VII.—*On the Mechanical Action of Heat, especially in Gases and Vapours*

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INTRODUCTION.

SUMMARY OF THE PRINCIPLES OF THE HYPOTHESIS OF MOLECULAR VORTICES, AND ITS APPLICATION TO THE THEORY OF TEMPERATURE, ELASTICITY, AND REAL SPECIFIC HEAT.

The ensuing paper forms part of a series of researches respecting the consequences of an hypothesis called that of Molecular Vortices, the object of which is, to deduce the laws of elasticity, and of heat as connected with elasticity, by means of the principles of mechanics, from a physical supposition consistent and connected with the theory which deduces the laws of radiant light and heat from the hypothesis of undulations. Those researches were commenced in 1842, and after having been laid aside for nearly seven years, from the want of experimental data, were resumed in consequence of the appearance of the experiments of M. REGNAULT on gases and vapours.

The investigation which I have now to describe, relates to the mutual conversion of heat and mechanical power by means of the expansion and contraction of gases and vapours.

In the introduction which I here prefix to it, I purpose to give such a summary of the principles of the hypothesis as is necessary to render the subsequent investigation intelligible.

The fundamental suppositions are the following:—

First,—That each atom of matter consists of a nucleus, or central physical point, enveloped by an elastic atmosphere, which is retained in its position by forces attractive towards the nucleus or centre.

Suppositions similar to this have been brought forward by FRANKLIN, ÆPINUS, MOSSOTTI, and others. They have in general, however, conceived the atmosphere of each nucleus to be of variable mass. I have treated it, on the contrary, as an essential part of the atom. I have left the question indeterminate, whether the nucleus is a small body of a character distinct from that of the atmosphere, or merely a portion of the atmosphere in a highly condensed state, owing to the mutual attraction of its parts.

According to this first supposition, the boundary between two contiguous atoms of a body is an imaginary surface at which the attractions of all the atomic

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centres of the body balance each other; and the elasticity of the body is made up of two parts: *First*, the elasticity of the atomic atmospheres at the imaginary boundaries of the atoms, which I shall call the superficial-atomic elasticity ; and, *secondly*, the force resulting from the mutual actions of distinct atoms. If the atmospheres are so much condensed round their nuclei or centres, that the superficial-atomic elasticity is insensible, and that the resultants of the mutual actions of all parts of the distinct atoms are forces acting along the lines joining the nuclei or centres, then the body is a perfect solid, having a tendency to preserve not only a certain bulk, but a certain figure; and the elasticity of figure, or *rigidity*, bears certain definite relations to the elasticity of volume.

If the atmospheres are less condensed about their centres, so that the mutual actions of distinct atoms are not reducible to a system of forces acting along the lines joining the atomic centres, but produce merely a cohesive force sufficient to balance the superficial-atomic elasticity, then the condition is that of a *perfect liquid;* and the intermediate conditions between this and perfect solidity constitute the gelatinous, plastic, and viscous states.

When the mutual actions of distinct atoms are very small as compared with the superficial-atomic elasticity, the condition is that of *gas* or *vapour;* and when the substance is so far rarefied that the influence of the atomic nuclei or centres in modifying the superficial elasticity of their atmospheres is insensible, it is then in the state of *perfect gas.*

So far as our experimental knowledge goes, the elasticity of a perfect gas at a given temperature varies simply in proportion to its density. I have therefore assumed this to be the law of the elasticity of the atomic atmospheres, ascribing a specific coefficient of elasticity to each substance.

The *second supposition*, being that from which the hypothesis of molecular vortices derives its name, is the following :—*That the elasticity due to heat arises from the centrifugal force of revolutions or oscillations among the particles of the atomic atmospheres ; so that quantity of heat is the* vis viva *of those revolutions or oscillations.*

This supposition appears to have been first definitely stated by Sir HUMPHRY DAVY. It has since been supported by Mr JOULE, whose valuable experiments to establish the convertibility of heat and mechanical power are well known. So far as I am aware, however, its consequences have not hitherto been mathematically developed.

To connect this hypothesis with the undulatory theory of radiation, I have introduced a *third supposition:—That the medium which transmits light and radiant heat consists of the* nuclei *of the atoms, vibrating independently, or almost independently, of their atmospheres ;*—so that the absorption of light and of radiant heat, is the transference of motion from the nuclei to their atmospheres, and the

emission of light and of radiant heat, the transference of motion from the atmospheres to their nuclei.

Although in all undulations of sensible length and amplitude, such as those of sound, the nuclei must carry their atmospheres along with them, and vibrating thus loaded, produce a comparatively slow velocity of propagation; yet in all probability the minute vibrations of light and radiant heat may be performed by the atomic nuclei in transparent and diathermanous bodies, without moving the atmospheres more than by that amount which constitutes absorption; and those vibrations will therefore be transmitted according to the laws of the elasticity of *perfect solids*, and with a rapidity corresponding to the extreme smallness of the masses set in motion, as compared with the mutual forces exerted by them.

This supposition is peculiar to my own view of the hypothesis, and is, in fact, the converse of the idea hitherto adopted, of an ether surrounding ponderable particles.

The second and third suppositions involve the assumption, that motion can be communicated between the nuclei and their atmospheres, and between the different parts of the atmospheres; so that there is a tendency to produce some permanent condition of motion, which constitutes equilibrium of heat. It is now to be considered what kind of motion is capable of producing increase of elasticity, and what are the conditions of permanency of that motion.'

It is obvious, that the parts of the atomic atmospheres may have motions of alternate expansion and contraction, or of rectilinear oscillation about a position of equilibrium, without affecting the superficial atomic elasticity, except by small periodical changes. Should they have motions, however, of *revolution* about centres, so as to form a group of *vortices*, the centrifugal force will have the effect of increasing the density of the atmosphere at what I have called the bounding surfaces of the atoms, and thus of augmenting the elasticity of the body.

In this summary, I shall not enter into the details of mathematical analysis, but shall state results only. The following, then, are the conditions which must be fulfilled, in order that a group of vortices, of small size as compared with the bulk of an atom, and of various diameters, may permanently coexist, whether side by side, or end to end, in the atomic atmospheres of one substance, or of various substances mixed.

First, The mean elasticity must vary continuously; which involves the condition, that at the surface of contact of two vortices of different substances, side by side, or end to end, the respective densities at each point of contact must be inversely proportional to the coefficients of elasticity. Hence *the specific gravities of the* atmospheric parts of *all substances, under precisely similar circumstances as to heat and molecular forces* (a condition realised in perfect gases at the same pressure and temperature), *are inversely proportional to the coefficients of atmospheric elasticity.* Therefore let μ represent the mass of the atmosphere of one atom of

any substance, b its coefficient of elasticity, and n the number of atoms which, in the state of perfect gas, occupy unity of volume under unity of pressure at the temperature of melting ice;—then

$$n \mu b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(I.)}$$

is a constant quantity for all substances.

Secondly, The superficial elasticity of a vortex must *not* be a function of its diameter: to fulfil which condition, the linear velocity of revolution must be equal throughout all parts of each individual vortex.

Thirdly, In all contiguous vortices of the same substance, the velocities of revolution must be equal; and in contiguous vortices of different substances, the squares of the velocities must be proportional to the coefficients of elasticity of the molecular atmospheres.

The second and third conditions are those of equilibrium of heat, and are equivalent to this law :—

TEMPERATURE *is a function of the square of the velocity of revolution in the molecular vortices divided by the coefficient of elasticity of the atomic atmospheres ;—*or

$$\text{Temperature} = \phi \left(\frac{w^2}{b} \right) \quad . \quad . \quad . \quad . \quad . \quad \text{(II.)}$$

where w represents that velocity.

The *mean* elasticity which a vortex exerts endways is not affected by its motion, being equal to

$$b \varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(III.)}$$

where ϱ is its mean density. The superficial elasticity at its lateral surfaces, however, is expressed by

$$\frac{w^2 \varrho}{2 g} + b \varrho \quad . \quad . \quad . \quad . \quad . \quad \text{(IV.)}$$

The additional elasticity $\frac{w^2 \varrho}{2 g}$, being that which is due to the motion, is independent of the diameter. The divisor g (the force of gravity) is introduced, on the supposition of the density ϱ being measured by weight.

Supposing the atmosphere of an atom to be divided into concentric spherical layers, it may be shewn that the effect of the coexistence of a great number of small vortices in one of those layers whose radius is r, and mean density ϱ, is to give it a centrifugal force, expressed by

$$\frac{w^2}{g r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(V.)}$$

which tends to increase the density and elasticity of the atmosphere at the surface, which I have called the boundary of the atom. The layer is also acted upon by the difference between the mean elasticities at its two surfaces, and by the attraction towards the atomic centre; and these three forces must balance each other.

I have integrated the differential equation which results from this condition, for substances in the gaseous state, in which the forces that interfere with the centrifugal force and atmospheric elasticity are comparatively small; and the result is

$$P = b\frac{\mu}{M}D\left(\frac{w^2}{3\,g\,b}+1\right)(1-F)+f(D) \quad . \quad . \quad . \quad (VI.)$$

P is the entire elasticity of the gas, and D its mean density. M represents the total mass of an atom, measured by weight, and μ that of its atmospheric part; so that $\frac{\mu}{M}D$ is the mean density of the atomic atmospheres.

$f(D)$ denotes the effect of the mutual actions of separate atoms.

The first term represents the superficial-atomic elasticity. F denotes the effect of the attraction of the nucleus in modifying that elasticity, and can be represented approximately by a converging series, in terms of the negative powers of $\frac{w^2}{3\,g\,b}+1$, commencing with the inverse square, the coefficients being functions of the density D.

By using the first term of such a series, and determining its coefficient, and the quantity $f(D)$ empirically, I have obtained formulæ agreeing closely with the results of M. REGNAULT's experiments on the Expansion of Atmospheric Air, Carbonic Acid, and Hydrogen.

In a perfect gas, the above expression is reduced to

$$P = b\frac{\mu}{M}D\left(\frac{w^2}{3\,g\,b}+1\right) \quad . \quad . \quad . \quad . \quad (VII.)$$

Let n, as before, denote the number of atoms of a substance which, in the state of perfect gas, occupy unity of volume under unity of pressure at the temperature of melting ice, so that $n\,M$ is its specific gravity in that state: then

$$P = \frac{D}{n\,M}n\,\mu\,b\left(\frac{w^2}{3\,g\,b}+1\right) \quad . \quad . \quad . \quad (VIII.)$$

The factor by which $\frac{D}{n\,M}$ is here multiplied fulfils the condition of being a function of $\frac{w^2}{b}$, and of constants which are the same for all substances, and is therefore fitted for a measure of temperature. It obviously varies proportionally to the pressure of a perfect gas of a given density, or its volume under a given pressure.

Let τ, therefore, denote temperature, as measured from an *imaginary zero*, C degrees of the scale adopted, below the temperature of melting ice, at which

$$\frac{w^2}{3\,g\,b}+1 = 0\,;$$

Then for all substances

$$\tau = C\,n\,\mu\,b\left(\frac{w^2}{3gb} + 1\right)$$

and in perfect gases $\left.\begin{array}{l} \\ \\ \\ \end{array}\right\}$ . . . (IX.)

$$P = \frac{\tau}{C}\,\frac{D}{n\,M}$$

τ may be termed *absolute temperature*, and the point from which it is measured, the *absolute zero of temperature*. This, as I have observed, is an imaginary point, being lower than the absolute zero of heat by the quantity $C\,n\,\mu\,b$, which is the same for all substances.

The value of C, or the absolute temperature of melting ice, as determined from M. REGNAULT's experiments, is

$$274°\cdot6 \text{ centigrade,}$$

being the reciprocal of

$$0\cdot00364166 \text{ per centigrade degree,}$$

the value to which the coefficients of dilatation of gases at the temperature of melting ice approximate as they are rarefied.

For FAHRENHEIT's scale $C = 494°\cdot28$.

In the sequel I shall represent temperatures measured from that of melting ice by

$$T = \tau - C$$

We have now to consider the absolute quantity of heat, or of molecular *vis viva*, which corresponds to a given temperature in a given substance. It is obvious that

$$\frac{\mu\,w^2}{2\,g}$$

represents, in terms of gravity, the portion of *vis viva*, in one atom, due to the molecular vortices; but besides the vortical motion, there may be oscillations of expansion and contraction, or of rectilinear vibration about a position of equilibrium. The velocity with which these additional motions are performed will be in a permanent condition, when the mean value of its square, independent of small periodic changes, is equal throughout the atomic atmosphere. We may therefore represent by

$$\frac{\mu\,v^2}{2\,g} = k\,\frac{\mu\,w^2}{2\,g} \quad . \quad . \quad . \quad . \quad (X.)$$

the total *vis viva* of the atomic atmosphere. To this we have to add that of the nucleus, raising the quantity of heat in one atom to

$$\frac{M\,v^2}{2\,g} = q \quad . \quad . \quad . \quad . \quad .$$

While the quantity of heat in unity of weight is $\left.\begin{array}{l} \\ \\ \\ \end{array}\right\}$ (XI.)

$$\frac{v^2}{2\,g} = Q \quad . \quad . \quad . \quad . \quad .$$

The coefficient k (which enters into the value of specific heat) being the ratio of the *vis viva* of the entire motion impressed on the atomic atmospheres by the action of their nuclei, to the *vis viva* of a peculiar kind of motion, may be conjectured to have a specific value for each substance depending in a manner as yet unknown on some circumstance in the constitution of its atoms. Although it varies in some cases for the same substance in the solid, liquid, and gaseous states, there is no experimental evidence that it varies for the same substance in the same condition. In the investigation which follows, therefore, I have treated it as sensibly constant.

The following, then, are the expressions for quantity of heat in terms of temperature. In one atom :—

$$q = \frac{v^2}{2g} M = \frac{3 k M}{2 C n \mu}(\tau - C n \mu b)$$

In unity of weight :—

$$Q = \frac{v^2}{2g} = \frac{3 k}{2 C n \mu}(\tau - C n \mu b)$$

(XII.)

Real specific heat is consequently expressed by the following equations:—
For one atom :—

$$\frac{dq}{d\tau} = \frac{3 k M}{2 C n \mu} \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

For unity of weight :—

$$\frac{dQ}{d\tau} = \frac{3 k}{2 C n \mu} \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

(XIII.)

