\left[\frac{d}{dy}\left(\frac{dw}{dx}\right)-\frac{d}{dx}\left(\frac{dw}{dy}\right)\right].$$

The expression standing on the left-hand side of this equation is $E_{\xi\eta}$, and that contained within square brackets on the right-hand side is $E_{xy}$. Hence we finally obtain

$$E_{\xi\eta}=\left(\frac{dx}{d\xi}\cdot\frac{dy}{d\eta}-\frac{dx}{d\eta}\cdot\frac{dy}{d\xi}\right)E_{xy}. \quad . \quad . \quad . \quad . \qquad (i)$$

Similarly we may also find

$$E'_{\xi\eta}=\left(\frac{dx}{d\xi}\cdot\frac{dy}{d\eta}-\frac{dx}{d\eta}\cdot\frac{dy}{d\xi}\right)E'_{xy}. \quad . \quad . \quad . \quad . \qquad (i')$$

If we replace only one of the variables by a new one—if, for instance, we retain the variable $x$ while putting the variable $\eta$ in place of $y$, we have in the two foregoing equations $x=\xi$, and consequently $\frac{dx}{d\xi}=1$, and $\frac{dx}{d\eta}=0$, whereby they become

$$E_{x\eta}=\frac{dy}{d\eta}E_{xy} \text{ and } E'_{x\eta}=\frac{dy}{d\eta}E'_{xy}. \quad . \quad . \quad . \qquad (k)$$

If, further, the original variables are retained but their order of succession altered, the magnitudes in question take the opposite sign, as may be seen at once from the expressions ($c$) and ($e$); that is to say, they become

$$E_{yx}=-E_{xy} \text{ and } E'_{yx}=-E'_{xy}. \quad . \quad . \quad . \quad . \qquad (l)$$

4. We now return again to the differential equations ($d$) and ($f$) that have been deduced for S and U.

These assume particularly simple forms when the temperature T is taken as one of the independent variables. If, for instance, we put $T=y$, it follows thence that $\frac{dT}{dy}=1$ and $\frac{dT}{dx}=0$; and we have also, in place of $E_{xy}$ and $E'_{xy}$, to write $E_{xT}$ and $E'_{xT}$. Equations ($d$) and ($f$) thus become

$$\left.\begin{aligned}\frac{dS}{dx}&=E_{xT},\\ \frac{dU}{dx}&=E'_{xT}.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (m)$$

These equations can at once be integrated with respect to $x$, and we thus deduce

$$\left.\begin{aligned} S&=\int E_{xT}dx+\phi(T), \\ U&=\int E'_{xT}dx+\psi(T), \end{aligned}\right\} \quad \ldots\ldots \quad (n)$$

where $\phi(T)$ and $\psi(T)$ are two arbitrary functions of T.

The last two equations can of course be easily changed back again by putting any other variable $y$ in place of the variable T. For this purpose we only require to substitute for T the function of $x$ and $y$ which represents this magnitude. The equations hence resulting are the same as those obtained when we start from the more general differential equations ($d$) and ($f$), and apply to them the common process of integration, keeping in mind, at the same time, that according to ($k$) we have to put

$$\frac{dy}{dT}E_{xy}=E_{xT} \text{ and } \frac{dy}{dT}E'_{xy}=E'_{xT}.$$

We have thus in what precedes arrived, by help of the partial differential equations deduced from equation ($a$), at expressions for S and U, each of which still contains an arbitrary function of T. If we wish to determine the functions, which are there left arbitrary, we must go back to equations (A) and (B), whence equation ($a$) was obtained by the elimination of $dQ$.

5. Let us assume that the condition of the body is determined by its temperature and any other variable $x$; we can then give to the two equations (A) and (B) the following form:

$$\frac{dS}{dT}dT+\frac{dS}{dx}dx=\frac{1}{T}\cdot\frac{dQ}{dT}dT+\frac{1}{T}\cdot\frac{dQ}{dx}dx,$$

$$\frac{dU}{dT}dT+\frac{dU}{dx}dx=\left(\frac{dQ}{dT}-\frac{dw}{dT}\right)dT+\left(\frac{dQ}{dx}-\frac{dw}{dx}\right)dx.$$

Since these equations must be true for any values of the differentials $dT$ and $dx$, each resolves itself, as has been already pointed out in a similar case above, into two equations. Of the four equations thus arising we will here employ only those two which can serve for the determination of $\frac{dS}{dT}$ and of $\frac{dU}{dT}$, namely

$$\left.\begin{aligned} \frac{dS}{dT}&=\frac{1}{T}\cdot\frac{dQ}{dT}, \\ \frac{dU}{dT}&=\frac{dQ}{dT}-\frac{dw}{dT}. \end{aligned}\right\} \quad \ldots\ldots \quad (o)$$

