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The Hon. Lord MURRAY in the Chair.

The following Communications were read :—

1. Abstract of a Paper on the Hypothesis of Molecular Vortices, and its Application to the Mechanical Theory of Heat. By William John Macquorn Rankine, Civil Engineer, F.R.S.E., F.R.S.S.A., &c.

The object of this paper is to shew how the laws of the phenomena of Elasticity and Expansion, as connected with heat, may be reduced to mechanical principles by means of an hypothesis called that of Molecular Vortices.

The author ascribes the first distinct statement of an hypothesis of this kind to Sir Humphrey Davy, and refers to Mr Joule as having supported it; but he states that its consequences, to the best of his knowledge, have not hitherto been developed by means of the principles of Analytical Mechanics.

The author has endeavoured to do this, so far as the present state of experimental knowledge enables him, introducing such modifications into the hypothesis as are necessary in order to connect it with the undulatory theory of radiation. His researches were commenced in 1842, but were laid aside for nearly seven years from the want of experimental data, which, however, have at length been to a great extent supplied, so far as gaseous bodies are concerned, by the ex-

periments of M. Regnault. The author has thus been enabled to resume his investigations, and has obtained formulæ, agreeing with experiment, and applicable to practice, for the expansion and elasticity of gases,—the elasticity of vapours in contact with their liquids,—the specific heat of gases,—the heat produced by their compression,—the latent and total heat of evaporation,—the expansive action of vapours,—the power of the steam-engine,—and the mechanical value of heat in general.

One of the most useful in practice of those formulæ,—that for calculating the elasticity of steam and other vapours in contact with their liquids,—was published separately in the *Edinburgh New Philosophical Journal* for July 1849, with tables and a diagram, shewing its agreement with experiment, but without any account of the reasoning from which it is deduced.

The theory of radiant heat, like that of light, having been reduced to a branch of mechanics by means of the hypothesis of undulations, it is the object of the hypothesis of Molecular Vortices to reduce the theory of stationary heat also to a branch of mechanics, and thus to make a further step towards the fulfilment of the wish of Newton,—“*UTINAM CÆTERA NATURÆ PHÆNOMENA EX PRINCIPIIS MECHANICIS DERIVARE LICERET.*”

The hypothesis of molecular vortices is defined to be that which assumes, *that each atom of matter consists of a nucleus or central point, enveloped by an elastic atmosphere, which is retained in its position by attractive forces, and that the elasticity due to heat arises from the centrifugal force of those atmospheres, revolving or oscillating about their nuclei or central points.* According to this hypothesis, *quantity of heat is the vis viva of the molecular revolutions or oscillations.*

The author, for the present, leaves indeterminate the following questions, as he has not as yet found it necessary to make any definite supposition respecting them.

First, Whether the elastic molecular atmospheres are continuous, or consist of discrete particles? This includes the question, Whether expansive elasticity is wholly the result of the mutual repulsions of particles, or is, to a certain extent, a primary quality of matter?

Secondly, Whether, at the centre of each atom, there is a real *nucleus* or extremely small central body, or a mere *centre* of condensation and force?

Thirdly, What are the figures of the orbits described by the particles of the atomic atmospheres in their revolutions or oscillations?

The author introduces into the hypothesis of molecular vortices a supposition peculiar to his own researches, for the purpose of connecting it with the undulatory hypothesis as to radiation. It is this : *That the vibration which, according to the undulatory hypothesis, constitutes radiant light and heat, is a motion of the atomic nuclei or centres, and is propagated by means of their mutual attractions and repulsions.* The absorption of light and of radiant heat, according to this supposition, is the transference of motion from the nuclei or centres to their atmospheres, and the emission of light and radiant heat, the transference of motion from the atmospheres to the nuclei or centres. The author enumerates several advantages which he conceives that this hypothesis possesses over the common supposition of a luminiferous ether pervading the spaces between ponderable particles.