For so much of a perfect gas as occupies unity of volume under unity of pressure at the temperature of melting ice :—

$$n\frac{dq}{d\tau} = \frac{3 k M}{2 C \mu} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

The laws established experimentally by DULONG, that the specific heats of simple atoms, and of certain groups of compound atoms, bear to each other simple ratios, generally that of equality, and that the specific heats of equal volumes of all simple gases are equal, shew that the specific factor $\frac{k M}{\mu}$ depends on the chemical constitution of the atom, and thus confirm the conjecture I have stated respecting the coefficient k.

As I shall have occasion, in the investigation which follows, to refer to and to use the equation for the elasticity of vapours in contact with their liquids, which I published in the *Edinburgh New Philosophical Journal for July* 1849, I shall here state generally the nature of the reasoning from which it was deduced.

The equilibrium of a vapour in contact with its liquid depends on three conditions.

First, The total elasticity of the substance in the two states must be the same.

Secondly, The superficial atomic elasticity must vary continuously; so that if at the surface which reflects light there is an abrupt change of density (which seems almost certain), there must there be two densities corresponding to the same superficial-atomic elasticity.

Thirdly, The two forces, which act on each stratum of vapour parallel to the surface of the liquid, namely, the preponderance of molecular attraction towards the liquid, and the difference of the superficial-atomic elasticities at the two sides of the stratum, must be in equilibrio.

Close to the surface of the liquid, therefore, the vapour is highly condensed. The density diminishes rapidly as the distance from the liquid increases, and at all appreciable distances has a sensibly uniform value, which is a function of the temperature and of certain unknown molecular forces.

The integration of a differential equation representing the third condition of equilibrium, indicates the *form* of the approximate equation.

$$\text{Log } P = a - \frac{\beta}{\tau} - \frac{\gamma}{\tau^2} \quad . \quad . \quad . \quad \text{(XIV.)}$$

The coefficients of which have been determined empirically by three experimental data for each fluid. For proofs of the extreme closeness with which the formulæ thus obtained agree with experiment, I refer to the Journal in which they first appeared.

I annex a table of the coefficients for water, alcohol, ether, turpentine, petroleum, and mercury, in the direct equation, and also in the inverse formula,

$$\frac{1}{\tau} = \sqrt{\frac{a - \log P}{\gamma} + \frac{\beta^2}{4\gamma^2}} - \frac{\beta}{2\gamma} \quad . \quad . \quad \text{(XV.)}$$

by which the temperature of vapour at saturation may be calculated from the pressure. In the ninth and tenth columns are stated the limits between which the formulæ have been compared with experiment.

For turpentine, petroleum, and mercury, the formula consists of two terms only,

$$\text{Log } P = a - \frac{\beta}{\tau} \quad . \quad . \quad . \quad \text{(XVI.)}$$

the small range of the experiments rendering the determination of γ impossible.

TABLE *of the Constants in the Formulæ for the Elasticities of Vapours in contact with their Liquids.*

(1.) Names of the Fluids.	(2.) Scale of Pressures.	(3.) Scale of Temperatures.	(4.) α.	(5.) Log. β.	(6.) Log. γ.	(7.) $\dfrac{\beta}{2\,\gamma}$	(8.) $\dfrac{\beta^2}{\pm\,\gamma^2}$	(9.) Range of Temperatures.	(10.) Range of Pressures.
Water	Millimètres of Mercury.	Centigrade.	7·831247	3·1851091	5·0327176	·0063294	·00004006	Centigrade. −30° to +230°	Millimètres. 0·35 to 20945
Do.	Inches of Mercury.	Fahrenheit.	6·426421	3·4403816	5·5932626	·0035163	·000012364	Fahrenheit. −22° to +446°	Inches. 0·014 to 824·63
Alcohol sp. gr. 0·813	do.	do.	6·16620	3·3165220	5·7602709	·0017998	·000003239	+32° to 264°	0·41 to 165·58
Ether boiling at 105° F.	do.	do.	5·33590	3·2084573	5·5119893	·0024856	·000006178	105° to 210°	30·00 to 163·27
Ether boiling at 104° F.	do.	do.	5·44580	3·2571312	5·3962460	·0036296	·000013174	34° to 104°	6·20 to 30·00
Turpentine	do.	do.	5·98187	3·5380701	......	......	......	304° to 362°	30·00 to 62·24
Petroleum	do.	do.	6·19451	3·5648490	......	......	......	316° to 375°	30·00 to 64·50
Mercury	Millimètres of Mercury.	Centigrade.	7·5305	3·4685511	......	......	......	Centigrade. 72°·74 to 358°	Millimètres. 0·115 to 760
Do.	Inches of Mercury.	Fahrenheit.	6·1259	3·7238236	......	......	......	Fahrenheit. 162°·93 to 676°·4	Inches. ·0046 to 29·92

The following are some additional values of the constant a for steam, corresponding to various units of pressure used in practice.

Units of Pressure.	Values of a.
ATMOSPHERES of 760 millimètres of mercury,	
$=29\cdot922$ inches of mercury,	
$=14\cdot7$ lb. on the square inch,	
$=1\cdot0333$ kilogrammes on the square centimètre, . .	$4\cdot950433$
ATMOSPHERES of 30 inches of mercury,	
$=761\cdot99$ millimètres,	
$=14\cdot74$ lb. on the square inch,	
$=1\cdot036$ kilogrammes on the square centimètre, . .	$4\cdot949300$
Kilogrammes on the square centimètre, ...	$4\cdot964658$
Kilogrammes on the circular centimètre, ...	$4\cdot859748$
Pounds avoirdupois on the square inch, ...	$6\cdot117662$
Pounds avoirdupois on the circular inch, ...	$6\cdot012752$
Pounds avoirdupois on the square foot, ...	$8\cdot276025$

All the numerical values of the constants are for common logarithms.

SECTION I.—OF THE MUTUAL CONVERSION OF HEAT AND EXPANSIVE POWER.

(1.) The quantity of heat in a given mass of matter, according to the hypothesis of molecular vortices, as well as every other hypothesis which ascribes the phenomena of heat to motion, is measured by the mechanical power to which that motion is equivalent, that being a quantity the total amount of which in a given system of bodies cannot be altered by their mutual actions, although its distribution and form may be altered. This is expressed in Equation XII. of the Introduction, where the quantity of heat in unity of weight, Q, is represented by the height $\frac{v^2}{2g}$, from which a body must fall in order to acquire the velocity of the molecular oscillations. This height, being multiplied by the weight of a body, gives the mechanical power to which the oscillations constituting its heat are equivalent. The real specific heat of unity of weight, as given in Equation XIII. of the Introduction,

$$\frac{dQ}{d\tau} = \frac{3k}{2Cn\mu}$$

represents the *depth of fall*, which is equivalent to *one degree of rise of temperature* in any given weight of the substance under consideration.

We know, to a greater or less degree of precision, the ratios of the specific heats of many substances to each other, and they are commonly expressed by taking that of water at the temperature of melting ice as unity; but their actual mechanical values have as yet been very imperfectly ascertained, and, in fact, the data necessary for their determination are incomplete.

(2.) Mr JOULE, indeed, has made several very interesting series of experiments, in order to ascertain the quantity of heat developed in various substances

by mechanical power employed in different ways, viz., by electric currents excited by the rotation of a magnet, by the forcing of water through narrow tubes, by the agitation of water and oil with a paddle, by the compression of air, and by the friction of air rushing through a narrow orifice. The value of the depth of fall equivalent to a rise of one degree of FAHRENHEIT's scale in the temperature of a mass of water, as determined by that gentleman, varies, in the different series of experiments, between the limits of 760 feet and 890 feet, the value in which Mr JOULE appears to place the greatest confidence being about 780 feet.

Although the smallness of the differences of temperature measured in those experiments renders the numerical results somewhat uncertain, it appears to me that, as evidence of the convertibility of heat and mechanical power, they are unexceptionable. Nevertheless, there is reason to believe that the true mechanical equivalent of heat is considerably less than any of the values deduced from Mr JOULE's experiments; for in all of them there are causes of loss of power, the effect of which it is impossible to calculate. In all machinery, a portion of the power which disappears is carried off by waves of condensation and expansion, along the supports of the machine, and through the surrounding air: this portion cannot be estimated, and is, of course, not operative in producing heat within the machine. It is also impossible to calculate, where friction is employed to produce heat, what amount of it has been lost in the production of electricity, a power which is, no doubt, convertible into heat, but which, in such experiments, probably escapes without undergoing that conversion. To make the determination of the mechanical equivalent of heat by electro-magnetic experiments correct, it is necessary that the whole of the mechanical power should be converted into magnetic power, the whole of the magnetic power into what are called electric currents, and the whole of the power of the electric currents into heat, not one of which conditions is likely to be exactly fulfilled. Even in producing heat by the compression of air, it must not be assumed that the whole of the mechanical power is expended in raising the temperature.

(3.) The best means of determining the mechanical equivalent of heat are furnished by those experiments in which no machinery is employed. Of this kind are experiments on the velocity of sound in air and other gases, which, according to the received and well-known theory of LAPLACE, is accelerated by the heat developed by the compression of the medium.

The accuracy of this theory has lately been called in question. There can be no doubt that it deviates from absolute exactness, in so far that the magnitude of the displacements of the particles of air is neglected in comparison with the length of a wave. It appears to me, however, that the Astronomer-Royal, in his remarks on the subject in the *London and Edinburgh Philosophical Magazine for July* 1849, has shewn, in a satisfactory manner, that although the effect of the appreciable magnitude of those displacements, as compared with the length of a

wave of sound, is to alter slowly the form of the function representing the wave, still that effect is not sufficiently great to make LAPLACE's theory practically erroneous. I have, therefore, in the sequel, adhered to the experiments of DULONG, and to those quoted by POISSON, on the velocity of sound, as the best data for determining the mechanical equivalent of heat.

(4.) The expression already given for the real specific heat of unity of weight of a given substance may be resolved into two factors, thus :—

$$\frac{d\,Q}{d\,\tau} = \frac{1}{C\,n\,M} \times \frac{3\,k\,M}{2\,\mu} \quad \cdot \quad \cdot \quad \cdot \quad (1.)$$

The first factor, $\dfrac{1}{C\,n\,M}$, may be considered in general as a known quantity; for C represents, as already stated, 274·6 centigrade degrees, the absolute temperature of melting ice, and $n\,M$ the theoretical weight, in the perfectly gaseous state, of unity of volume of the substance, under unity of pressure, at that temperature; or what is the same thing, $\dfrac{1}{n\,M}$ is the height of an imaginary column of the substance, of uniform density, and at the temperature of melting ice, whose pressure by weight upon a given area of base is equal to its pressure by elasticity, supposing it to be perfectly gaseous. The determination of the ratio $\dfrac{3\,k\,M}{2\,\mu}$ is necessary, to complete the solution of the problem.

(5.) The relation now to be investigated between heat and mechanical power, is that which exists between the power expended in compressing a body into a smaller volume, and the increase of heat in consequence of such a compression, and conversely, between the heat which disappears, or, as it is said, becomes *latent*, during the expansion of a body to a greater volume, and the mechanical power gained or developed by that expansion. Those phenomena, according to the hypothesis now under consideration, as well as every hypothesis which ascribes heat to motion, are simply the transformation of mechanical power from one shape into another.

It is obvious, in the first place, without the aid of algebraical symbols, that the general effect of the compression of an oscillating atomic atmosphere, or molecular vortex, must be to accelerate its motion, and of its dilatation, to retard its motion; for every portion of such an atmosphere is urged towards the nucleus or atomic centre by a centripetal force equal to the centrifugal force arising from the oscillation; so that when, by compression, each portion of the atmosphere is made to *approach* the centre by a given distance, the *vis viva* of its motion will be *increased* by the amount corresponding to the centripetal force acting through that distance; and conversely, when by expansion each portion of the atmosphere is made to *retreat* from the centre, the *vis viva* of its motion will be *diminished* by a similar amount.

It is not, however, to be taken for granted, that *all* the power expended in

compressing a body appears in the form of heat. More or less power may be consumed or developed by changes of molecular arrangement, or of the internal distribution of the density of the atomic atmospheres; and changes of molecular arrangement or distribution may develope or consume heat, independently of changes of volume.

(6.) We shall now investigate, according to the hypothesis of molecular vortices, the amount of heat produced by an indefinitely small compression of one atom of a body in that state of perfect fluidity which admits of the bounding surface of the atom being treated as if it were spherical: its radius being denoted by R, and the radius of any internal spherical layer of the atmosphere by multiplying R by a fraction u.

I shall denote by the ordinary symbol of differentiation d, such changes as depend on the various positions of portions of the atomic atmosphere relatively to each other, when changes of volume and temperature are not taken into consideration; while by the symbol δ of the calculus of variations, I shall represent such changes as arise from the variations of volume and temperature.

Let us consider the case of an indefinitely thin spherical layer of the atomic atmosphere, whose distance from the nucleus is $R\,u$, its thickness $R\,d\,u$, its area $4\,\pi\,R^2\,u^2$, and its density $\frac{\mu}{M}\,D\,\psi\,(u, D, \tau)$.

