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I. *On the Moving Force of Heat, and the Laws regarding the Nature of Heat itself which are deducible therefrom. By* R. CLAUSIUS[*].

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 instructive experiments 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 permanent alteration of the body in action does not at the same time take place, a certain quantity of heat passes

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[*] Translated from Poggendorff's *Annalen*, vol. lxxix. p. 368.

[†] *Reflexions sur la puissance motrice du feu, et sur les Machines propres à déveloper cette puissance*, par S. Carnot. Paris, 1824.

[‡] *Journ. de l'École Polytechnique*, vol. xix. (1834); and Taylor's Scientific Memoirs, Part III. p. 347.

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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 consumption 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

* *Ueber die Wärme und Elasticität der Gase und Dämpfe,* von C. Holtzmann. Manheim, 1845. Also Taylor's Scientific Memoirs, Part XIV. p. 189.

combined with an increase of elasticity, or a mechanical work,
or a combination of both ; a mechanical work being the equiva-
lent 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 completely agrees with that obtained in a manner
totally different by Joule. In carrying out the theory, however,
that is, in developing the equations by means of which his con-
clusions are arrived at, he proceeds in a manner similar to Cla-
peyron, so that the assumption that the quantity of heat is con-
stant is still tacitly retained.

The difference between both ways of regarding the subject has
been laid hold of with much greater clearness by W. Thomson,
who has applied the recent discoveries 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,
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 trans-
mission 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 abso-
lute 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 prin-
ciple 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 investiga-
tions, 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

* *Ann. der Chim. und Pharm.*, vol. xlii. p. 239.
† Transactions of the Royal Society of Edinburgh, vol. xvi.

it or refuting it. Besides this, I do not imagine that the diffi-
culties are so great as Thomson considers them to be; for although
a certain alteration in our way of regarding the subject is neces-
sary, still I find that this is in no case contradicted by *proved
facts.* It is not even requisite to cast the theory of Carnot over-
board; a thing difficult to be resolved upon, inasmuch as expe-
rience 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.

## 1. *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 general,
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 expended; 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 considera-
tion; 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 quan-
tity 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 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 $t_1$ ; the quantity of heat varying in all cases with the manner in which the alterations succeed each other.

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 $t_1$ ; 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 second 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 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 per-

[*] 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. From this it follows, that of the heat which the water receives from without, only one portion must be regarded as sensible, while the other portion goes to loosen the cohesion. This view is in harmony with the fact, that water possesses a so much greater specific heat than ice, and probably than steam also.

manent 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:

$$pv = R(a+t), \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

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, $\dfrac{p_0 v_0}{a+t_0}$, 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 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. Its accuracy for permanent gases in their common state is so great, that 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 $\dfrac{1}{a}$ 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 $\dfrac{1}{a}$ 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 $0^\circ$ under the pressure of *one* atmosphere, heated to a temperature

[*] 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.

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 regarded 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 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.

In the annexed figure let *oe* represent the volume, and *ea* the pressure of the unit weight of gas when its 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 being added, the temperature will fall. To avoid

Fig. 1.
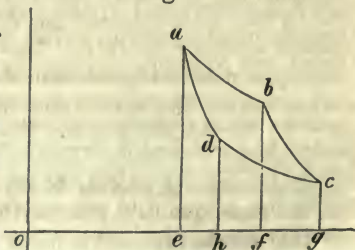
this, let the bag during the expansion be brought into contact with a body A of the temperature *t*, from which it shall receive heat sufficient to preserve it constant at the same temperature. While this expansion by constant temperature proceeds, the pressure decreases according to the law of M., and may be represented by the ordinate of a curve *ab*, which is a portion of an equilateral hyperbola. When the gas has increased in volume from *oe* to *of*, 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 *bc*. When the volume of the gas has increased from *of* to *og*, and its temperature is lowered from *t* to *τ*, 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 *τ*, to which any excess of heat will be immediately imparted, the gas being thus preserved constantly at *τ*. 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 *he* shall be just sufficient to raise the gas from *τ* 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 *cd* of another equilateral hyperbola. At the end the increase is quicker, and may be represented by the curve *da*. 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 product is represented geometrically by the quadrilaterals *ea*, *bf* and *fbcg*. During the compression, however, work will be *expended*, which is represented by the quadrilaterals *gcdh* and *hdae*. 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 *abcd*.