The present paper refers solely to the condition of bodies in the state of gas or vapour. It is divided into two parts, the first of which treats of the Statical Relations of Heat and Elasticity, or their relations when both are invariable; and the second, of their Dynamical Relations, which take place when gaseous bodies expand or contract, and involve the principles of the mutual conversion of heat and expansive power, and those of the latent heat of expansion and evaporation.

The first section of the first part explains the general principles of the hypothesis, of which a summary has just been given.

The second section contains the mathematical investigation of the general equation between the heat and the elasticity of a gas. The total elasticity is divided into two parts, — the *superficial atomic elasticity*, being the elasticity of the atomic atmospheres at the bounding surfaces of the atoms, which is always expansive, and a function of density and heat, and an elasticity arising from the mutual forces exerted by separate atoms, which may be expansive or contractive, and in the perfectly fluid state is a function of density only.

The more substances are rarefied, that is to say, the more the forces which interfere with the operation of the elasticity of the atomic atmospheres are weakened, the more nearly do they approach to a condition called that of perfect gas, in which the total elasticity

at a given temperature, is simply proportional to the density. This is therefore assumed to be the law of the elasticity of the atomic atmosphere of any given substance; so that the superficial atomic elasticity is held to be proportional to the density of the atomic atmosphere, at its bounding surface.

It is shewn, that although the form of such bounding surfaces in a perfect fluid is a rhombic dodecahedron, it may be treated without sensible error, in calculation, as if it were spherical, and the atmosphere of each atom may be conceived to be composed of concentric spherical layers, the density being uniform for each layer, but varying for different layers.

An oscillatory movement is supposed to be propagated from the nucleus or atomic centre in an inappreciably short time, to every part of the atmosphere, so that the mean velocity of movement is uniform throughout. The quantity of heat in one atom, or any other mass of matter, is expressed in terms of the force of gravity, by the weight of that mass, multiplied by the height through which it must fall at the earth's surface, in order to acquire that velocity. This oscillatory movement is conceived to be resolved into two components, one in the direction of radii passing through the atomic centre, the other performed in spherical surfaces described round that centre. The latter component alone produces centrifugal force; and it is afterwards shewn to be probable, that the ratio which the *vis viva* of this latter component bears to the whole *vis viva* of the oscillations, depends on the chemical constitution of the substance. The centrifugal force thus arising, has a tendency to increase the superficial density and elasticity of the atomic atmosphere, and must, at each layer of that atmosphere, be *in equilibrio* with the forces arising from the elastic pressure of the adjacent layers, and from the attraction towards the nucleus or centre. The condition of this equilibrium is expressed by a differential equation, which at the same time shews it to be stable. By the integration of that equation, there is obtained a general expression for the elasticity of a gas, in terms of its density and heat.

The first and largest term is simply proportional to the density of the gas, multiplied by a function, which varies as a certain fraction of the heat increased by a constant. In a perfect gas, this term constitutes the whole elasticity.

It is followed by an approximative converging series, chiefly de-

gative, in terms of the reciprocals of the powers of the function of the heat before mentioned, representing the effect of the actions of the nuclei or centres in modifying the superficial-atomic elasticity. The numerators of the terms of this series are functions of the density, diminishing along with it, and requiring to be determined by experiment.

The last term of the expression represents the effect of the mutual action of separate atoms, and is a function of the density, to be determined by experiment.

The third section treats of Temperature and of Real Specific Heat. Bodies are defined to be *at the same temperature*, when the powers of their atoms to communicate heat are equal; and the proper *measure* of temperature is defined to be the elasticity of a perfect gas at constant volume, or its volume under constant pressure. Those quantities are, in all perfect gases, proportional to the temperature, as measured from a point 274·6 centigrade degrees, or 494·28 degrees of Fahrenheit's scale, below the temperature of melting ice. This point is called the *absolute zero*, and temperatures, as measured from it, *absolute temperatures*.

It is shewn from the equations in the preceding section, that absolute temperature, as thus defined, is simply proportional to the quantity of heat in one atom, *plus* a constant, multiplied by a constant coefficient. The constants depend on the nature of the substance, and the coefficient especially on its chemical constitution.