In order to determine the two other differential coefficients $\frac{dS}{dx}$ and $\frac{dU}{dx}$, we will apply the equations ($m$) deduced above. With the aid of these expressions of the four differential coefficients we can form the following complete differential equations of S and U:

$$\left.\begin{aligned} dS &= \frac{1}{T}\cdot\frac{dQ}{dT}dT + E_{xT}dx, \\ dU &= \left(\frac{dQ}{dT} - \frac{dw}{dT}\right)dT + E'_{xT}dx. \end{aligned}\right\} \quad . \quad . \quad . \quad (p)$$

Since the magnitudes S and U must be capable of being represented by functions of T and $x$, in which the two variables T and $x$ may be looked upon as independent of each other, the known equation of condition of integrability must apply to both the foregoing equations. For the first equation this is

$$\frac{d}{dx}\left(\frac{1}{T}\cdot\frac{dQ}{dT}\right) = \frac{dE_{xT}}{dT},$$

or, differently written,

$$\frac{d}{dx}\left(\frac{dQ}{dT}\right) = T\frac{dE_{xT}}{dT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (q)$$

which is equation (15) of the foregoing Memoir. For the second equation the equation of condition is

$$\frac{d}{dx}\left(\frac{dQ}{dT}\right) - \frac{d}{dx}\left(\frac{dw}{dT}\right) = \frac{dE'_{xT}}{dT}. \quad . \quad . \quad . \quad . \quad . \quad (r)$$

These two equations of condition are connected with each other in such a manner that from either of them the necessity of the other can be immediately deduced. Between the two magnitudes $E_{xT}$ and $E'_{xT}$, which occur in them, the following relation subsists, which results from ($g$) if we therein place $T=y$:

$$E'_{xT} = TE_{xT} - \frac{dw}{dx}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (s)$$

Differentiating this equation with respect to T, we have

$$\frac{dE'_{xT}}{dT} = T\frac{dE_{xT}}{dT} + E_{xT} - \frac{d}{dT}\left(\frac{dw}{dx}\right).$$

Now bearing in mind that

$$E_{xT} = \frac{d}{dT}\left(\frac{dw}{dx}\right) - \frac{d}{dx}\left(\frac{dw}{dT}\right),$$

the last equation becomes

$$\frac{dE'_{xT}}{dT}=T\frac{dE_{xT}}{dT}-\frac{d}{dx}\left(\frac{dw}{dT}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (t)$$

By aid of this equation we can immediately refer either of the equations ($q$) and ($r$) to the other.

By the integration of the complete differential equations ($p$) each of the two magnitudes S and U can be determined, except as to a constant that still remains unknown.

Of course any other variable $y$ might be substituted for the variable T in these complete differential equations, if it appeared appropriate for special purposes to make the substitution; this could be done without any difficulty, if T were supposed to be a known function of $x$ and $y$, and therefore does not require to be further dwelt upon.

6. All the foregoing equations are developed in such a way that no limiting conditions are set up in relation to the external forces which act upon the body, and to which the external ergon has reference. We will now consider the particular case rather more closely, where the only external force which acts either to hinder or promote the change of condition in the body, and so occasions the production of positive or negative ergon, is a pressure uniformly distributed over the whole surface of the body, and everywhere directed perpendicularly to the surface of the body.

In this case, in accordance with equations (17) of the foregoing Memoir, if $p$ denote the pressure and $v$ the volume, we must put

$$\frac{dw}{dx}=Ap\frac{dv}{dx},$$

$$\frac{dw}{dy}=Ap\frac{dv}{dy}.$$

By introducing these values into the expressions given for $E_{xy}$ and $E'_{xy}$ in ($c$) and ($e$), we have

$$E_{xy}=A\left[\frac{d}{dy}\left(p\frac{dv}{dx}\right)-\frac{d}{dx}\left(p\frac{dv}{dy}\right)\right],$$

$$E'_{xy}=AT^2\left[\frac{d}{dy}\left(\frac{p}{T}\cdot\frac{dv}{dx}\right)-\frac{d}{dx}\left(\frac{p}{T}\cdot\frac{dv}{dy}\right)\right].$$

In the last of these equations we will put, for shortness,

$$\pi=\frac{p}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (u)$$