The weight, then, of this layer is

$$4\,\pi\,R^3\,\frac{\mu}{M}\,D\,u^2\,\psi\,(u, D, \tau)\,d\,u.$$

Its velocity of oscillation is v, and having, in virtue of that velocity, a mean centrifugal force, as explained in the Introduction (Equation V.), equal to

$$\text{its weight} \times \left(\frac{v^2}{g\,k\,R\,u} = \frac{2\,Q}{k\,R\,u}\right)$$

it is kept in equilibrio by an equal and opposite centripetal force, arising from attraction and elastic pressure, which is consequently represented by

$$4\,\pi\,R^2\,\frac{\mu}{M}\,\frac{v^2}{g\,k}\,D\,u\,\psi\,(u, D, \tau)\,d\,u$$

$$=8\,\pi\,R^2\,\frac{\mu}{k\,M}\,Q\,D\,u\,\psi\,(u, D, \tau)\,d\,u.$$

Let the mean density of the atom now be increased by the indefinitely small quantity δD. Then the layer will approach the nucleus through the distance $-\delta\,(R\,u) = -u\,\delta\,R - R\,\delta\,u$, and being acted upon through that distance by the centripetal force already stated, the *vis viva* of oscillation will be increased by a quantity corresponding to the mechanical power (that is to say, the *heat*), represented by the product of that distance by that force, or by

$$-8\,\pi\,R^2\,\frac{\mu}{k\,M}\,Q\,D\,u\,\psi\,(u, D, \tau)\,d\,u \times \delta\,(R\,u)$$

2 U

$$= -8\,\pi\,R^3\,\frac{\mu}{k\,M}\,Q\,D\,\psi\,(u,\,D,\,\tau)\,u^2\left(\frac{\delta\,R}{R} + \frac{\delta\,u}{u}\right)d\,u$$

which, because $\dfrac{\delta\,R}{R} = -\dfrac{1}{3}\cdot\dfrac{\delta\,D}{D}$, and $\dfrac{4\,\pi\,R^3\,D}{3} = M$ is equal to

$$+\,Q\,M\,\cdot\,\frac{2\,\mu}{k\,M}\,\psi\,(u,\,D,\,\tau)\,u^2\left(\frac{\delta\,D}{D} - 3\,\frac{\delta\,u}{u}\right)d\,u.$$

We must suppose that the velocity of oscillation is equalised throughout the atomic atmosphere, by a propagation of motion so rapid as to be practically instantaneous.

Then if the above expression be integrated with respect to $d\,u$, from $u = 0$ to $u = 1$, the result will give the whole increase of heat in the atom arising from the condensation $\delta\,D$; and dividing that integral by the atomic weight M, we shall obtain the corresponding development of heat in unity of weight. This is expressed by the following equation :—

$$\delta\,Q' = 2\,Q\,\frac{\mu}{k\,M}\left\{\frac{\delta\,D}{D}\int_0^1 d\,u\,\cdot\,u^2\,\psi\,(u,\,D,\,\tau)\right.$$
$$\left. -3\int_0^1 d\,u\,\cdot\,u\,\delta\,u\,\psi\,(u,\,D,\,\tau)\right\}\quad\cdot\quad\cdot\quad(2.)$$

The letter Q′ is here introduced to denote, when negative, that heat which is consumed in producing changes of volume and of molecular arrangement, and when positive, as in the above equation, the heat which is produced by such changes.

The following substitutions have to be made in Equation (1.) of this Section.

For Q is to be substituted its value, according to Equation XII. of the Introduction; or abbreviating $C\,n\,\mu\,b$ into κ:—

$$Q = \frac{3\,k}{2\,C\,n\,\mu}\,(\tau - \kappa)\quad\cdot\quad\cdot\quad\cdot\quad(3.)$$

The value of the first integral in Equation (2.) of this Section is

$$\int_0^1 d\,u\,\cdot\,u^2\,\psi\,(u,\,D,\,\tau) = \frac{1}{3}$$

The value of the second integral

$$-3\int_0^1 d\,u\,\cdot\,u\,\delta\,u\,\psi\,(u,\,D,\,\tau)$$

remains to be investigated. The first step in this inquiry is given by the condition, that whatsoever changes of magnitude a given spherical layer undergoes, the portion of atmosphere between it and the nucleus is invariable. This condition is expressed by the equation

$$0 = \left(\delta\,u\frac{d}{d\,u} + \delta\,\tau\,\frac{d}{d\,\tau} + \delta\,D\frac{d}{d\,D}\right)\int_0^u d\,u\,\cdot\,u^2\,\psi\,(u,\,D,\,\tau)\quad\cdot\quad\cdot\quad\cdot\quad(4.)$$

from which it follows that

$$\delta\,u = -\frac{1}{u^2\,\psi\,(u,\,D,\,\tau)}\left(\delta\,\tau\,\frac{d}{d\,\tau} + \delta\,D\,\frac{d}{d\,D}\right)\int_0^u d\,u\,\cdot\,u^2\,\psi\,(u,\,D,\,\tau)$$

and consequently that

$$-3\int_0^1 du \, . \, u \, \delta u \, \psi \, (u, D, \tau) =$$

$$+ \left(\delta \tau \, . \, \frac{d}{d\tau} + \delta D \frac{d}{dD} \right) 3 \int_0^1 \frac{du}{u} \int_0^u du \, . \, u^2 \psi \, (u, D, \tau)$$

Hence, making

$$9 \int_0^1 \frac{du}{u} \int_0^u du \, . \, u^2 \psi \, (u, D, \tau) = U \quad . \quad . \quad . \quad (5.)$$

The second integral in Equation (2.) is transformed into

$$+ \frac{1}{3} \left(\delta \tau \frac{d}{d\tau} + \delta D \frac{d}{dD} \right) U.$$

By means of those substitutions we obtain, for the mechanical value of the heat developed in unity of weight of a fluid by any indefinitely small change of volume or of molecular distribution—

$$\left. \begin{aligned} \delta Q' &= \frac{\tau - \kappa}{C \, n \, M} \left(\delta D \left(\frac{1}{D} + \frac{dU}{dD} \right) + \delta \tau \frac{dU}{d\tau} \right) \\ \end{aligned} \right\}$$

or taking $V = \frac{1}{D}$ to denote the volume of unity of weight of the substance,

$$\left. \begin{aligned} \delta Q' &= -\frac{\tau - \kappa}{C \, n \, M} \left(\delta V \left(\frac{1}{V} - \frac{dU}{dV} \right) - \delta \tau \frac{dU}{d\tau} \right) \\ \end{aligned} \right\} \quad (6.)$$

Of this expression, the portion $\frac{\tau - \kappa}{C \, n \, M} \cdot \frac{\delta D}{D} = -\frac{\tau - \kappa}{C \, n \, M} \cdot \frac{\delta V}{V}$ represents the variation of heat arising from mere change of volume.

$\frac{\tau - \kappa}{C \, n \, M} \delta V \frac{dU}{dV} = \frac{\tau - \kappa}{C \, n \, M} \delta D \frac{dU}{dD}$, denotes the variation of heat produced by change of molecular distribution dependent on change of volume.

$\frac{\tau - \kappa}{C \, n \, M} \delta \tau \frac{dU}{d\tau}$ expresses the variation of heat due to change of molecular distribution dependent on change of temperature.

(7.) The function U is one depending on molecular forces, the nature of which is as yet unknown. The only case in which it can be calculated directly is that of a perfect gas. Without giving the details of the integration, it may be sufficient to state, that in this case

$$\left. \begin{aligned} U &= \frac{\kappa}{\tau} \\ \\ \frac{dU}{d\tau} &= -\frac{\kappa}{\tau^2} \, ; \quad \frac{dU}{dV} = 0 \end{aligned} \right\} \quad . \quad . \quad . \quad (7.)$$

and therefore that

In all other cases, however, the value of this function can be determined indirectly, by introducing into the investigation the principle of the *conservation of vis viva.*

Suppose a portion of any substance, of the weight *unity*, to pass through a variety of changes of temperature and volume, and at length to be brought back to its primitive volume and temperature. Then the absolute quantity of heat in the substance, and the molecular arrangement and distribution, being the same as at first, the effect of their changes is eliminated; *and the algebraical sum of the vis viva expended and produced, whether in the shape of expansion and compression, or in that of heat, must be equal to zero:*—that is to say, if, on the whole, any mechanical power has appeared, and been given out from the body, in the form of expansion, an equal amount must have been communicated to the body, and must have disappeared in the form of heat; and if any mechanical power has appeared and been given out from the body in the form of heat, an equal amount must have been communicated to the body, and must have disappeared in the form of compression. This principle expressed symbolically is

$$\Delta \, \Pi + \Delta \, Q' = 0 \quad . \quad . \quad . \quad . \quad (8.)$$

Where Π, when positive, represents expansive power given out, when negative, compressive power absorbed; and Q' represents, when positive, heat given out, when negative, heat absorbed.

To take the simplest case possible, let the changes of temperature and of volume be supposed to be indefinitely small, and to occur during distinct intervals of time, so that τ and V are independent variables. Let the initial absolute temperature be τ, the initial volume V, and the initial total elasticity P; and let the substance go through the following four changes.

First, Let its temperature be raised from τ to $\tau + \delta \tau$, the volume remaining unchanged. Then the quantity of heat absorbed is

$$- \delta \tau \left(\frac{d \, Q}{d \, \tau} - \frac{\tau - \kappa}{C \, n \, M} \frac{d \, U}{d \, \tau} \right)$$

and there is no expansion nor compression.

Secondly, Let the body expand, without change of temperature, from the volume V to the volume $V + \delta V$. Then the quantity of heat absorbed is

$$- \delta V \cdot \frac{\tau + \delta \tau - \kappa}{C \, n \, M} \left(\frac{1}{V} - \frac{d}{d V} \cdot \left(U + \frac{d \, U}{d \, \tau} \delta \, \tau \right) \right)$$

while the power given out by expansion is

$$\delta \, V \left(P + \frac{d \, P}{d \, \tau} \delta \, \tau \right)$$

Thirdly, Let the temperature fall from $\tau + \delta \tau$ to its original value τ, the volume $V + \delta V$ continuing unchanged; then the heat given out is

$$+ \delta \, \tau \left(\frac{d \, Q}{d \, \tau} - \frac{\tau - \kappa}{C \, n \, M} \frac{d}{d \, \tau} \left(U + \frac{d \, U}{d \, V} \delta \, V \right) \right)$$

and there is no expansion nor compression.

Fourthly, Let the body be compressed, without change of temperature, to its original volume V; then the heat given out is

$$+ \delta V \frac{\tau - \kappa}{C n M} \left(\frac{1}{V} - \frac{dU}{dV} \right)$$

while the power absorbed in compression is

$$- \delta V . P$$

The body being now restored in all respects to its primitive state, the sum of the two portions of power connected with change of volume, must, in virtue of the principle of *vis viva*, be equal to the sum of the four quantities of heat with their signs reversed. Those additions being made, and the sums divided by the common factor $\delta V \, \delta \tau$, the following equation is obtained:—

$$\frac{dP}{d\tau} = \frac{1}{C n M} \left(\frac{1}{V} - \frac{dU}{dV} \right) \quad \cdot \cdot \cdot \quad (9.)$$

The integral of this partial differential equation is

$$U = \phi . \tau + \int dV \left(\frac{1}{V} - C n M \frac{dP}{d\tau} \right) \quad \cdot \cdot \cdot \quad (10.)$$

Now $\phi . \tau$ being the same for all densities, is the value of U for the perfectly gaseous state, or $\frac{\kappa}{\tau}$; for in that state, the integral $= 0$.

The values of the partial differential coefficients are accordingly—

$$\left. \begin{array}{l} \dfrac{dU}{dV} = \dfrac{1}{V} - C n M \dfrac{dP}{d\tau} \\[2mm] \dfrac{dU}{d\tau} = -\dfrac{\kappa}{\tau^2} - C n M \displaystyle\int dV . \dfrac{d^2 P}{d\tau^2} \end{array} \right\} \quad \cdot \cdot \cdot \quad (11.)$$

and they can, therefore, be determined in all cases in which the quantity $\kappa = C n \mu b$, and the law of variation of the total elasticity with the volume and temperature are known, so as to complete the data required in order to apply equation 6 of this section to the calculation of the mechanical value of the variations of heat due to changes of volume and molecular arrangement.

The total elasticity of an imperfect gas, according to Equations VI. and XII. of the introduction, being

$$P = \frac{\tau}{C n M V} \left(1 - F \left(D, \frac{\tau}{\kappa} \right) \right) + f(D)$$

its first and second partial differential coefficients with respect to the temperature are,—

$$\frac{dP}{d\tau} = \frac{1}{C n M V} \left(1 - \left(1 + \tau \frac{d}{d\tau} \right) F \left(D, \frac{\tau}{\kappa} \right) \right)$$

$$\frac{d^2 P}{d\tau^2} = -\frac{1}{C n M V} \left(2 \frac{d}{d\tau} + \tau \frac{d^2}{d\tau^2} \right) F \left(D, \frac{\tau}{\kappa} \right)$$

Consequently, for the imperfectly gaseous state,

$$
\left.
\begin{aligned}
\mathrm{U} &= \frac{\kappa}{\tau} + \left(1 + \tau \frac{d}{d\tau}\right) \int d\mathrm{V} \cdot \frac{\mathrm{F}\left(\mathrm{D}, \frac{\tau}{\kappa}\right)}{\mathrm{V}} \\[2mm]
\frac{d\mathrm{U}}{d\mathrm{V}} &= \frac{1}{\mathrm{V}} \cdot \left(1 + \tau \frac{d}{d\tau}\right) \mathrm{F}\left(\mathrm{D}, \frac{\tau}{\kappa}\right) \\[2mm]
\frac{d\mathrm{U}}{d\tau} &= -\frac{\kappa}{\tau^2} + \left(2\frac{d}{d\tau} + \tau \frac{d^2}{d\tau^2}\right) \int d\mathrm{V} \cdot \frac{\mathrm{F}\left(\mathrm{D}, \frac{\tau}{\kappa}\right)}{\mathrm{V}}
\end{aligned}
\right\} \quad . \quad . \ (12.)
$$

(8.) It is to be observed that the process followed in ascertaining the nature of the function U is analogous to that employed by M. CARNÔT in his theory of the motive power of heat, although founded on contrary principles, and leading to different results.

CARNÔT, in fact, considers heat to be something of a peculiar kind, whether a condition or a substance, the total amount of which in nature is incapable of increase or of diminution. It is not, therefore, according to his theory, convertible into mechanical power; but is capable, by its transmission through substances under particular circumstances, of causing mechanical power to be developed. He supposes a body to go through certain changes of temperature and volume, and to return at last to its primitive volume and temperature, and conceives, in accordance with his view of the nature of heat, that it must have given out exactly the same quantity of heat that it has absorbed. The transmission of this heat he regards as the cause of the production of an amount of mechanical power, depending on the quantity of heat transmitted and on the temperature at which the transmission has taken place. According to these principles, a body, having received a certain quantity of heat, is capable of giving out not only all the heat it has received, but also a quantity of mechanical power which did not before exist.