The reciprocal of this coefficient is, of course, the *real specific heat of one atom*, which, being divided by the atomic weight, gives the *real specific heat of unity of weight*.

The following laws, which have been to a great extent established experimentally by Dulong, are inferred from the theory—

That the specific heats of all simple atoms are either the same, or vary only in certain simple numerical ratios.

That the specific heats of atoms of similar chemical constitution are either the same, or vary only in simple numerical ratios.

The fourth section relates to the actual coefficients of elasticity and expansion of gases. The coefficient of increase of elasticity with temperature at constant volume, and the coefficient of expansion under constant pressure, are the same, and equal to each other, for every substance in the state of perfect gas, being the reciprocal of the absolute temperature of melting ice, (or ·00364166 per centi-

grade degree), when the volume and pressure at that temperature are respectively taken as units. The state of perfect gas, however, can be only approximated to in nature; for in all gases, especially the more dense and composite, the actions of the atomic nuclei or centres on their atmospheres, and of separate atoms upon each other, have more or less influence on the elasticity.

M. Regnault has made several elaborate series of experiments, to determine the deviations from uniform expansibility thus produced, in various gases.

The author, by applying his theory to data furnished by the experiments of M. Regnault, has obtained formulæ for the coefficients of expansion of atmospheric air, carbonic acid gas, and hydrogen, the results of which agree closely with those of observation, in every case in which a comparison is possible.

The fifth section treats of the elasticity of vapour in contact with the same substance in the liquid or solid state, or what is called the pressure of vapour at saturation.

The equilibrium of a substance filling a limited space, partly in the form of vapour, and partly in that of liquid or solid, is shewn to depend on three conditions.

The first condition of equilibrium is, that the total elasticity of the substance in the two states must be the same.

The second condition of equilibrium is, that the superficial elasticities of every two contiguous atoms must be the same at their surface of contact, and hence, that the superficial-atomic elasticity must vary continuously; so that, if, at the bounding surface between the liquid or solid and its vapour, there is an abrupt change of density, (as the reflection of light renders probable) there must there be two densities corresponding to the same superficial atomic elasticity.

The third condition of equilibrium is deduced from the mutual attractions and repulsions of the atoms of liquid or solid and those of vapour. In a gas in which the atomic centres are equidistant, the actions of the several atoms on each individual particle at an appreciable distance from the bounding surface of the gas, balance each other, and are accordingly treated as merely affecting the total elasticity by a quantity which is a function of the density; but near the bounding surface between a liquid or solid and its vapour, the action of the liquid or solid upon any atom must be greater than that of the vapour. A force is thus produced which acts on each particle in a

line perpendicular to that bounding surface, and which is probably attractive towards the liquid or solid, very intense close to the bounding surface, but inappreciable at all perceptible distances from it. Such a force can be balanced only by a gradual increase of superficial-atomic elasticity in a direction towards the liquid or solid. Hence, although at perceptible distances from the liquid or solid, the density of vapour is sensibly uniform, the layers close to that surface are probably in a state of condensation by attraction, analogous to that of the earth's atmosphere under the influence of gravity.

Professor Faraday has expressed an opinion that certain well-known phenomena arise from a state of condensation of this kind, produced in gases by the superficial attraction of various solid substances.

This third condition of equilibrium is expressed by a differential equation, the integral of which, taken in conjunction with the first two conditions, would be sufficient to determine the respective densities, and the total elasticity of a liquid or solid and its vapour, when in contact with each other in a limited space at any temperature, provided we had a complete knowledge of the laws of molecular force. In the present imperfect state of that knowledge, the integral in question indicates the *form* of an approximate equation, expressing the logarithm of the elasticity of vapour at saturation, in terms of the reciprocals of the first and second powers of the absolute temperature, the coefficients of which the author has calculated empirically, for water and mercury, from the experiments of M. Regnault, and for alcohol, ether, turpentine, and petroleum, from those of Dr Ure,—three experimental data being required for each fluid, to calculate three constants. The agreement of the results of the formulæ thus obtained with those of experiment is as close as the uncertainties of observation render possible, throughout the whole range of pressures and temperatures observed. For steam, in particular, the coincidence is almost perfect. The author gives a table of the constants for the fluids enumerated, and refers to the Edinburgh New Philosophical Journal for July 1849, for the details of the comparison between calculation and experiment.