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*.

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 *abcd*

Fig. 2.
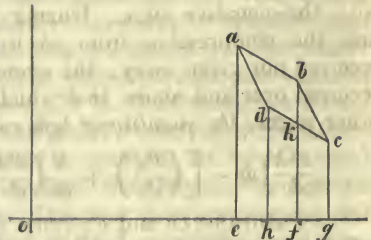


may be regarded as a parallelogram, for the error in this case can only amount to a differential of the *third* order, while the area itself is a differential of the *second* order. The latter may therefore be expressed by the product *ef.bk*, where *k* marks the point at which the ordinate *bf* cuts the lower side of the parallelogram. The quantity *bk* is the increase of pressure due to the raising of 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 *dv*, we obtain the content of the quadrilateral, and with it

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

We must now determine the quantity of heat consumed during those alterations. Let the amount of heat which must be imparted to change the gas by a definite process 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

$$\left(\frac{d\mathrm{Q}}{dv}\right)dv ;$$

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

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

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

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

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 *oh* to *oe*, consequently during its expansion under the same circumstances from *oe* to *oh*, and during the expansion from *of* to *og*, 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

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

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:

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

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

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

or

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

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 matter of indifference, the right side of the equation must be equal 0.

The equation can be brought under the form of a *complete differential*, thus:

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

where U denotes an arbitrary function of $v$ and $t$. This differential 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 (IIa.), 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 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 make this equation suited to 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 *oe,* and the pressure of the steam by the ordinate *ea.* Let the vessel be now supposed to expand, while both fluid and steam are kept in contact with a body A of the constant temperature *t.* As the space increases, more fluid is evaporated, the necessary amount of latent heat being supplied by the body A ; so that the temperature, and consequently



Fig. 3.
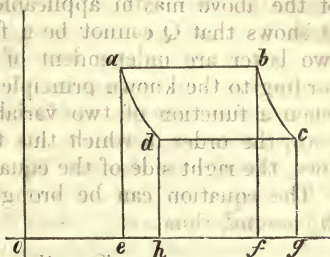
the pressure of the steam, may remain unchanged. When the entire volume is increased in this manner from *oe* to *of,* an exterior work is produced which is represented by the rectangle *ea bf.* Let the body A be now taken away, and let the vessel continue to expand without heat being either given or 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 *τ,* and let *og* represent the volume at this temperature. If the decrease of pressure during this expansion be represented by the curve *bc,* the exterior work produced by it will be represented by *fbcg.*

Let the vessel be now pressed together so as to bring the fluid and vapour to their original volume *oe,* and during a portion of the process let the vessel be in contact with a body, B, of the temperature *τ,* to which any excess of heat shall be immediately imparted, and the temperature of the fluid and vapour kept constant at *τ.* 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 *oh,* it being so arranged that the remaining space *he* shall be just sufficient to raise the temperature from *τ* to *t.* During the first decrease of volume the pressure remains constant at *gc,* and the quantity of exterior work expended is equal to the rectangle *gc dh.* During the last decrease of volume the pressure increases, and may be represented by the curve *da,* which must terminate exactly in the point *a,* as the original temperature *t* must again correspond to the original pressure *ea.* The exterior work expended in this case is = *hdae.*

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 *abcd,* the content of which must therefore be compared with the *heat expended* at the same time.

For this purpose let it be as-
sumed, as before, that the de-
scribed alterations are infinitely
small, and under this view let
the process be represented by
the annexed figure, in which the
curves *ad* and *bc* shown in fig. 3
have passed into straight lines.
With regard to the content of
the quadrilateral *abcd*, it may be
again regarded as a parallelogram,

Fig. 4.



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 tempera-
ture $t - \tau$ be expressed by *dt*, we have

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

*ef* is the increase of volume caused by the passing of a certain
quantity of fluid 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 fluid at the temperature *t* be called $\sigma$; then is

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

and hence the content of the rectangle, or

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

To express the amount of heat, we will introduce the following
notation :—Let the quantity of heat rendered latent by the pas-
sage of a unit weight of fluid at the temperature *t*, and under a
corresponding pressure into a state of vapour, be called *r*, and
the specific heat of the fluid *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
refer the question as to whether its value is positive or negative
to future consideration.