According to the theory of this Essay, on the contrary, and to every conceivable theory which regards heat as a modification of motion, no mechanical power can be given out in the shape of expansion unless the quantity of heat emitted by the body in returning to its primitive temperature and volume is *less* than the quantity of heat originally received: the excess of the latter quantity above the former disappearing as heat, to appear as expansive power, so that the sum of the *vis viva* in those two forms continues unchanged.

Section II.—Of Real and Apparent Specific Heat, especially in the State of Perfect Gas.

(9.) The apparent specific heat of a given substance is found by adding to the real specific heat (or the heat which retains its form in producing an elevation of one degree of temperature in unity of weight) that additional heat which disappears in producing changes of volume and of molecular arrangement, and which is determined by reversing the sign of Q^1 in equation 6 of Section I. (so as to transform it from heat evolved to heat absorbed), and taking its *total* differential coefficient with respect to the temperature. Hence, denoting total apparent specific heat by K,—

$$K = \frac{d\,Q}{d\,\tau} - \frac{d\,.\,Q^1}{d\,\tau} = \frac{d\,Q}{d\,\tau} - \frac{d\,Q^1}{d\,\tau} - \frac{d\,Q^1}{d\,V}\cdot\frac{d\,V}{d\,\tau}$$

$$= \frac{1}{C\,n\,M}\left\{ \frac{3\,k\,M}{2\,\mu} + (\tau - \kappa)\left(\frac{d\,V}{d\,\tau}\left(\frac{1}{V} - \frac{d\,U}{d\,V}\right) - \frac{d\,U}{d\,\tau}\right) \right\} \quad (13.)$$

Another mode of expressing this coefficient is the following :—

Denote the ratio $\qquad \dfrac{2\,\mu}{3\,k\,M}$ by N,

and the real specific heat by k $\qquad\qquad\qquad\qquad\quad . \quad . \quad (14.)$

$$= \frac{1}{C\,n\,M\,N}$$

Then

$$K = \text{k}\left\{ 1 + N\,(\tau - \kappa)\left(\frac{d\,V}{d\,\tau}\left(\frac{1}{V} - \frac{d\,U}{d\,V}\right) - \frac{d\,U}{d\,\tau}\right) \right\} \quad (15.)$$

The value of $\dfrac{d\,V}{d\,\tau}$ is to be determined from the conditions of each particular case; so that each substance may have a variety of apparent specific heats, according to the manner in which the volume varies with the temperature.

If the volume is not permitted to vary, so that $\dfrac{d\,V}{d\,\tau} = 0$, there is obtained the following result, being the apparent specific heat at constant volume :—

$$K_v = \frac{1}{C\,n\,M}\left(\frac{1}{N} - (\tau - \kappa)\frac{d\,U}{d\,\tau}\right)$$

$$= \text{k}\left(1 - N\,(\tau - \kappa)\frac{d\,U}{d\,\tau}\right) \quad . \quad . \quad (16.)$$

(10.) When the substance under consideration is a perfect gas, it has already been stated (Eq. 7), that $\dfrac{d\,U}{d\,\tau} = -\dfrac{\kappa}{\tau^2}, \dfrac{d\,U}{d\,V} = 0$; and because the volume of unity of weight is directly as the absolute temperature and inversely as the pressure,

$$\frac{1}{V}\frac{d\,V}{d\,\tau} = \frac{1}{\tau} - \frac{1}{P}\frac{d\,P}{d\,\tau} \quad . \quad . \quad . \quad (17.)$$

Hence the following are the values of the apparent specific heats of unity of weight of a theoretically perfect gas under different circumstances :—

General value of the total apparent specific heat :—

$$
\begin{aligned}
\mathrm{K} &= \frac{1}{C\,n\,\mathrm{M}} \left\{ \frac{1}{\mathrm{N}} + (\tau - \kappa)\left(\frac{\kappa}{\tau^2} + \frac{d\,\mathrm{V}}{\mathrm{V}\,d\tau} \right) \right\} \\
&= \frac{1}{C\,n\,\mathrm{M}} \left\{ \frac{1}{\mathrm{N}} + (\tau - \kappa)\left(\frac{\kappa}{\tau^2} + \frac{1}{\tau} - \frac{d\,\mathrm{P}}{\mathrm{P}\,d\tau} \right) \right\}
\end{aligned}
$$

Apparent specific heat at constant volume :—

$$
\begin{aligned}
\mathrm{K_v} &= \frac{1}{C\,n\,\mathrm{M}} \left\{ \frac{1}{\mathrm{N}} + \frac{\kappa}{\tau} - \frac{\kappa^2}{\tau^2} \right\} \\
&= \Bbbk \left(1 + \mathrm{N}\left(\frac{\kappa}{\tau} - \frac{\kappa^2}{\tau^2} \right) \right)
\end{aligned}
$$

Apparent specific heat under constant pressure :—

$$
\begin{aligned}
\mathrm{K_p} &= \frac{1}{C\,n\,\mathrm{M}} \left(\frac{1}{\mathrm{N}} + 1 - \frac{\kappa^2}{\tau^2} \right) \\
&= \Bbbk \left\{ 1 + \mathrm{N}\left(1 - \frac{\kappa^2}{\tau^2} \right) \right\}
\end{aligned}
$$

. . . (18.)

The ratio of the apparent specific heat under constant pressure to the apparent specific heat at constant volume is the following :—

$$
\frac{\mathrm{K_p}}{\mathrm{K_v}} = \frac{1 + \mathrm{N}\left(1 - \frac{\kappa^2}{\tau^2} \right)}{1 + \mathrm{N}\left(\frac{\kappa}{\tau} - \frac{\kappa^2}{\tau^2} \right)} = 1 + \mathrm{N}\frac{1 - \frac{\kappa}{\tau}}{1 + \mathrm{N}\left(\frac{\kappa}{\tau} - \frac{\kappa^2}{\tau^2} \right)} \quad \cdots \quad (19.)
$$

The value of κ is unknown; and, as yet, no experimental data exist from which it can be determined. I have found, however, that practically, results of sufficient accuracy are obtained by regarding κ as so small in comparison with τ, that $\frac{\kappa}{\tau}$, and à *fortiori* $\frac{\kappa^2}{\tau^2}$, may be neglected in calculation.

Thus are obtained the following *approximate* results, for perfect gases, and gases which may without material error be treated as perfect.

General value of the total apparent specific heat :—

$$
\begin{aligned}
\mathrm{K} &= \frac{1}{C\,n\,\mathrm{M}} \left(\frac{1}{\mathrm{N}} + \frac{\tau}{\mathrm{V}}\frac{d\,\mathrm{V}}{d\tau} \right) = \Bbbk + \mathrm{P}\frac{d\,\mathrm{V}}{d\tau} \\
&= \frac{1}{C\,n\,\mathrm{M}} \left(\frac{1}{\mathrm{N}} + 1 - \frac{\tau}{\mathrm{P}}\frac{d\,\mathrm{P}}{d\tau} \right)
\end{aligned}
$$

Apparent specific heat at constant volume :—

$$
\mathrm{K_v} = \frac{1}{C\,n\,\mathrm{M}\,\mathrm{N}} = \Bbbk
$$

being equal to the real specific heat.

Apparent specific heat under constant pressure :—

$$
\mathrm{K_p} = \frac{1}{C\,n\,\mathrm{M}} \left(\frac{1}{\mathrm{N}} + 1 \right) = \Bbbk\,(1 + \mathrm{N})
$$

. . (20.)

Ratio of those two specific heats :—

$$\frac{K_P}{K_V} = 1 + N \quad . \quad . \quad . \quad (21.)$$

This ratio is the quantity called by POISSON γ, in his researches on the propagation of sound.

(11.) It is unnecessary to do more than to refer to the researches of POISSON, and to those of LAPLACE, for the proof that the effect of the production of heat by the compression of air is the same as if the elasticity varied in proportion to that power of the density whose index is the ratio of the two specific heats; so that the actual velocity of sound is greater than that which it would have if there were no such development of heat, in the proportion of the square root of that ratio.

The following is the value of the velocity of sound in a gas, as given by POISSON, in the second volume of his *Traité de Mécanique* :—

$$a = \sqrt{g \, . \, \gamma \, . \, (1 + E\,T)\frac{m\,h}{\Delta}} \quad . \quad . \quad . \quad (22.)$$

where a denotes the velocity of sound, g the velocity generated by gravity in unity of time, E the coefficient of increase of elasticity with temperature, at the freezing point of water, T the temperature measured from that point, m the specific gravity of mercury, Δ that of the gas at the temperature of melting ice, and pressure corresponding to a column of mercury of the height h. It follows that the ratio γ is given by the formula

$$\gamma = 1 + N \text{ nearly} = \frac{a^2 \, \Delta}{g \, m \, h \, (1 + E\,T)} \quad . \quad . \quad . \quad (23.)$$

Calculations have been made to determine the ratio γ from the velocity of sound; but as many of them involve erroneous values of the coefficient of elasticity E, the experiments have to be reduced anew.

The following calculation is founded on an experiment quoted by POISSON on the velocity of sound in atmospheric air, the values of E, m, and Δ being taken from the experiments of M. REGNAULT.

$$a = 340\cdot89 \text{ mètres per second.}$$
$$g = 9^{m}\cdot80896. \qquad h = 0^{m}\cdot76. \qquad T = 15°\cdot9 \text{ Centigrade.}$$
$$E = 0\cdot003665; \; \frac{m}{\Delta} = 10513.$$

Consequently, for atmospheric air,
$$\gamma = 1\cdot401.$$

The results of a reduction, according to correct data, of the experiments of DULONG upon the velocity of sound in atmospheric air, oxygen, and hydrogen, are as follows :—

Atmospheric air,	.	.	.	$\gamma = 1\cdot410$		
Oxygen,	.	.	.	.	.	1·426
Hydrogen,	.	.	.	.	.	1·426

Thus it appears, that for the simple substances, oxygen and hydrogen, the ratio N is the same, while for atmospheric air it is somewhat smaller.[*]

(12.) The ordinary mode of expressing the specific heats of gases is to state their ratios to that of an *equal volume* of atmospheric air at the same pressure and temperature.

When $\frac{\kappa}{\tau}$ is a very small fraction, specific heats of *unity of volume* of a perfect gas are given by the equations

$$\left. \begin{aligned} n \, M \, K_v &= \frac{1}{C \, N} \\[2mm] n \, M \, K_P &= \frac{1}{C} \left(\frac{1}{N} + 1 \right) \end{aligned} \right\} \quad \ldots \quad (24.)$$

That is to say, the specific heat of unity of volume at constant volume is inversely proportional to the fraction by which the ratio of the two specific heats exceeds unity; a conclusion already deduced from experiment by DULONG.

The following is a comparison of the ratios of the apparent specific heats under constant pressure, of unity of volume of oxygen and hydrogen respectively, to that of atmospheric air, as deduced from Equation (24.), with those determined experimentally by DE LA ROCHE and BÉRARD.

<div align="center">

Ratio $\dfrac{n \, M \, K_P \, (\text{Gas})}{n \, M \, K_P \, (\text{Atmos. air})}$

</div>

Gas.	By Theory.	By Experiment.
Oxygen, ...	0·973	0·9765
Hydrogen, ...	0·973	0·9033

This comparison exhibits a much more close agreement between theory and experiment than has been hitherto supposed to exist, the errors in the constants employed having had the effect of making the ratio $1 + N$ seem greater for atmospheric air than for oxygen and hydrogen, while in fact it is smaller.

To treat the other substances on which both M. DULONG and MM. DE LA

---

[*] The following are some additional determinations of the value of γ for atmospheric air, founded upon experiments on the velocity of sound :—

Observers.	T Centigrade.	a Mètres per second.	γ
Bravais and Martins : mean of several experiments at temperatures varying from 5° to 11° centigrade, reduced to 0° (Comptes Rendus, xix.) . .	0°	332·37	1·40955
Moll and Van Beek : reduced to	0°	332·25	1·40853
Stampfer and Myrbach : reduced to 0° (not corrected for moisture)	0°	332·96	1·41456
Académie des Sciences, 1738 : (not corrected for moisture)	6°·1	337·10	1·418

A variation of one mètre per second in the velocity of sound at 0° corresponds to a variation of ·0085 in the value of γ.

Roche and Bérard made experiments as perfect gases, would lead to sensible errors. I have, therefore, confined my calculations for the present to oxygen, hydrogen, and atmospheric air.

(13.) The heat produced by compressing so much of a perfect gas as would occupy unity of volume under the pressure unity, at the temperature $0°$ centigrade, from its actual volume $n \, M \, V_1 = \frac{\tau}{PC}$ into a volume which is less in a given ratio s (when κ is neglected as compared with τ), is expressed by the following motion :—

$$n \, M \, Q' = -\frac{1}{C} \int_{V_1}^{s \, V_1} dV \, . \, \frac{\tau}{V} = - n \, M \, V_1 \int_{1}^{s} P \, ds \quad . \quad . \quad . \quad (25.)$$

being, in fact, equal to the mechanical power used in the compression. When the temperature is maintained constant, this becomes

$$n \, M \, Q'_{(\tau)} = \frac{\tau}{C} \log_e \, . \, \frac{1}{s} \quad . \quad . \quad . \quad (26.)$$

which is obviously independent of the nature of the gas.

Hence *equal volumes of all substances in the state of perfect gas, at the same pressure and at equal and constant temperatures, being compressed by the same amount, disengage equal quantities of heat;* a law already deduced from experiment by Dulong.

(14.) The determination of the fraction N affords the means of calculating the mechanical or absolute value of specific heat, as defined by Equation 1. Section First. The data for atmospheric air being taken as follows:—

$$N = 0.4, \qquad C = 274°.6 \text{ centigrade,}$$

$\frac{1}{n \, M}$ = height of an imaginary column of air of uniform density, at the temperature $0°$ cent., whose pressure by weight on a given base is equal to its pressure by elasticity, ... = 7990 mètres,
= 26214 feet:—

the real specific heat of atmospheric air, or the depth of fall equivalent to one centigrade degree of temperature in that gas, is found to be

$$k = \frac{1}{C \, n \, M \, N} = 72.74 \text{ mètres} = 238.66 \text{ feet} \quad . \quad . \quad (27.)$$

The apparent specific heat of atmospheric air, under constant pressure, according to De la Roche and Bérard, is equal to that of liquid water at $0°$ centigrade $\times$ 0.2669. The ratio of its real specific heat to the apparent specific heat of water at $0°$ centigrade, is, therefore,

$$.2669 \times \frac{1.0}{1.4} = .1906,$$

And, consequently, the mechanical value of the apparent specific heat of liquid water, at the temperature of melting ice, is

$$\frac{k \text{ (at. air)}}{\cdot 1906} = 381 \cdot 64 \text{ mètres} = 1252 \text{ feet per centigrade degree,} \left.\begin{array}{c} \\ \\ \end{array}\right\} \quad \cdot \quad \cdot \quad \cdot \quad (28.)$$
$$\text{or } 695 \cdot 6 \text{ feet per degree of Fahrenheit's scale,}$$

This quantity we shall denote by K_w. It is the mechanical equivalent of the ordinary *thermal unit*.