The section concludes with a speculation as to the probable effects of the atmospheres of dense vapours supposed to exist at the surfaces of solid and liquid bodies. The author conjectures that the presence of such atmospheres may be the cause which prevents solid

bodies from cohering when brought together, and produces that resistance to contact which is visible not only in them but in drops of liquid. He conceives it possible that it may also be the cause of the "spheroidal state" of liquids at high temperatures, and may assist in maintaining the vesicular state, if such a state exists.

The sixth and last section of the first part relates to mixtures of gases and vapours of different kinds.

The principle stated in the second section *that the elasticity of the atomic atmosphere is proportional to its density*, is here expressed in the form, *that the elasticity of any number of portions of atomic atmosphere, compressed into a given space, is equal to the sum of the elasticities which such portions would respectively have if they occupied the same space separately*. It is shewn, that if this principle be considered true, not only of portions of atomic atmosphere of one kind of substance, but also of portions of atomic atmospheres of substances of different kinds, when mixed, it leads to the well-known laws of the elasticity and diffusion of mixed gases and vapours. He also speculates on the possibility of solid bodies, which have no perceptible vapours of their own at ordinary temperatures, acquiring the power of resisting cohesion by means of a superficial atmosphere of foreign substances.

The second part of the paper treats of the dynamical relations of the heat and the elasticity of bodies in the gaseous state.

The first section contains the general theory of the mutual conversion of heat and expansive power.

After recapitulating the mode of expressing quantities of heat in terms of gravity, the author refers to the experiments of Mr. Joule on the production of heat by electro-magnetic currents, by friction, and by the compression of air, as proving the convertibility of heat and mechanical power. He states reasons, however, for believing that the mechanical value of heat as deduced from those experiments (viz., from 760 feet to 890 feet per degree of Fahrenheit, applied to liquid water) is too large, owing to various causes of loss of power, and gives the preference to experiments in which no machinery is used, such as those on the velocity of sound, as data for such a calculation.

The laws of the production of heat by compression, and its consumption by expansion, are then deduced from the following two principles, the first of which is peculiar to the hypothesis of mole-

cular vortices, while the second is a consequence of the law of the conservation of *vis viva*.

First, As every portion of an atomic atmosphere is urged towards the nucleus or atomic centre by a centripetal force equal to the centrifugal force arising from the oscillation which constitutes heat, it follows that, when by compression, each portion of such an atmosphere is made to *approach* the centre by a certain distance, the *vis viva* of its oscillation will be *increased* by the amount corresponding to that centrifugal force, acting through that distance; and conversely, that, 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.

Secondly, Let a portion of any substance undergo any changes of temperature, volume, and figure, and at length return to its primitive volume, figure, and temperature. Then, the absolute quantity of heat in the substance, the arrangement of the atoms, and the distribution of their atmospheres, being the same as at first, it follows that *the algebraical sum of the vires vivæ consumed and produced during the changes, 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, a certain amount of 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 a certain amount of 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 expansion.

From those principles the author deduces an algebraical expression of three terms. The first term represents the variation of heat arising from mere change of volume; the second, the variation of heat produced by change of the distribution of the density of the atomic atmospheres dependent on change of volume; and the third, the variation of heat due to change of the distribution of the density of the atomic atmospheres, dependent on change of temperature. In all those terms there is a common factor, bearing a constant ratio to the absolute quantity of heat in the body. In the first term, that factor is multiplied by the variation of the logarithm of the density of the body, and in the second and third by certain functions of the density

and temperature depending on the law of the influence of molecular attraction and repulsion upon the superficial-atomic elasticity.

