Brought forward, 356

Deduct Deceased—Rev. Dr Guthrie; Prof. John
Hunter; Very Rev. Dean Ramsay; Prof.
Macquorn Rankine; Arch. Smith, Esq.;
Rev. Prof. Stevenson; Dr J. L. Stewart; R.
W. Thomson, Esq., ... 8
Resigned—J. F. M·Lennan, Esq.; Dr Alex. Wood, 2
Cancelled—Dr Richardson, Dr Foulerton, . . 2
 ── 12

Total number of Ordinary Fellows at Nov. 1873, . 344

The following Communications were read:—

9. The Kinetic Theory of the Dissipation of Energy. By Sir William Thomson.

In abstract dynamics the instantaneous reversal of the motion of every moving particle of a system causes the system to move backwards, each particle of it along its old path, and at the same speed as before, when again in the same position. That is to say, in mathematical language, any solution remains a solution when t is changed into $-t$. In physical dynamics this simple and perfect reversibility fails, on account of forces depending on friction of solids; imperfect fluidity of fluids; imperfect elasticity of solids; inequalities of temperature, and consequent conduction of heat produced by stresses in solids and fluids; imperfect magnetic retentiveness; residual electric polarisation of dielectrics; generation of heat by electric currents induced by motion; diffusion of fluids, solution of solids in fluids, and other chemical changes; and absorption of radiant heat and light. Consideration of these agencies in connection with the all-pervading law of the conservation of energy proved for them by Joule, led me twenty-three years ago to the theory of the dissipation of energy, which I communicated first to the Royal Society of Edinburgh in 1852, in a paper entitled "On a Universal Tendency in Nature to the Dissipation of Mechanical Energy."

The essence of Joule's discovery is the subjection of physical phenomena to dynamical law. If, then, the motion of every par-

ticle of matter in the universe were precisely reversed at any instant, the course of nature would be simply reversed for ever after. The bursting bubble of foam at the foot of a waterfall would reunite and descend into the water; the thermal motions would reconcentrate their energy, and throw the mass up the fall in drops re-forming into a close column of ascending water. Heat which had been generated by the friction of solids and dissipated by conduction, and radiation with absorption, would come again to the place of contact, and throw the moving body back against the force to which it had previously yielded. Boulders would recover from the mud the materials required to rebuild them into their previous jagged forms, and would become reunited to the mountain peak from which they had formerly broken away. And if also the materialistic hypothesis of life were true, living creatures would grow backwards, with conscious knowledge of the future, but no memory of the past, and would become again unborn. But the real phenomena of life infinitely transcend human science, and speculation regarding consequences of their imagined reversal is utterly unprofitable. Far otherwise, however, is it in respect to the reversal of the motions of matter uninfluenced by life, a very elementary consideration of which leads to the full explanation of the theory of dissipation of energy.

To take one of the simplest cases of the dissipation of energy, the conduction of heat through a solid—consider a bar of metal warmer at one end than the other, and left to itself. To avoid all needless complication, of taking loss or gain of heat into account, imagine the bar to be varnished with a substance impermeable to heat. For the sake of definiteness, imagine the bar to be first given with one-half of it at one uniform temperature, and the other half of it at another uniform temperature. Instantly a diffusing of heat commences, and the distribution of temperature becomes continuously less and less unequal, tending to perfect uniformity, but never in any finite time attaining perfectly to this ultimate condition. This process of diffusion could be perfectly prevented by an army of Maxwell's "intelligent demons,"* stationed at the

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* The definition of a demon, according to the use of this word by Maxwell, is an intelligent being endowed with free-will and fine enough tactile and perceptive organisation to give him the faculty of observing and influencing individual molecules of matter.

surface, or interface as we may call it with Professor James Thomson, separating the hot from the cold part of the bar. To see precisely how this is to be done, consider rather a gas than a solid, because we have much knowledge regarding the molecular motions of a gas, and little or no knowledge of the molecular motions of a solid. Take a jar with the lower half occupied by cold air or gas, and the upper half occupied with air or gas of the same kind, but at a higher temperature, and let the mouth of the jar be closed by an air-tight lid. If the containing vessel were perfectly impermeable to heat, the diffusion of heat would follow the same law in the gas as in the solid, though in the gas the diffusion of heat takes place chiefly by the diffusion of molecules, each taking its energy with it, and only to a small proportion of its whole amount, by the interchange of energy between molecule and molecule; whereas in the solid there is little or no diffusion of substance, and the diffusion of heat takes place entirely, or almost entirely, through the communication of energy from one molecule to another. Fourier's exquisite mathematical analysis expresses perfectly the statistics of the process of diffusion in each case, whether it be "conduction of heat," as Fourier and his followers have called it, or the diffusion of substance in fluid masses (gaseous or liquid), which Fick showed to be subject to Fourier's formulæ. Now, suppose the weapon of the ideal army to be a club, or, as it were, a molecular cricket bat; and suppose. for convenience, the mass of each demon with his weapon to be several times greater than that of a molecule. Every time he strikes a molecule he is to send it away with the same energy as it had immediately before. Each demon is to keep as nearly as possible to a certain station, making only such excursions from it as the execution of his orders requires. He is to experience no forces except such as result from collisions with molecules, and mutual forces between parts of his own mass, including his weapon. Thus his voluntary movements cannot influence the position of his centre of gravity, otherwise than by producing collision with molecules.