I have already pointed out (in Article 2. of the First Section) the causes which tend to make the apparent value of the mechanical equivalent of heat, in Mr JOULE's experiments, greater than the true value. The differences between the result I have just stated, and those at which he has arrived, do not seem greater than those causes are capable of producing, when combined with the uncertainty of experiments, like those of Mr JOULE, on extremely small variations of temperature.

(15.) Besides the conditions of constant volume and constant pressure, there is a third condition in which it is of importance to know the apparent specific heat of an elastic fluid, namely, the condition of vapour at saturation, or in contact with its liquid.

The apparent specific heat of a vapour at saturation, is the quantity of heat which unity of weight of that vapour receives or gives out, while its temperature is increased by one degree, its volume being at the same time compressed so as to bring it to the maximum pressure corresponding to the increased temperature.

It has been usually taken for granted, that this quantity is the same with the variation for one degree of temperature, of what is called the *total heat* of evaporation. Such is, indeed, the case according to the theory of CARNÔT; but I shall shew that, according to the mechanical theory of heat, these two quantities are not only distinct, but in general of contrary signs.

I shall, for the present, consider such vapours only as may be treated in practice as perfect gases, so as to make the first of the Equations (20.) applicable.

It has been shewn that the logarithm of the maximum elasticity of a vapour in contact with its liquid may be represented by the expression

$$\log P = a - \frac{\beta}{\tau} - \frac{\gamma}{\tau^2}$$

The coefficients a, β, γ, being those adapted for calculating the common logarithm of the pressure, I shall use the accented letters a', β', γ', to denote those suited to calculate the hyperbolic logarithm, being equal respectively to the former coefficients $\times 2 \cdot 3025851$.

Then for vapour at saturation,

$$\frac{d P}{P d \tau} = \frac{\beta'}{\tau^2} + \frac{2 \gamma'}{\tau^3} \quad \cdot \quad \cdot \quad \cdot \quad (29.)$$

Making this substitution in the general Equation (21.), we find the following value for the apparent specific heat of perfectly gaseous vapour at saturation :—

$$
\left.
\begin{aligned}
K_s &= k + P \frac{dV}{d\tau} = k \left(1 + N \cdot \frac{\tau}{V} \frac{dV}{d\tau}\right) \\
&= k \left\{1 + N \left(1 - \frac{\tau}{P} \frac{dP}{d\tau}\right)\right\} \\
&= \frac{1}{C\,n\,M} \left(\frac{1}{N} + 1 - \frac{\beta'}{\tau} - \frac{2\gamma'}{\tau^2}\right)
\end{aligned}
\right\}
\qquad \cdot \quad \cdot \quad \cdot \quad (30.)
$$

(16.) For the vapours of which the properties are known, the negative terms of this expression exceed the positive at all ordinary temperatures, so that the kind of apparent specific heat now under consideration is a negative quantity :— that is to say, that if a given weight of vapour at saturation is increased in temperature, and at the same time maintained by compression at the maximum elasticity, the heat generated by the compression is greater than that which is required to produce the elevation of temperature, and a surplus of heat is given out ; and on the other hand, if vapour at saturation is allowed to expand, and at the same time maintained at the temperature of saturation, the heat which disappears in producing the expansion is greater than that set free by the fall of temperature, and the deficiency of heat must be supplied from without, *otherwise a portion of the vapour will be liquefied, in order to supply the heat necessary for the expansion of the rest.*

This circumstance is obviously of great importance in meteorology, and in the theory of the steam-engine. There is as yet no experimental proof of it. It is true, that, in the working of non-condensing engines, it has been found that the steam which escapes is always at the temperature of saturation corresponding to its pressure, and carries along with it a portion of water in the liquid state ; but it is impossible to distinguish between the water which has been liquefied by the expansion of the steam, and that which has been carried over mechanically from the boiler.

The calculation of the proportion of vapour liquefied by a given expansion, requires the knowledge of the latent heat of evaporation, which forms the subject of the next section.

SECTION III.—OF THE LATENT AND TOTAL HEAT OF EVAPORATION, ESPECIALLY FOR WATER.

(17.) The latent heat of evaporation of a given substance at a given temperature, is the amount of heat which disappears in transforming unity of weight of the substance from the liquid state, to that of vapour of the maximum density for the given temperature, being consumed in producing an increase of volume, and an unknown change of molecular arrangement.

It is obvious, that if the vapour thus produced is reconverted into the liquid state *at the same temperature*, the heat given out during the liquefaction must be

equal to that consumed during the evaporation; for as the sum of the expansive and compressive powers, and of those dependent on molecular arrangement during the whole process, is equal to zero, so must the sum of the quantities of heat absorbed and evolved.

The heat of liquefaction, at a given temperature, is therefore equal to that of evaporation, with the sign reversed.

(18.) If to the latent heat of evaporation at a given temperature, is added the quantity of heat necessary to raise unity of weight of the liquid from a certain fixed temperature (usually that of melting ice) to the temperature at which the evaporation takes place, the result is called the total heat of evaporation from the fixed temperature chosen.

According to the theory of CARNÔT, this quantity is called the constituent heat of vapour; and it is conceived, that if liquid at the temperature of melting ice be raised to any temperature and evaporated, and finally brought in the state of vapour to a certain given temperature, the whole heat expended will be equal to the constituent heat corresponding to that given temperature, and will be the same, whatsoever may have been the intermediate changes of volume, or the temperature of actual evaporation.

According to the mechanical theory of heat, on the other hand, the quantity of heat expended must vary with the intermediate circumstances; for otherwise no power could be gained by the alternate evaporation and liquefaction of a fluid at different temperatures.

(19.) The law of the latent and total heat of evaporation is immediately deducible from the principle of the constancy of the total *vis viva* in the two forms of heat and expansive power, when the body has returned to its primitive density and temperature, as already laid down in Article 7.

That principle, when applied to evaporation and liquefaction, may be stated as follows :—

Let a portion of fluid in the liquid state be raised from a certain temperature to a higher temperature : let it be evaporated at the higher temperature : let the vapour then be allowed to expand, being maintained always at the temperature of saturation for its density, until it is restored to the original temperature, at which temperature let it be liquefied :—then *the excess of the heat absorbed by the fluid above the heat given out, will be equal to the expansive power generated.*

To represent those operations algebraically,—let the lower absolute temperature be τ_0 :—the volume of unity of weight of liquid at that temperature, v_0, and that of vapour at saturation, V_0 : let the pressure of that vapour be P_0 : the latent heat of evaporation of unity of weight, L_0 ; and let the corresponding quantities for the higher absolute temperature τ_1, be v_1, V_1, P_1, L_1. Let K_L represent the mean apparent specific heat of the substance in the liquid form between the temperatures τ_0 and τ_1. Then,—

First, Unity of weight of liquid being raised from the temperature τ_0 to the temperature τ_1, absorbs the heat,

$$K_L (\tau_1 - \tau_0)$$

and produces the expansive power,

$$\int_{v_0}^{v_1} dv \cdot P$$

Secondly, It is evaporated at the temperature τ_1, absorbing the heat

$$L_1$$

and producing the expansive power,

$$P_1 (V_1 - v_1)$$

Thirdly, The vapour expands, at saturation, until it is restored to the original temperature τ. In this process it absorbs the heat,

$$-\int_{\tau_0}^{\tau_1} d\tau \cdot K_s$$

and produces the expansive power,

$$\int_{V_1}^{V_0} dV \cdot P$$

Fourthly, It is liquefied at the original temperature, giving out the heat

$$L_0$$

and consuming the compressive power,

$$P_0 (V_0 - v_0).$$

The equation between the heat which has disappeared, and the expansive power which has been produced, is as follows:—

$$\left.\begin{array}{l} L_1 - L_0 + K_L (\tau_1 - \tau_0) - \int_{\tau_0}^{\tau_1} d\tau \cdot K_s \\[2mm] = P_1 (V_1 - v_1) - P_0 (V_0 - v_0) + \int_{v_0}^{v_1} dv \cdot P + \int_{V_1}^{V_0} dV \cdot P \end{array}\right\} \quad \ldots \quad (31.)$$

If the vapour be such that it can be regarded as a perfect gas without sensible error, the substitution of $k + P\dfrac{dV}{d\tau}$ for K_s, and of $\dfrac{\tau}{C\,n\,M} = k\,N\,\tau$ for $P\,V$, transforms the above to

$$\left.\begin{array}{l} L_1 - L_0 + \{K_L - k(1 + N)\}(\tau_1 - \tau_0) \\[2mm] = - P_1 v_1 + P_0 v_0 + \int_{v_0}^{v_1} dv \cdot P = - \int_{P_0}^{P_1} dP \cdot v \end{array}\right\} \quad \ldots \ldots \quad (32.)$$

In almost all cases which occur in practice, v is so small as compared with V, that $-\int dP \cdot v$ may be considered as sensibly $= 0$; and therefore (sensibly)

$$L_1 + K_L(\tau_1 - \tau_0) = L_0 + k(1 + N)(\tau_1 - \tau_0) \quad \ldots \quad (33.)$$

Now this quantity, which I shall denote by H, is the total heat required to raise unity of weight of liquid from τ_0 to τ_1 of absolute temperature, and to evaporate it at the latter temperature. Therefore *the total heat of evaporation, where the vapour may be treated as a perfect gas, increases sensibly at an uniform rate with the temperature of evaporation ; and the coefficient of its increase with temperature is equal to the apparent specific heat of the vapour at constant pressure*, k $(1 + N)$.

(20.) There have never been any experiments from which the apparent specific heat of steam under constant pressure can be deduced in the manner in which that of permanent gases has been ascertained.

The experiments of M. REGNAULT, however, prove that the total heat of evaporation of water increases uniformly with the temperature from 0° to 200° centigrade, and thus far fully confirm the results of this theory.

The coefficient of increase is equal to

$$K_w \times 0{\cdot}305$$

Its mechanical value is consequently

$$116{\cdot}4 \text{ metres} = 382 \text{ feet per centigrade degree, or}$$
$$212 \text{ feet per degree of Fahrenheit.}$$

$\left.\begin{array}{c} \\ \\ \\ \end{array}\right\} \quad \cdots \quad (34.)$

Although the principle of the conservation of *vis viva* has thus enabled us to ascertain the *law of increase* of the total heat of evaporation, it does not enable us to calculate *à priori* the constant L_0 of the formula, being the latent heat of evaporation at the fixed temperature from which the total heat is measured ; for the changes of molecular arrangement which constitute evaporation are unknown.

When the fixed temperature is that of melting ice, M. REGNAULT's experiments give 606·5 centigrade degrees, applied to liquid water as the value of this constant ; so that

$$H = K_w \,(606°{\cdot}5 + {\cdot}305 \; T^0)$$
For the centigrade scale,
$$H = K_w \,(1091°{\cdot}7 + {\cdot}305 \,(T^0 - 32°)\,)$$
For Fahrenheit's scale.

$\left.\begin{array}{c} \\ \\ \\ \end{array}\right\} \quad \cdots \quad (35.)$

is the complete expression for the heat required to raise unity of weight of water from the temperature of melting ice to T^0 above the ordinary zero, and to evaporate it at the latter temperature. This formula has been given by M. REGNAULT as merely empirical ; but we have seen that it closely represents the physical law, when quantities depending on the expansion of water are neglected.

It must be remarked, that the unit of heat in M. REGNAULT's tables is not precisely the specific heat of water at 0° centigrade, but its mean specific heat between the initial and final temperatures of the water in the calorimeter. The utmost error, however, which can arise from this circumstance, is less than $\frac{1}{1200}$ of the total heat of evaporation, so that it may safely be neglected.

The coefficient $\cdot305\ K_w = 382$ feet per centigrade degree is the apparent specific heat of steam at constant pressure; that is to say, for steam,—

$$\mathfrak{k} + \frac{1}{C\,n\,M} = 382 \text{ feet per centigrade degree,}$$

$$\text{but } \frac{1}{C\,n\,M} = 153 \text{ feet.}$$

Therefore the real specific heat of steam is

$$\mathfrak{k} = \frac{1}{C n M N} = 229 \text{ feet per centigrade degree,}$$

$$= 127\cdot4 \text{ feet per deg. of Fahrenheit,}$$

$$= K_w \times \cdot183$$

$$\text{and } N = \frac{153}{229} = \frac{2}{3}.$$

$$\quad\quad\quad\quad \cdot\ \cdot\ \cdot\ (36.)$$

The quantity $-\int_{P_0}^{P_1} d\,P\ .\ v$ has been neglected, as already explained, in these calculations, on account of its smallness. When $\tau_0 = C$, or the fixed point is $0°$ centigrade, this integral is nearly equal to

$$-v\,P_1 = -\frac{v}{V_1} \cdot \frac{\tau_1}{C\,n\,M} = -\mathfrak{k}\,N \cdot \frac{v}{V_1}\,\tau_1 \quad \cdot\ \cdot\ \cdot\ (37.)$$

which, for steam, is equal to

$$-K_w \times \cdot122 \frac{v}{V_1}\,\tau_1.$$

For a pressure of eight atmospheres,

$$\frac{v}{V_1} = \frac{1}{252} \text{ nearly, } \tau_1 = 445°\cdot5 \ (T = 170°\cdot9 \text{ cent.})$$

consequently, $\quad\quad -v\,P_1 = -K_w \times 0°\cdot22$ cent.

a quantity much less than the limit of errors of observation in experiments on latent heat.