If we name the mass of fluid originally present in the vessel
$\mu$, and the mass of the vapour *m*; further, the mass evaporated
during the expansion from *oe* to *of*, *dm*, and the mass precipi-
tated by the compression from *og* to *oh*, *d'm*, we obtain in the
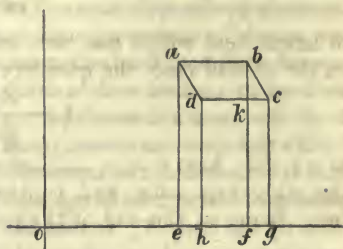
first case the quantity

$$rdm$$

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

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

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

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

In this equation the differential $d'm$ must be expressed through $dm$ and $dt$ ; the conditions under which the second expansion and the second contraction have been carried out enables 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 fluid 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 order than the second be neglected, we have

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

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

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

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

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

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

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

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

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

it must be inferred that for this fluid $h$ also is equal 0; this, indeed, has been often 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

$$\frac{dr}{dt} + c = 0{\cdot}305,$$

the equation (8.) gives for $h$ also the value $0{\cdot}305$. 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 $0{\cdot}305$. It will be shown further on that the value of the said expression is so great that $h$ becomes even negative. Hence we must conclude that the above quantity 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.

This result is indeed directly opposed to the notions generally

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

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.

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 (IIa.) 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 fluid bodies is in their case annulled; so that while with solids and fluids the heat necessary to effect an expansion has to contend with both an inner and an outer 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 all gases in the same degree as the law of M. and G.

From this immediately follows

$$\left(\frac{d\mathrm{Q}}{dv}\right) = \mathrm{A.R}\,\frac{a+t}{v}; \quad . \quad . \quad . \quad . \quad (9.)$$

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

for, as already mentioned, $R \dfrac{a+t}{v} dv$ represents the quantity of exterior work produced by the expansion $dv$. According to this, the function $U$, which appears in equation (IIa.), cannot contain $v$, and hence the equation changes to

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

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 we set in equation (II$b$.) $v =$ const. and $p =$ const., we 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

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

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

$$dv = \frac{Rdt}{p},$$

or

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

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

$$\frac{dQ}{dt} = c' = c + AR. \quad . \quad . \quad . \quad \text{(10}a.\text{)}$$

From this it may be inferred *that the difference of both specific heats for every gas is a constant quantity* $AR$. But this quantity expresses a simple relation for different gases also. The complete expression for $R$ is $\dfrac{p_0 v_0}{a+t_0}$, where $p_0$, $v_0$, and $t_0$ denote the contemporaneous values of $p$, $v$, and $t$ for a unit of weight of the gas in question ; and from this follows, as already mentioned in expressing equation (I.), that $R$ is inversely proportional to the specific heat of the gas ; the same must be true of the difference $c' - c = AR$, as $A$ is for all gases the same.

If it be desired to calculate the specific heat of the gas, not by the unit of weight, but by the method more in use, 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

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

In this last expression nothing appears which is dependent on the peculiar nature of the gas; *the difference of the specific heats reckoned according 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 constant found above is not given by the difference $c' - c$, 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

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

wherein $k$ is set for shortness' sake 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. *The excess of this quotient above unity in the case of different gases is therefore inversely proportional to their specific heats, reckoned according to the unit of volume when the latter is constant.* 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 heat 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 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 $c$ of the gases by constant volume is constant, 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

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

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 $Q = $ const., we then obtain the following equation between $v$ and $t$:

$$c\,dt + A \cdot R \frac{a+t}{v}\,dv = 0; \quad . \quad . \quad . \quad (13.)$$

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

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

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

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

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

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

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

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

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

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

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

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 $Q_0$,

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

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[*] *Traité de Mécanique,* 2nd edit. vol. ii. p. 646.
[†] *Traité de Mécanique,* vol. ii. p. 647.

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 $R = \dfrac{p_0 v_0}{a+t}$ be set in equation (18.), and we obtain

$$Q - Q_0 = A p_0 v_0 \log \frac{v}{v_0}. \quad \dots \quad (19.)$$

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.*

[To be continued.]