This section concludes by contrasting the author's theory with that of Carnôt, which has hitherto been followed, either explicitly or virtually, in all calculations respecting the motive power of heat (except in the investigations of Mr Joule, already referred to), and of which a very clear and able account, with copious illustrations, was read before the Royal Society of Edinburgh, in January 1849, by Professor Thomson. Carnôt 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 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 which did not before exist. According to the author's theory, on the contrary, as well as to every conceivable theory which regards heat as a modification of motion, the production of expansion by heat, and of heat by compression, consist in the transformation of mechanical power from one shape into another.

The second section relates to real and apparent specific heat, especially in the state of perfect gas. The apparent specific heat of a given substance is defined to be the sum of the real specific heat, and of that heat which is employed in producing those changes of volume and of molecular condition which accompany an elevation of one degree in the temperature of the substance. The same substance may therefore have different apparent specific heats, according to the manner in which the volume is made to vary with the temperature. The general algebraical expression for apparent specific heat is deduced from the equations of the preceding section. That expression being applied to the case of a perfect gas, or of a gas which may be treated in practice as sensibly perfect, it is shewn that the apparent specific heat of such a gas, at constant volume, is sensibly equal to the real specific heat, and that the apparent specific heat at constant pressure exceeds the specific heat at constant volume in a ratio which is sensibly constant for a given gas. Laplace's method of calculating this ratio from the velocity of sound is referred to, and applied to atmospheric air, oxygen, and hydrogen, using the correct coefficients of dilatation of those gases, as determined by M. Regnault.

The following laws, which have already been inferred from experiment by Dulong, are then deduced from the theory :

The specific heat of unity of volume, at constant volume, varies for different perfect gases inversely as the fraction by which the ratio of the two specific heats exceeds unity.

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.

The data now obtained being employed to calculate the value of heat in terms of the force of gravity, it is found that the real specific heat of atmospheric air is equivalent to a fall of 238·66 feet per centigrade degree, and the apparent specific heat of liquid water at the temperature of melting ice (being what is commonly termed a thermal unit) to a fall of 1252 feet per centigrade degree, or 695·6 feet per degree of Fahrenheit.

The author next investigates the apparent specific heat of vapour at saturation. This quantity, according to his theory, is altogether different from the variation of the total heat of evaporation, with which, according to the theory of Carnôt, it is identical. It is in general *negative* ; so that if vapour at saturation is allowed to expand, being cut off from external sources of heat, a portion of it must be liquefied in order to supply the heat necessary for the expansion of the rest, in addition to the heat set free by the fall of temperature.

The third section treats of the latent and total heat of evaporation, especially for water.

It is in the first place proved, from the principle of *vis viva*, that the latent heats of evaporation and liquefaction, at a given temperature, are equal, with contrary signs.

The total heat of evaporation is defined to be the sum of the latent heat of evaporation, and of the heat required to raise the liquid to the temperature at which it is evaporated, from some arbitrary fixed temperature—(generally that of melting ice).

The law of variation of the total heat of evaporation with temperature is then deduced from the principle of the conservation of *vis viva*, which, as applied to this subject, takes the following form :—

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 its 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.

From this principle it is deduced that when a vapour is sensibly in the state of perfect gas, and of very small density as compared with its liquid, the total heat of evaporation increases uniformly with the temperature, and the rate of increase is sensibly equal to the apparent specific heat of the vapour at constant pressure. This conclusion is verified by the experiments of M. Regnault upon the evaporation of water. As an additional verification of the theory, the real specific heat of steam is calculated from the total heat of evaporation, and also from the specific heat of atmospheric air; and the results of these two processes are found to agree exactly, being equal to 0.183 of the apparent specific heat of liquid water.

The fourth and last section of the second part is an investigation of the mechanical action of steam, treated as a perfect gas, and the power of the steam-engine.

The density of steam of saturation at 100° centigrade, is calculated from its chemical composition on the assumption of its being a perfect gas, and found to agree with the result of experiment, being $\frac{1}{1696}$ of the maximum density of water; and thence it is inferred that, in the absence of more precise data, steam at ordinary pressures may be treated in practice as a perfect gas, without material error.