This shews that in practice we are justified in overlooking the influence of the volume of the liquid water on the heat of evaporation.

SECTION IV.—OF THE MECHANICAL ACTION OF STEAM, TREATED AS A PERFECT GAS, AND THE POWER OF THE STEAM-ENGINE.

(21.) In the present limited state of our experimental knowledge of the density of steam at pressures differing much from that of the atmosphere, it is desirable to ascertain whether any material error is likely to arise from treating it as a perfect gas. For this purpose the ratio of the volume of steam at $100°$ centigrade, under the pressure of one atmosphere, to that of the water which produces it at $4°\cdot1$ centigrade, as calculated theoretically on the supposition of steam being a perfect gas, is to be compared with the actual ratio.

The weight of one volume of water at 4°·1 centigrade being taken as unity, that of half a volume of oxygen at 0° centigrade, under the pressure of one atmosphere, according to the experiments of M. REGNAULT, is   0·000714900

That of one volume of hydrogen, ...   0·000089578

The sum being   .   .   .   .   .   .   0·000804478

The reciprocal of this sum being multiplied by $\dfrac{374\cdot6}{274\cdot6} = 1\cdot364166$ the ratio of dilatation of a perfect gas from 0° to 100° centigrade) the result gives, for the volume of steam of saturation at 100° centigrade as compared with that of water at

4°·1   .   .   .   .   .   1695·72
And for its density,   .   .   0·00058972

The agreement of those results with the known volume and density of steam is sufficiently close to shew, that at pressures less than one atmosphere, it may be regarded as a gas sensibly perfect; from which it may be concluded, that in the absence of more precise data, the errors arising from treating it as a perfect gas at such higher pressures as occur in practice, will not be of much importance.

Representing, then, by v the volume of unity of weight of water at 4°·1 centigrade, that of unity of weight of steam at any pressure and temperature will be given by the formula

$$V = \frac{1696\, v\, \varpi}{(\tau)} \cdot \frac{\tau}{P} \quad . \quad . \quad . \quad (38.)$$

ϖ representing the number of units of weight per unit of area in the pressure of one atmosphere, and (τ) the absolute temperature at which the pressure of saturation is one atmosphere; being for the centigrade scale 374°·6, and for Fahrenheit's scale 674°·28.

The mechanical action of unity of weight of steam at the temperature τ and pressure P, during its entrance into a cylinder, before it is permitted to expand, is represented by the product of its pressure and volume, or by

$$PV = \frac{1696\, v\, \varpi}{(\tau)} \cdot \tau \quad . \quad . \quad . \quad (39.)$$

The coefficient $\dfrac{1696\, v\, \varpi}{(\tau)}$ represents a certain depth of fall per degree of absolute temperature, and is the same with the coefficient $\dfrac{1}{C\, n\, M}$ already referred to. By taking the following values of the factors :—

$v = 0·016$ cubic foot per pound avoirdupois,

$\varpi = 2117$ pounds avoirdupois per square foot,

we find this coefficient to be

153·35 feet = 46·74 mètres per centigrade degree, ⎱
85·19 feet per degree of Fahrenheit;   ⎰   .   .   (40.)

this determination may be considered correct to about $\frac{1}{1200}$ part. When French measures are used in the calculation, the following is the result :—

$$v = 1 \text{ cubic centimètre per gramme,}$$
$$\varpi = 1033\cdot3 \text{ grammes per square centimètre,}$$

$$\left.\begin{aligned} \frac{1}{C\,n\,M} &= 46\cdot78 \text{ mètres per centigrade degree,} \\ &= 153\cdot48 \text{ feet} \qquad \ldots \qquad \ldots \qquad \ldots \\ & \text{or } 85\cdot27 \text{ feet per degree of Fahrenheit.} \end{aligned}\right\} \quad \cdot \quad \cdot \quad \cdot \quad (41.)$$

The difference, which is of no practical importance in calculating the power of the steam-engine, arises in the estimation of the density of liquid water.

(22.) Unit of weight of steam at saturation, of the elasticity P_1 and volume V_1 corresponding to the absolute temperature τ_1, being cut off from external sources of heat, it is now to be investigated what amount of power it will produce in expanding to a lower pressure P_2 and temperature τ_2.

It has already been shewn, at the end of the second section, that if vapour at saturation is allowed to expand, it requires a supply of heat from without to maintain it at the temperature of saturation, otherwise a portion of it must be liquefied to supply the heat required to expand the rest. Hence, when unity of weight of steam at saturation, at the pressure P_1 and volume V_1, expands to a lower pressure P, being cut off from external sources of heat, it will not occupy the entire volume V corresponding to that pressure, according to Equation (38.), but a less volume

$$S = m\,V,$$

where m represents the weight of water remaining in the gaseous state, the portion $1 - m$ having been liquefied during the expansion of the remainder. The expansive action of the steam will therefore be represented by

$$\int_{V_1}^{S_2} d\,S\,.\,P \quad \cdot \quad \cdot \quad \cdot \quad (42.)$$

The law of variation of the fraction m flows from the following considerations :—

Let δm represent the indefinitely small variation of m corresponding to the indefinitely small change of temperature $\delta \tau$; L, the latent heat of evaporation of unity of weight; K_s, as in Equation (30.), the specific heat of vapour at saturation, which is a negative coefficient varying with the temperature; then we must have

$$-L\,\delta m = m\,K_s\,\delta\tau, \quad \text{or} \quad \frac{\delta m}{m} = -\frac{K_s}{L}\,\delta\tau.$$

in order that the heat produced by the liquefaction of δm may be equal to the heat required to expand m. Hence making, according to Equation (30.)—

$$K_s\,\delta\tau = k\left(\delta\tau + N\frac{\tau}{V}\,\delta V\right)$$

and
$$\delta\,\tau = -\,\frac{\tau}{V}\,\delta\,V\,\frac{1}{\dfrac{\beta'}{\tau}+\dfrac{2\gamma'}{\tau^{2}}-1}$$

we obtain

$$\frac{\delta\,m}{m}=-\,\frac{\kappa\,\tau}{L}\left(N-\frac{1}{\dfrac{\beta'}{\tau}+\dfrac{2\gamma'}{\tau^{2}}-1}\right)\frac{\delta\,V}{V}\quad\ldots\quad(43.)$$

and denoting the coefficient of $\dfrac{\delta\,V}{V}$ by $-\nu$,

$$\frac{d\log m}{d\log V}=-\nu\ ;\ \frac{d\log S}{d\log V}=1-\nu$$

and because
$$\frac{d\log V}{d\log P}=-1+\frac{1}{\dfrac{\beta'}{\tau}+\dfrac{2\gamma'}{\tau^{2}}}$$

$$\frac{d\log m}{d\log P}=+\nu\left(1-\frac{1}{\dfrac{\beta'}{\tau}+\dfrac{2\gamma'}{\tau^{2}}}\right)$$

$$\frac{d\log S}{d\log P}=-(1-\nu)\left(1-\frac{1}{\dfrac{\beta'}{\tau}+\dfrac{2\gamma'}{\tau^{2}}}\right)=-\sigma$$

$$\left.\vphantom{\begin{array}{c}1\\1\\1\\1\end{array}}\right\}\quad\ldots\quad(44.)$$

As the mean temperature of the liquid thus produced more or less exceeds that of the remaining vapour, a small fraction of it will be reconverted into vapour, if the expansion is carried on slowly enough; but its amount is so small, that to take it into account would needlessly complicate the calculation, without making it to any material extent more accurate.

(23.) The extreme complexity of the exponent σ, considered as a function of the pressure P, would render a general formula for the expansive action $\int P\,d\,S$ very cumbrous in its application. For practical purposes, it is sufficient to consider the exponent σ as constant during the expansion which takes place in any given engine, assigning it an average value suitable to the part of the scale of pressures in which the expansion takes place. For engines in which the steam is introduced at pressures not exceeding four atmospheres, I conceive that it will be sufficiently accurate to make

$$\sigma=\frac{6}{7};$$

while for engines in which the initial pressure lies between four and eight atmospheres, the suitable value is

$$\sigma=\frac{5}{6}.$$

The utmost error which can arise from using these exponents is about $\frac{1}{100}$ of the whole power of the engine, and that only in extreme cases.

Making, therefore,

$$P=P_{1}\left(\frac{S}{V_{1}}\right)^{-\frac{1}{\sigma}}$$

we obtain for the value of the expansive action of unity of weight of steam,

$$\int_{V_1}^{S_2} d\,S\,.\,P = P_1\,V_1\,\frac{\sigma}{1-\sigma}\left(1-\left(\frac{S_2}{V_1}\right)^{1-\frac{1}{\sigma}}\right) \left.\vphantom{\int}\right\}$$

$$= P_1\,V_1\,\frac{\sigma}{1-\sigma}\left(1-s^{1-\frac{1}{\sigma}}\right) \qquad \cdots \quad (45.)$$

s being used to denote $\frac{S_2}{V_1}$, or the ratio of the volumes occupied by steam at the end and at the beginning of the expansion respectively.

A table to facilitate the computation is given in the Appendix.

The gross mechanical action of unity of weight of steam on one side of the piston is found by adding to the above quantity the action of the steam before it begins to expand, or $P_1\,V_1$, and is therefore

$$P_1\,V_1\,\left(\frac{1}{1-\sigma}-\frac{\sigma}{1-\sigma}\,s^{1-\frac{1}{\sigma}}\right) \qquad \cdots \quad (46.)$$

The values of the coefficients and exponent being

	$\dfrac{1}{1-\sigma}$	$\dfrac{\sigma}{1-\sigma}$	$1-\dfrac{1}{\sigma}$
For initial pressures between			
1 and 4 atmospheres, ...	7	6	$-\dfrac{1}{6}$
4 and 8 atmospheres, ...	6	5	$-\dfrac{1}{5}$

(24.) The following deductions have to be made from the gross action, in order to obtain the action effective in overcoming resistance.

First, For loss of power owing to a portion of the steam being employed in filling steam-passages, and the space called the *clearance* of the cylinder at one end. Let the bulk of steam so employed be the fraction $c\,S_2$ of the space filled by steam at the end of the expansion; then the loss of power from this cause is

$$P_1\,c\,S_2 = c\,s\,P_1\,V_1.$$

Secondly, For the pressure on the opposite side of the piston, of the steam which escapes into the condenser, or into the atmosphere, as the case may be. Let P_3 be the pressure of this steam; the deduction to be made for its action is

$$P_3\,S_2\,(1-c) = P_3\,V_1\,(1-c)\,s.$$

These deductions having been made, there is obtained for the effect of unity of weight of water evaporated,

$$V_1\left\{P_1\left(\frac{1}{1-\sigma}-\frac{\sigma}{1-\sigma}\,s^{1-\frac{1}{\sigma}}-c\,s\right)-P_3\,(1-c)\,s\right\} \quad \cdots \quad (47.)$$

(25.) The effect of the engine in unity of time is found by multiplying the

above quantity by the number of units of weight of water evaporated in unity of time.

If this number be denoted by W,

$$W\,S_2\,(1-c) = W\,V_1\,(1-c)\,s = A\,u \quad . \quad . \quad . \quad (48.)$$

will represent the cubical space traversed by the piston in unity of time, A denoting the area of the piston, and u its mean velocity.

Now let the whole resistance to be overcome by the engine be reduced by the principles of statics to a certain equivalent pressure per unit of area of piston, and let this pressure be denoted by R. Then,

$$R\,A\,u = R\,W\,V_1\,(1-c)\,s \quad . \quad . \quad . \quad (49.)$$

expresses the effect of the engine in terms of the gross resistance.

We have now the means of calculating the circumstances attending the working of a steam-engine according to the principle of the conservation of *vis viva*, or, in other words, of the equality of power and effect, which regulates the action of all machines that move with an uniform or periodical velocity.

This principle was first applied to the steam-engine by the COUNT DE PAMBOUR; and accordingly, the formulæ which I am about to give only differ from those of his work in the expressions for the maximum pressure at a given temperature, and for the expansive action of the steam, which are results peculiar to the theory of this essay.

In the first place, the effect, as expressed in terms of the pressure, is to be equated to the effect as expressed in terms of the resistance, as follows:—

$$R\,A\,u = R\,W\,V_1(1-c)\,s = W\,V_1\left\{P_1\left(\frac{1}{1-\sigma} - \frac{\sigma}{1-\sigma}\,s^{1-\frac{1}{\sigma}} - c\,s\right) - P_3\,(1-c)\,s\right\} \quad . \quad . \quad (50.)$$

This is the fundamental equation of the action of the steam-engine, and corresponds with Equation A. of M. DE PAMBOUR's theory.

(26.) Dividing both sides of Equation (50.) by the space traversed by the piston in unity of time $W\,V_1\,(1-c)\,s$, and transferring the pressure of the waste steam, P_3, to the first side, we obtain this equation:—

$$R + P_3 = P_1\,\frac{\dfrac{1}{1-\sigma} - \dfrac{\sigma}{1-\sigma}\,s^{1-\frac{1}{\sigma}} - c\,s}{(1-c)\,s} \quad . \quad . \quad . \quad (51.)$$

which gives the means of determining the pressure P_1 at which the steam must enter the cylinder, in order to overcome a given resistance and counter-pressure with a given expansion; or supposing the expansion s to be variable at pleasure, and the initial pressure P_1 fixed, the equation gives the means of finding, by approximation, the expansion best adapted to overcome a given resistance and counter-pressure.

The next step is to determine, from Equations XV. of the Introduction and

(35.) of this section, the volume V_1 of unity of weight of steam corresponding to the maximum pressure P_1. Then Equation (48.) gives the space traversed by the piston in unity of time, which, being multiplied by the resistance R per unit of area of piston, gives the gross effect of the engine.

(27.) If, on the other hand, the space traversed by the piston in unity of time is fixed, Equation (48.) gives the means of determining, from the evaporating power of the boiler W, either the volume V_1 of unity of weight of steam required to work the engine at the given velocity with a given expansion, or the expansion *s* proper to enable steam of a given initial density to work the engine at the given velocity. The initial pressure P_1 being then determined from the volume V_1, the resistance which the engine is capable of overcoming with the given velocity is to be calculated by means of Equation (51.)