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## II. *On the Beudantite of* Levy. *By* H. J. Brooke, *F.R.S.*[*]

HAVING had the pleasure last week of a personal communication with M. Des Cloizeaux, and having shown him Levy's specimen of this mineral, he at once stated that it differed entirely from that examined by himself and M. Damour as Beudantite, as well as from every other specimen under the same name which he had seen. He said that he was not aware of the existence of any mineral resembling Levy's in any collection on the Continent, and that he was inclined with Levy to regard his specimen as belonging to a separate species. The mineral known as Beudantite on the continent appears to be only an impure variety of cube ore of the usual form.

June 9, 1851.

XVIII. *On the Moving Force of Heat, and the Laws regarding the Nature of Heat itself which are deducible therefrom. By* R. Clausius.

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 reason-

ably be assumed, with Carnot, that the work depends solely upon the quantity of heat transmitted, on the temperatures $t$ and $\tau$ of both bodies A and B, and 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 of 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.

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,

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

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

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

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

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

or

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

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

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

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

$$r\,dm.$$

The quantity of work thereby produced was

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

and hence we obtain the equation

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

or

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

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 original maxim, commencing with those which have reference to permanent gases.

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

$$dQ = \left[\,B + R\left(\frac{dC}{dt} - A\right)\log v\,\right]dt + \frac{R.C}{v}\cdot dv, \quad (IIc.)$$

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 unneces-
sary for the nearer determination of (IIa.), inasmuch as the same
object is arrived at in a much more complete manner by equa-
tion (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 princi-
ples to a reciprocal trial. The equation (9.) was thus expressed,

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

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 $\mathrm{A}(a+t)$.

To this surprising coincidence the equation (V.) adds its testi-
mony, and confirms the result that $\mathrm{R}(a+t)$ is the true expres-
sion for the function C. This equation is used by Clapeyron
and Thomson in determining the values of C for single tempe-
ratures. The temperatures chosen by Clapeyron were the boiling-
points of æther, of alcohol, of water, and of oil of turpentine. He
determined by experiment the values of $\frac{dp}{dt}$, $s$ and $r$, for these
fluids at their boiling-points; and setting these values in equa-
tion (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 has observed it at
various temperatures, and in this way calculated the value of
C for every single degree from 0° to 230° Cent. The observa-
tions 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 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. t in Cent. degrees. | 2. C according to Clapeyron. | 3. 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 the principle of Carnot may be applicable, 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

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

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

$$ps = R(a+t). \quad . \quad . \quad . \quad . \quad (20.)$$

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

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

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

$$\log\frac{p}{p_1} = \frac{r(t-100)}{\mathrm{A.R}(a+100)(a+t)},$$

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

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

we have then

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

This equation cannot of course be strictly correct, because the two assumptions made during its development are not so.    As however the latter approximate at least in some measure to the truth, the formula $\dfrac{\beta.\tau}{\alpha+\tau}$ expresses in a rough manner, so to speak, the route of the quantity $\log\dfrac{p}{p_1}$; 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 equation (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 :

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

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

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

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 equation 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[*].

With regard to the *latent heat*, moreover, according to Regnault[†] the quantity of heat $\lambda$ necessary to raise a unit of weight of water from $0°$ to $t°$, and then to evaporate it at this temperature, may be represented with tolerable accuracy by the following formula:

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

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

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

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

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

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

$$r = 606 \cdot 5 - 0 \cdot 695 . t - 0 \cdot 00002 . t^2 - 0 \cdot 000000 . t^3 §. \quad . \quad (24.)$$

Further, with regard to the pressure, Regnault has had recourse to a diagram to obtain the most probable value out of his nume-

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* *Mém. de l'Acad. de l'Inst. de France*, vol. xxi. (1847).
† Ibid. Mem. IX.; also Pogg. *Ann.*, vol. lxxviii.
‡ *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.

rous 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 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, 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:

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

* 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.

or

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

wherein log is the sign of Briggs's logarithms, and 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 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.