The mechanical action of unity of weight of steam while entering a cylinder, and before it has begun to expand, is found by multiplying its pressure by its volume. The expansive action is next investigated, taking into account the liquefaction of a portion of the steam in supplying the heat required to expand the rest. The exact expression of this action is extremely complicated; but approximate formulæ of a more simple kind are given, suitable for calculating its amount with accuracy sufficient for practice, in different portions of the scale of pressures. From the sum of those two portions of power, deductions are made for the loss of power arising from clearance, and for the effect of the counter-pressure of the escaping steam. Thus is obtained the complete expression for the gross effect of unity of weight of steam, which, being multiplied by the weight of water effectively

evaporated in unity of time gives the gross effect of the engine in unity of time. The result affords the means of calculating all the circumstances connected with 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 a uniform or periodical velocity. This principle was first applied to the steam-engine by the Count de Pambour, and, accordingly, the formulæ of this paper only differ from those of his work in the expressions for the pressure and expansive action of the steam, which are results peculiar to the author's theory. As an illustration of the use of the formulæ, the maximum useful effect of a double-acting Cornish engine is computed, and compared with the result of the calculation of M. de Pambour for the same engine, shewing the latter to be too large by about one-fifteenth.

In an Appendix are given two tables; one for calculating the volume of steam from its pressure, and *vice versa*, and its mechanical action at full pressure, the other for computing the amount of its action in expansive engines.

In order to shew the limit of the possible effect from the expenditure of a given quantity of heat in evaporating water under given circumstances, the maximum gross effect of unity of weight of steam, evaporated at a higher temperature, and liquefied at a lower, is computed in two examples, and compared with the heat which disappears during the action of the steam, as calculated directly. In the first example, the water is supposed to be evaporated at the pressure of four atmospheres, and condensed at that of half an atmosphere; in the second, to be evaporated at eight atmospheres, and condensed at one atmosphere.

In both these examples, the direct calculation of the heat rendered effective, agrees with the calculation from the power developed, thus verifying the methods of computation founded on the author's theory.

The heat converted, in those examples, into engine-power amounts to only about *one-sixth part* of the heat expended in evaporating the water, the remainder being carried off by the steam and liquid water which escape from the cylinder. In practice, the proportion of heat rendered effective is still smaller, and in some unexpansive engines amounts to only *one twenty-fourth part*, or even less. It is thus

shewn, that there is a waste of heat in the steam-engine, which is a necessary consequence of its nature. It can be reduced only by increasing the initial pressure of steam, and the extent of the expansive action; and to both these resources there are practical limits.

In conclusion of the present paper, the author states, that, from his equations, many additional formulæ are deducible, with respect to the specific heat of imperfect gases, to certain questions in meteorology, and to the specific heat of liquids; but from the want of sufficient experimental data, he conceives that they are not as yet capable of being usefully applied.

2. On Probable Inference. By Bishop Terrot.

The paper commenced with a suggestion, that, as the inferences of ordinary logic admitted no premises but such as were absolutely certain, and as the premises with which we have to deal in the business of life were not certain, but only probable, therefore it was highly desirable that we should have a logic, or rules for drawing inferences on the case of probable premises.

The attention of the Society was then drawn to the 15th section of the article Probabilities, in the *Encyclopædia Metropolitana*, and especially to the following passage: "It is an even chance that A is B, and the same that B is C; and therefore, 1 to 3 from these grounds only that A is C. But other considerations of themselves give an even chance that A is C. What is the resulting degree of evidence that A is C?" To which query the answer in the *Encyclopædia* is $\frac{5}{8}$.

On this passage it was observed, in the first place, that the asserted ratio of 1 to 3, or the probability $\frac{1}{4}$ in the first syllogism, was true only on the hypothesis that A can be C only through the intervention of the middle term B. But that when such is not the case, when other ways are conceivable but totally unknown, the probability is not $\frac{1}{4}$ but $\frac{1}{2}$; these two fractions representing, the one the probability of the evidence of a complete proof that A is C, the other the probability that A is C; and it was observed, that, in practical questions, it is the latter probability alone which we have an interest in determining.