(28.) This calculation involves the determination of the pressure P_1 from the volume V_1 of unity of weight of steam at saturation, which can only be done by approximation. The following formula will be found useful for this purpose :—

$$P_1 = \varpi \left(\frac{V_0}{V_1}\right)^{\frac{12}{11}} \quad . \quad . \quad . \quad (52.)$$

where ϖ represents the pressure of one atmosphere, V_0 the volume of steam of saturation at that pressure (being 1696 times the volume of water at $4°·1$ cent., or $27·136$ cubic feet per pound avoirdupois), and V_1 the volume of steam of saturation at the pressure P_1. This formula is only applicable between the pressures of one and eight atmospheres: that is to say, when the volume of steam is not greater than 27 cubic feet per pound, nor less than 4, and the temperature not lower than $100°$ centigrade, nor higher than $171°$ centigrade (which correspond to $212°$ and $340°$ Fahrenheit).

The greatest error in computing the pressure by means of this formula is about $\frac{1}{50}$ of an atmosphere, and occurs at the pressure of four atmospheres, so that it is $\frac{1}{200}$ of the whole pressure. This is sufficiently accurate for practice, in calculating the power of steam-engines; but should a more accurate result be required, the approximate value of the pressure may be used to calculate the temperature by means of Equation XV.; and the temperature thus determined (which will be correct to $\frac{1}{5}$ of a centigrade degree) may then be used in conjunction with the volume to compute a corrected value of the pressure, according to Equation (38.) The pressure, as thus ascertained, will be correct to $\frac{1}{2000}$ of its amount, which may be considered the greatest degree of accuracy attainable.

The most convenient and expeditious mode, however, of computing the pressure from the volume, or *vice versâ*, is by interpolation from the table given in the Appendix to this paper.

(29.) The resistance denoted by R may be divided into two parts; that which arises from the *useful work performed*, and that which is independent of it, being,

in fact, the resistance of the engine when unloaded. Now it is evident, that the maximum *useful* effect of the steam has been attained, as soon as it has expanded to a pressure which is in equilibrio with the pressure of the waste steam added to the resistance of the engine when unloaded; for any further expansion, though increasing the total effect, diminishes the useful effect. Therefore if we make

$$R = R' + f,$$

R' being the resistance arising from the useful work, and f the resistance of the engine when unloaded, both expressed in the form of pressure on the piston, the expansion corresponding to the maximum of useful effect will take place when

$$P_2 = P_3 + f \quad . \quad . \quad . \quad . \quad \Big\}$$

the corresponding ratio of expansion being $\qquad\qquad\Big\} \quad . \quad . \quad (53.)$

$$s = \left(\frac{P_1}{P_3 + f}\right)^\sigma \quad . \quad . \quad . \quad . \quad \Big\}$$

The maximum useful effect with a given pressure on the safety-valve has been so fully discussed by M. DE PAMBOUR, that it is unnecessary to do more than to state that it takes place when the initial pressure in the cylinder is equal to that at the safety-valve: that is to say, when it and the useful resistance are the greatest that the safety-valve will permit.

(30.) Annexed is a table of the values of some of the quantities which enter into the preceding equations in the notation of the COUNT DE PAMBOUR's works.

Expression in the Notation of this paper.	Equivalent Expression in M. DE PAMBOUR's Notation.
$R = R' + f$	$(1 + \delta)\, r + f$
$A u$	$a v$
W	$S \times$ weight of one cubic foot of water.
P_3	p
s	$\dfrac{l + c}{l' + c}$
c	$\dfrac{c}{l' + c}$

(31.) As an illustration, I shall calculate the maximum useful effect of one pound, and of one cubic foot of water, in a Cornish double-acting engine, in the circumstances taken by M. DE PAMBOUR as an example for that kind of engine: that is to say,—

Clearance one-twentieth of the stroke, or $c = \dfrac{1}{21}$

Resistance not depending on the useful load, $f = $ 72 lb. per square foot.

Pressure of condensation, . . . $P_3 = $ 576 lb.   ...   ...

Consequently to give the maximum useful effect,

$$P_2 = P_3 + f \qquad = 648 \text{ lb. per square foot.}$$

Total pressure of the steam when first admitted, $P_1 = 7200$ lb. $\quad \cdots \qquad \cdots$

Volume of 1 lb. of steam $V_1 = 8{\cdot}7825$ cubic feet.

Therefore $P_1 V_1 = 63234$ lbs. raised one foot.

$$\frac{P_1}{P_2} = \frac{7200}{648} \text{ and consequently,}$$

Expansion to produce the maximum useful effect $s = \left(\frac{P_1}{P_2}\right)^{\frac{6}{7}} = 7{\cdot}877$

Space traversed by the piston during the action of one pound of steam,

$$= V_1 (1-c) \, s = 65{\cdot}886 \text{ cubic feet.}$$

Gross effect of one pound of steam, in pounds raised one foot high,

$$= P_1 V_1 \left(7 - 6s^{-\frac{1}{6}} - \frac{s}{21}\right) - P_3 V_1 (1-c) s \qquad . \qquad . \qquad = 112004$$

Deduct for resistance of engine when unloaded $f V_1 (1-c) s \qquad . \qquad = \quad 4744$

Effect of one pound of steam in overcoming resistance depending $\Big\}$ on useful load, $\quad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad \Big\} \quad 107260$

This being multiplied by $62\frac{1}{2}$, gives for the effect of one cubic foot of water evaporated, in pounds raised one foot, $\quad . \qquad . \qquad . \qquad . \qquad 6{,}703{,}750$

It is here necessary to observe, that M. DE PAMBOUR distinguishes the useful resistance into two parts, the resistance of the useful load independently of the engine, and the increase in the resistance of the engine, arising from the former resistance, and found by multiplying it by a constant fraction which he calls δ. In calculating the net useful effect, he takes into account the former portion of the resistance only; consequently,

Net useful effect as defined by M. DE PAMBOUR $= \dfrac{\text{Gross effect} - f V_1 (1-c) s}{1 + \delta} \quad . \quad$ (54.)

The value of δ, for double acting steam-engines generally, is considered by M. DE PAMBOUR to be $\frac{1}{7}$; consequently, to reduce the effect of one cubic foot of water as calculated above to that which corresponds with his definition, we must deduct $\frac{1}{8}$, which leaves,

$$5{,}865{,}781 \text{ lb. raised one foot.}$$

M. DE PAMBOUR's own calculation gives,

$$6{,}277{,}560$$

being too large by about one-fifteenth.

(32.) In order to shew the limit of the effect which may be expected from the expenditure of a given quantity of heat in evaporating water, and also to verify the approximate method employed in calculating the expansive action of the steam, I shall now investigate the *maximum gross effect*, including resistance of all kinds, producible by evaporating unity of weight of water at a higher temperature and liquefying it at a lower, and compare, in two examples, the power produced, with the heat which disappears during the action of the steam, as calculated directly.

To obtain the maximum gross effect, the steam must continue to act expansively until it reaches the pressure of condensation, so that $P_2 = P_3$. The clearance must also be null, or $c = 0$. Making those substitutions in the formula (47.), we find, for the maximum gross effect of unity of weight of water, evaporated under the pressure P_1 and liquefied under the pressure P_2,

$$P_1 V_1 \frac{1}{1-\sigma} \left(1 - s^{1-\frac{1}{\sigma}} \right) = P_1 V_1 \frac{1 - \left(\frac{P_2}{P_1}\right)^{1-\sigma}}{1-\sigma} \quad \cdots \quad (55.)$$

In order to calculate directly the heat which is converted into power in this operation, let τ_1, τ_2, respectively represent the absolute temperatures of evaporation and liquefaction, and L_2 the latent heat of evaporation at the lower temperature τ_2; then the total heat of evaporation at τ_1, starting from τ_2 as the fixed point, by Equation (33.), is

$$H_{2, 1} = L_2 + \cdot 305 \, K_w \, (\tau_1 - \tau_2).$$

This is the heat communicated to the water in raising it from τ_2 to τ_1 and evaporating it. Now a weight $1 - m$ of the steam is liquefied during the expansion at temperatures varying from τ_1 to τ_2, so that it may be looked upon as forming a mass of liquid water approximately at the mean temperature $\frac{\tau_1 + \tau_2}{2}$, and from which a quantity of heat, approximately represented by

$$K_w \, (1 - m) \, \frac{\tau_1 - \tau_2}{2}$$

must be abstracted, to reduce it to the primitive temperature τ_2.

Finally, the weight of steam remaining, m, has to be liquefied at the temperature τ_2, by the abstraction of the heat

$$m \, L_2.$$

The difference between the heat given to the water, and the heat abstracted from it, or

$$\left. \begin{array}{l} H_{2, 1} - K_w \, (1 - m) \, \frac{\tau_1 - \tau_2}{2} - m \, L_2 \\[2mm] = (1 - m) \, L_2 + K_w \left(\cdot 305 - \frac{1-m}{2} \right) (\tau_1 - \tau_2) \end{array} \right\} \quad \cdots \quad (56.)$$

is the heat which has disappeared, and ought to agree with the expression (55.) for the power produced, if the calculation has been conducted correctly.

As a first example, I shall suppose unity of weight of water to be evaporated under the pressure of four atmospheres, and liquefied under that of half an atmosphere; so that the proper values of the coefficients and exponent are

$$\frac{1}{1-\sigma} = 7 \qquad 1 - \sigma = \frac{1}{7}$$

The data in this case for calculating the power, are,

$$P_1 = 8468 \text{ lb. per square foot.}$$
$$V_1 = 7\text{·}584 \text{ cubic feet for one lb. of steam.}$$
$$P_1 V_1 = 64221 \text{ lb. raised one foot.}$$
$$\frac{P_2}{P_1} = \frac{1}{8}, \text{ whence } s = 8^{\frac{6}{7}} = 5\text{·}944.$$

Maximum possible effect of one pound of water,

$$= P_1 V_1 \times 7 \left(1 - \left(\frac{1}{8}\right)^{\frac{1}{7}}\right) = 115600 \text{ lb. raised one foot.}$$

Being the mechanical equivalent of 92°·3 centigrade degrees applied to one pound of liquid water at 0° C. ; or,

$$92°\text{·}3 \text{ K}_w$$

Maximum possible effect of one cubic foot of water, 7,225,000 lb. raised one foot.

In order to calculate directly the heat converted into power, we have,

$$\tau_1 = C + 144°\text{·}1 \text{ cent. } \tau_2 = C + 81°\text{·}7$$
$$L_2 = 549°\text{·}7 \text{ K}_w$$
$$H_{2, 1} = 568°\text{·}7 \text{ K}_w = \text{ heat expended in the boiler.}$$
$$1 - m = \text{·}14 \text{ nearly} = \text{ proportion of steam liquefied during the expansion.}$$

The heat converted into mechanical power, as calculated from these data, is found to be,

$$91°\text{·}6 \text{ K}_w$$

differing by only 0°·7 from the amount as calculated from the power produced.

The direct method, however, is much less precise than the other, and is to be regarded as only a verification of the general principle of calculation.

The heat rendered effective, in the above example, is $\frac{92\text{·}3}{568\text{·}7}$, or less than *one-sixth* of that expended in the boiler.

As a second example, I shall suppose the steam to be produced at a pressure of eight atmospheres, and to expand to that of one atmosphere. In this case,

$$P_1 = 16936 \text{ lbs. per square foot.}$$
$$V_1 = 4\text{·}03 \text{ cubic feet per lb. of steam.}$$
$$P_1 V_1 = 68252 \text{ lbs. raised one foot.}$$
$$\frac{P_2}{P_1} = \frac{1}{8} \quad \therefore \quad s = 5\text{·}657 = 8^{\frac{5}{6}}$$

Maximum possible effect of one pound of water,

$$= P_1 V_1 \times 6 \left(1 - \left(\frac{1}{8}\right)^{\frac{1}{6}}\right) = 119{,}942 \text{ lb. raised one foot.}$$

Being the equivalent of 95°·8 K$_w$ (Centigrade).

Maximum possible effect of one cubic foot of water = 7,496,375 lb. raised one foot.

The data for calculating directly the heat rendered effective are,

$$\tau_1 = C + 170°\text{·}9 \text{ cent. } \tau_2 = C + 100°$$
$$L_2 = 537° \text{ K}_w$$
$$H_{2, 1} = 558°\text{·}6 \text{ K}_w = \text{ heat expended in the boiler.}$$
$$1 - m = \text{·}148 \text{ nearly} = \text{ steam liquefied during the expansion.}$$

Whence, the heat converted in power, as calculated directly, is,

$$95°\cdot8\,K_w$$

agreeing with the calculation from the power produced.

In this example, the heat rendered effective is $\frac{95\cdot8}{558\cdot6}$, or somewhat more than one-sixth of that expended in the boiler.

(33.) The results of the calculations of maximum possible effect, of which examples have just been given, are *limits* which may be approached in practice by Cornish and similar engines, but which cannot be fully realised; and yet it has been shewn, that in those theoretical cases only about *one-sixth* of the heat expended in the boiler is rendered effective. In practice, of course, the proportion of heat rendered effective must be still smaller; and, in fact, in some unexpansive engines, it amounts to only one-twenty-fourth, or even less.

Dr Lyon Playfair, in a memoir on the Evaporating Power of Fuel, has taken notice of the great disproportion between the heat expended in the steam-engine and the work performed. It has now been shewn that this waste of heat is, to a great extent, a necessary consequence of the nature of the machine. It can only be reduced by increasing the initial pressure of the steam, and the extent of the expansive action; and to both of those resources there are practical limits, which have already in some instances been nearly attained.

APPENDIX TO THE FOURTH SECTION,

CONTAINING TABLES TO BE USED IN CALCULATING THE PRESSURE, VOLUME, AND MECHANICAL ACTION OF STEAM, TREATED AS A PERFECT GAS.

The object of the first of the annexed tables is to facilitate the calculation of the volume of steam of saturation at a given pressure, of the pressure of steam of saturation at a given volume, and of its mechanical action at full pressure.

The pressures are expressed in pounds avoirdupois per square foot, and the volumes by the number of cubic feet occupied by one pound avoirdupois of steam, when considered as a perfect gas; those denominations being the most convenient for mechanical calculations in this country.

The columns to be used in determining the pressure from the volume, and *rice versâ*, are the third, fourth, sixth, and seventh.