Table III.

| 1. | 2. | | 3. | 4. | |
|---|---|---|---|---|---|
| $t$ in Cent. degrees of the air-thermometer. | $Ap(s-\sigma)\frac{a}{a+t}$. | | | Differences. | |
| | According to the values observed. | | 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 | $-0·32$ | $-0·18$ |

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 90° 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 show, however, a *general* correspondence; and particularly when a diagram is made, it is found that the curve, which almost exactly connects the points within these limits, as determined from the numbers contained in the foregoing table, may be carried forward to 230°, the points being at the same time equally 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

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

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

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

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

$$\log\left[31 \cdot 549 - Ap(s-\sigma)\frac{a}{a+t}\right] = 0 \cdot 0206 + 0 \cdot 003100t. \quad (27.)$$

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 set in agreement with (20.),

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

and would therefore 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 $\frac{1}{a} = 0·003665$. Instead of this we derive from (26.), when in the place of $s-\sigma$ we set $s$ itself simply, the equation

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

and from this follows

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

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 (26a.) 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 quotients $\frac{d}{dt}\left(\frac{ps}{ps_0}\right)$, 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 $129\frac{1}{2}°$ a tension of 2 metres. We will therefore inquire how carbonic acid acts when heated to $21\frac{1}{2}°$, and the pressure thus 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 increase 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 $21\frac{1}{2}°$, the quantity $\frac{pv}{pv_0}$ would be thus increased from 1 to $1 + 0·003767 \times 21·5$ = 1·08099. 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 $21\frac{1}{2}$, 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 $1·08099 \times 0·99131 = 1·071596$; and from this we obtain, as the mean value of the differential quotients $\frac{d}{dt}\left(\frac{pv}{pv_0}\right)$,

$$\frac{0·071596}{21·5} = 0·00333.$$

We see, therefore, that for the case under contemplation a value is obtained for carbonic acid also which is less than 0·003665;

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

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 and in a state of maximum density, and 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.

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 weight 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

$$\frac{2 \times 0\cdot06926 + 1\cdot10563}{2} = 0\cdot622.$$

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

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

existing at the time; with proportionately greater tension, the 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 heat 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 neither from these, however important they may be in other respects, can a safe conclusion 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 weight 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.),

$$d = 0.622 \, \frac{m-n}{m-ne^{kt}} \quad (30.)$$

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 weight 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, $m = 31.549$, and we could then set in the place

of (30.) the equation

$$d = 0.622 \cdot \frac{m}{m - n e^{\kappa t}} \quad (31.)$$

From this we should derive for 0° the specific weight 0·643 instead of 0·622, and the other numbers of the above table would have to be increased proportionately. But we are not yet 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 $\Lambda(s - \sigma) \dfrac{a}{a + t}$ as unknown, and content 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 immediately derived from the original maxim, we can eliminate $\Lambda(s - \sigma)$, and we have remaining

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

By means of this equation, 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

$$h = 0.305 - \frac{606.5 - 0.695t - 0.0000t^2 - 0.0000003t^3}{273 + t}; \quad (33.)$$

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

### Table VI.

| $t$. | 0°. | 50°. | 100°. | 150°. | 200°. |
|------|-----|------|-------|-------|-------|
| $h$. | $-1.916$ | $-1.465$ | $-1.133$ | $-0.879$ | $-0.676$ |

In a manner similar to that already pursued in the case of water-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 $\Lambda$, or, what is more useful, the value of the fraction $\dfrac{1}{\Lambda}$; 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 $\dfrac{c'}{k}$ is introduced, we have

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

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 $R = \dfrac{p_0 v_0}{a + t_0}$, we know that the pressure of one atmosphere (760 millims.) on a square metre amounts to 10333 kils.; and the volume of 1 kil. atmospheric air under the said pressure and at the temperature of the freezing-point is $= 0·7733$ cubic metres.  From this follows

$$R = \frac{10333 \cdot 0·7733}{273} = 29·26,$$

and hence

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

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

$$\frac{1}{A} = 257 \cdot (s - \sigma). \quad \cdots \quad (35.)$$

If it now be assumed with Gay-Lussac that the specific weight of the water-vapour is 0·6235, we obtain $s = 1·699$, 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 weight of the vapour of water at its maximum density given by Gay-Lussac is probably a little too small, and the same may be said of the specific weights 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 $s = 1·638$, 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,

$$\frac{1}{A} = 438†;$$

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 original maxim.

* Phil. Mag., vol. xxiii. p. 441. The English measure has been reduced to the French standard.
† Ibid. vol. xxvi. p. 381. ‡ Ibid. vol. xxxv. p. 534.