The third column contains the common logarithms of the pressures of steam of saturation for every fifth degree of the centigrade thermometer from $-30°$ to $+260°$: that is to say, for every ninth degree of Fahrenheit's thermometer from $-22°$ to $+500°$.

The fourth column gives the differences of the successive terms of the third column.

The sixth column contains the common logarithms of the volume of one pound of steam of saturation corresponding to the same temperatures.

The seventh column contains the differences of the successive terms of the sixth column, which are negative; for the volumes diminish as the pressures increase.

By the ordinary method of taking proportional parts of the differences, the logarithms of the volumes corresponding to intermediate pressures, or the logarithms of the pressures corresponding to intermediate volumes, can be calculated with great precision. Thus, let $X + h$ be the logarithm of a pressure not found in the table, X being the next less logarithm which is found in the table; let Y be the logarithm of the volume corresponding to X, and $Y - k$ the logarithm of the volume corresponding to $X + h$; let H be the difference between X and the next greater logarithm in the table, as given in the fourth column, and K the corresponding difference in the seventh column; then by the proportion

$$H : K :: h : k$$

either $Y - k$ may be found from $X + h$, or $X + h$ from $Y - k$.

In the fifth and eighth columns respectively, are given the actual pressures and volumes corresponding to the logarithms in the third and sixth columns, to five places of figures.

In the ninth column are given the values of the quantity denoted by $P_1 V_1$ in the formulæ, which represents the mechanical action of unity of weight of steam at full pressure, or before it has begun to expand, in raising an equal weight. Those values are expressed in feet, being the products of the pressures in the fifth column by the volumes in the eighth, and have been found by multiplying the absolute temperature in centigrade degrees by 153·48 feet. Intermediate terms in this column, for a given pressure or a given volume, may be approximated to by the method of differences, the constant difference for 5° centigrade being 767·4 feet; but it is more accurate to calculate them by taking the product of the pressure and volume.

When the pressure is given in other denominations, the following logarithms are to be added to its logarithm, in order to reduce it to pounds avoirdupois per square foot:—

For Millimètres of mercury, ... 0·44477
    Inches of mercury, ... 1·84960
    Atmospheres of 760 millimètres, ... 3·32559
    Atmospheres of 30 inches, ... 3·32672
    Kilogrammes on the square centimètre, . . . 3·31136
    Kilogrammes on the circular centimètre, . . . 3·41627
    Kilogrammes on the square mètre, ... $\overline{1}$·31136
    Pounds avoirdupois on the square inch, . . . 2·15836
    Pounds avoirdupois on the circular inch, . . . 2·26327

To reduce the logarithm of the number of cubic mètres occupied by one kilogramme to that of the number of cubic feet occupied by one pound avoirdupois, add 1·20463.

The logarithms are given to five places of decimals only, as a greater degree of precision is not attainable in calculations of this kind.

The second table is for the purpose of calculating the mechanical action of steam in expansive engines.

The first column contains values of the fraction of the entire capacity of the cylinder which is filled with steam before the expansion commences (being the quantity $\frac{1}{s}$ of the formulæ), for every hundredth part, from 1·00, or the whole cylinder, down to 0·10, or one-tenth.

If l be the entire length of stroke, l' the portion performed at full pressure, and c the fraction of the entire capacity of the cylinder allowed for clearance, then

$$\frac{l'}{l} = \frac{\frac{1}{s} - c}{1 - c}, \quad \text{and} \quad \frac{1}{s} = (1 - c)\frac{l'}{l} + c.$$

The *entire capacity of the cylinder* is to be understood to include clearance at one end only.

The second column gives the reciprocals of the quantities in the first, or the values of the ratio of expansion s.

The third and fourth columns, headed Z, give the values of the quantity $\frac{1}{1-\sigma} - \frac{\sigma}{1-\sigma} s^{1-\frac{1}{\sigma}}$ of Article 23, which represents the ratio of the entire gross action of the steam to its action at full pressure, without allowing for clearance. The third column is to be used for initial pressures of from one to four atmospheres; and the fourth for initial pressures of from four to eight atmospheres.

The deduction to be made from the quantity Z for clearance is $c\,s$, or the product of the fraction of the cylinder allowed for clearance by the ratio of expansion. Hence, to calculate from the tables the net mechanical action of unity of weight of steam, allowing for the counter-pressure of the waste steam P_3, as well as for clearance, we have the formula

$$P_1 V_1 (Z - c\,s) - P_3 V_1 (1 - c)\,s$$

being equivalent to the formula (47.) of this paper.

TABLE I.—*Pressure and Volume of Steam, and its Action at Full Pressure.*

(1.) Temperature Fahrenheit.	(2.) Temperature Centigrade.	(3.) Logarithm of pressure in lbs. per square foot.	(4.) Differences.	(5.) Pressure in lbs. per square foot.	(6.) Logarithm of volume of one lb. of Steam in cubic feet.	(7.) Differences.	(8.) Volume of one lb. of Steam in cubic feet.	(9.) Action of a given weight of Steam in raising an equal weight in feet, at full pressure $= P_1 V_1$
− 22°	− 30°	$\bar{1}$·99278	0·20563	0·9835	4·58173	0·19684	38171	37541
− 13	− 25	0·19841	0·19602	1·5791	4·38489	0·18741	24260	38309
− 4	− 20	0·39443	0·18710	2·4799	4·19748	0·17865	15757	39076
+ 5	− 15	0·58153	0·17864	3·8153	4·01883	0·17036	10443	39843
14	− 10	0·76017	0·17085	5·7567	3·84847	0·16272	7054·6	40611
23	− 5	0·93102	0·16348	8·5314	3·68575	0·15550	4850·1	41378
32	0	1·09450	0·15661	12·431	3·53025	0·14877	3390·4	42146
41	+ 5	1·25111	0·15012	17·828	3·38148	0·14242	2407·0	42913
50	10	1·40123	0·14404	25·190	3·23906	0·13648	1734·0	43680
59	15	1·54527	0·13836	35·097	3·10258	0·13093	1266·4	44448
68	20	1·68363	0·13284	48·265	2·97165	0·12553	936·81	45215
77	25	1·81647	0·12780	65·535	2·84612	0·12061	701·65	45983
86	30	1·94427	0·12297	87·957	2·72551	0·11590	531·51	46750
95	35	2·06724	0·11842	116·75	2·60961	0·11146	407·01	47517
104	40	2·18566	0·11410	153·34	2·49815	0·10725	314·88	48285
113	45	2·29976	0·11002	199·42	2·39090	0·10328	245·98	49052
122	50	2·40978	0·10614	256·91	2·28762	0·09950	193·92	49820
131	55	2·51592	0·10247	328·04	2·18812	0·09593	154·21	50587
140	60	2·61839	0·09897	415·33	2·09219	0·09253	123·65	51354
149	65	2·71736	0·09566	521·63	1·99966	0·08931	99·922	52122
158	70	2·81302	0·09250	650·16	1·91035	0·08625	81·349	52889
167	75	2·90552	0·08953	804·49	1·82410	0·08336	66·696	53657
176	80	2·99505	0·08658	988·67	1·74074	0·08050	55·048	54424
185	85	3·08163	0·08388	1206·8	1·66024	0·07788	45·734	55191
194	90	3·16551	0·08129	1463·9	1·58236	0·07538	38·226	55959
203	95	3·24680	0·07879	1765·2	1·50698	0·07295	32·135	56726
212	100	3·32559	0·07640	2116·4	1·43403	0·07064	27·166	57494
221	105	3·40199	0·07415	2523·4	1·36339	0·06847	23·088	58261
230	110	3·47614	0·07196	2993·2	1·29492	0·06635	19·721	59028
239	115	3·54810	0·06988	3532·6	1·22857	0·06434	16·927	59796
248	120	3·61798	0·06788	4149·3	1·16423	0·06241	14·596	60563
257	125	3·68586	0·06597	4851·3	1·10182	0·06057	12·642	61331
266	130	3·75183	0·06414	5647·2	1·04125	0·05881	10·996	62098
275	135	3·81597	0·06238	6545·9	0·98244	0·05711	9·6037	62865
284	140	3·87835	0·06069	7557·0	0·92533	0·05548	8·4204	63633
293	145	3·93904	0·05907	8690·4	0·86985	0·05393	7·4105	64400
302	150	3·99811	0·05751	9956·6	0·81592	0·05242	6·5452	65168
311	155	4·05562	0·05601	11366	0·76350	0·05099	5·8010	65935
320	160	4·11163	0·05456	12931	0·71251	0·04959	5·1583	66702
329	165	4·16619	0·05319	14662	0·66292	0·04828	4·6017	67470
338	170	4·21938	0·05184	16572	0·61464	0·04698	4·1176	68237
347	175	4·27122	0·05056	18673	0·56766	0·04576	3·6954	69005
356	180	4·32178	0·04932	20979	0·52190	0·04457	3·3258	69772
365	185	4·37110	0·04812	23502	0·47733	0·04342	3·0014	70539
374	190	4·41922	0·04696	26256	0·43391	0·04231	2·7159	71307
383	195	4·46618	0·04586	29254	0·39160	0·04126	2·4638	72074
392	200	4·51204	0·04478	32512	0·35034	0·04023	2·2405	72842
401	205	4·55682	0·04375	36043	0·31011	0·03924	2·0423	73609
410	210	4·60057	0·04274	39863	0·27087	0·03829	1·8663	74376
419	215	4·64331	0·04176	43986	0·23258	0·03734	1·7084	75144
428	220	4·68507	0·04085	48425	0·19524	0·03649	1·5676	75911
437	225	4·72592	0·03994	53201	0·15875	0·03561	1·4413	76679
446	230	4·76586	0·03906	58326	0·12314	0·03478	1·3278	77446
455	235	4·80492	0·03819	63815	0·08836	0·03395	1·2256	78213
464	240	4·84311	0·03740	69680	0·05441	0·03320	1·1335	78981
473	245	4·88051	0·03660	75947	0·02121	0·03244	1·0501	79748
482	250	4·91711	0·03582	82625	$\bar{1}$·98877	0·03170	0·97447	80516
491	255	4·95293	0·03507	89728	$\bar{1}$·95707	0·03099	0·90588	81283
500	260	4·98800		97275	$\bar{1}$·92608		0·84349	82050

TABLE II.—*Expansive Action of Steam.*

(1.) Fraction of Cylinder filled with Steam at full pressure $= \frac{1}{s}$	(2.) Ratio of Expansion $= s.$	(3.) Coefficient of gross action $= Z.$ Initial Pressure one to four Atmospheres.	(4.) Initial Pressure four to eight Atmospheres.	(1.) Fraction of Cylinder filled with Steam at full pressure $= \frac{1}{s}$	(2.) Ratio of Expansion $= s.$	(3.) Coefficient of gross action $= Z.$ Initial Pressure one to four Atmospheres.	(4.) Initial Pressure four to eight Atmospheres.
1·00	1·000	1·000	1·000	·54	1·852	1·586	1·580
·99	1·010	1·010	1·010	·53	1·887	1·602	1·596
·98	1·020	1·020	1·020	·52	1·923	1·620	1·613
·97	1·031	1·030	1·030	·51	1·961	1·637	1·630
·96	1·042	1·041	1·041	·50	2·000	1·655	1·647
·95	1·053	1·051	1·051	·49	2·041	1·673	1·665
·94	1·064	1·062	1·062	·48	2·083	1·691	1·683
·93	1·075	1·072	1·072	·47	2·128	1·709	1·701
·92	1·087	1·083	1·083	·46	2·174	1·728	1·719
·91	1·099	1·094	1·093	·45	2·222	1·748	1·738
·90	1·111	1·104	1·104	·44	2·273	1·767	1·757
·89	1·124	1·115	1·115	·43	2·326	1·787	1·777
·88	1·136	1·126	1·126	·42	2·381	1·808	1·796
·87	1·149	1·138	1·137	·41	2·439	1·829	1·817
·86	1·163	1·149	1·149	·40	2·500	1·850	1·837
·85	1·176	1·160	1·160	·39	2·564	1·871	1·858
·84	1·190	1·172	1·171	·38	2·632	1·894	1·880
·83	1·205	1·183	1·183	·37	2·703	1·916	1·902
·82	1·220	1·195	1·195	·36	2·778	1·939	1·924
·81	1·235·	1·207	1·206 ·	·35	2·857	1·963	1·947
·80	1·250	1·219	1·218	·34 ·	2·941	1·987	1·970
·79	1·266	1·231	1·230	·33	3·030	2·012	1·994
·78	1·282	1·243	1·242	·32	3·125	2·038	2·019
·77	1·299	1·256	1·255	·31	3·225	2·064	2·044
·76	1·316	1·268	1·267	·30	3·333	2·091	2·070
·75	1·333	1·281	1·280	·29	3·448	2·119	2·097
·74	1·351	1·294	1·292	·28	3·571	2·147	2·124
·73	1·370	1·307	1·305	·27	3·704	2·176	2·152
·72	1·389	1·320	1·318	·26	3·846	2·207	2·181
·71	1·408	1·333	1·331	·25	4·000	2·238	2·211
·70	1·429	1·346	1·344	·24	4·167	2·270	2·242
·69	1·449	1·360	1·358	·23	4·348	2·304	2·273
·68	1·471	1·374	1·371	·22	4·545	2·338	2·306
·67	1·493	1·387	1·385	·21	4·762	2·374	2·341
·66	1·515	1·401	1·399	·20	5·000	2·412	2·376
·65	1·538	1·416	1·413	·19	5·263	2·451	2·413
·64	1·533	1·430	1·427	·18	5·556	2·492	2·452
·63	1·587	1·445	1·441	·17	5·882	2·534	2·492
·62	1·613	1·459	1·456	·16	6·250	2·579	2·434
·61	1·640	1·474	1·471	·15	6·667	2·626	2·579
·60	1·667	1·490	1·486	·14	7·143	2·676	2·626
·59	1·695	1·505	1·501	·13	7·692	2·730	2·675
·58	1·724	1·521	1·516	·12	8·333	2·786	2·728
·57	1·754	1·537	1·532	·11	9·091	2·847	2·784
·56	1·786	1·553	1·547 ،	·10	10·000	2·912	2·845
·55	1·818	1·569	1·563				