The whole interface between hot and cold is to be divided into small areas, each allotted to a single demon. The duty of each demon is to guard his allotment, turning molecules back, or allowing them to pass through from either side, according to certain

definite orders. First, let the orders be to allow no molecules to pass from either side. The effect will be the same as if the interface were stopped by a barrier impermeable to matter and to heat. The pressure of the gas being, by hypothesis, equal in the hot and cold parts, the resultant momentum taken by each demon from any considerable number of molecules will be zero; and therefore he may so time his strokes that he shall never move to any considerable distance from his station. Now, instead of stopping and turning all the molecules from crossing his allotted area, let each demon permit a hundred molecules chosen arbitrarily to cross it from the hot side; and the same number of molecules, chosen so as to have the same entire amount of energy and the same resultant momentum, to cross the other way from the cold side. Let this be done over and over again within certain small equal consecutive intervals of time, with care that if the specified balance of energy and momentum is not exactly fulfilled in respect to each successive hundred molecules crossing each way, the error will be carried forward, and as nearly as may be corrected, in respect to the next hundred. Thus, a certain perfectly regular diffusion of the gas both ways across the interface goes on, while the original different temperatures on the two sides of the interface are maintained without change.

Suppose, now, that in the original condition the temperature and pressure of the gas are each equal throughout the vessel, and let it be required to disequalise the temperature, but to leave the pressure the same in any two portions A and B of the whole space. Station the army on the interface as previously described. Let the orders now be that each demon is to stop all molecules from crossing his area in either direction except 100 coming from A, arbitrarily chosen to be let pass into B, and a greater number, having among them less energy but equal momentum, to cross from B to A. Let this be repeated over and over again. The temperature in A will be continually diminished and the number of molecules in it continually increased, until there are not in B enough of molecules with small enough velocities to fulfil the condition with reference to permission to pass from B to A. If after that no molecule be allowed to pass the interface in either direction, the final condition will be very great condensation and very low temperature in

A; rarefaction and very high temperature in B; and equal temperature in A and B. The process of disequalisation of temperature and density might be stopped at any time by changing the orders to those previously specified (2), and so permitting a certain degree of diffusion each way across the interface while maintaining a certain uniform difference of temperatures with equality of pressure on the two sides.

If no selective influence, such as that of the ideal "demon," guides individual molecules, the average result of their free motions and collisions must be to equalise the distribution of energy among them in the gross; and after a sufficiently long time, from the supposed initial arrangement, the difference of energy in any two equal volumes, each containing a very great number of molecules, must bear a very small proportion to the whole amount in either; or, more strictly speaking, the probability of the difference of energy exceeding any stated finite proportion of the whole energy in either is very small. Suppose now the temperature to have become thus very approximately equalised at a certain time from the beginning, and let the motion of every particle become instantaneously reversed. Each molecule will retrace its former path, and at the end of a second interval of time, equal to the former, every molecule will be in the same position, and moving with the same velocity, as at the beginning; so that the given initial unequal distribution of temperature will again be found, with only the difference that each particle is moving in the direction reverse to that of its initial motion. This difference will not prevent an instantaneous subsequent commencement of equalisation, which, with entirely different paths for the individual molecules, will go on in the average according to the same law as that which took place immediately after the system was first left to itself.

By merely looking on crowds of molecules, and reckoning their energy in the gross, we could not discover that in the very special case we have just considered the progress was towards a succession of states, in which the distribution of energy deviates more and more from uniformity up to a certain time. The number of molecules being finite, it is clear that small finite deviations from absolute precision in the reversal we have supposed would not

obviate the resulting disequalisation of the distribution of energy. But the greater the number of molecules, the shorter will be the time during which the disequalising will continue; and it is only when we regard the number of molecules as practically infinite that we can regard spontaneous disequalisation as practically impossible. And, in point of fact, if any finite number of perfectly elastic molecules, however great, be given in motion in the interior of a perfectly rigid vessel, and be left for a sufficiently long time undisturbed except by mutual impact and collisions against the sides of the containing vessel, it must happen over and over again that (for example) something more than $\frac{9}{10}$ths of the whole energy shall be in one-half of the vessel, and less than $\frac{1}{10}$th of the whole energy in the other half. But if the number of molecules be very great, this will happen enormously less frequently than that something more than $\frac{6}{10}$ths shall be in one-half, and something less than $\frac{4}{10}$ths in the other. Taking as unit of time the average interval of free motion between consecutive collisions, it is easily seen that the probability of there being something more than any stated percentage of excess above the half of the energy in one-half of the vessel during the unit of time, from a stated instant, is smaller the greater the dimensions of the vessel and the greater the stated percentage. It is a strange but nevertheless a true conception of the old well-known law of the conduction of heat, to say that it is very improbable that in the course of 1000 years one-half of the bar of iron shall of itself become warmer by a degree than the other half; and that the probability of this happening before 1,000,000 years pass is 1000 times as great as that it will happen in the course of 1000 years, and that it certainly will happen in the course of some very long time. But let it be remembered that we have supposed the bar to be covered with an impermeable varnish. Do away with this impossible ideal, and believe the number of molecules in the universe to be infinite; then we may say one-half of the bar will never become warmer than the other, except by the agency of external sources of heat or cold. This one instance suffices to explain the philosophy of the foundation on which the theory of the dissipation of energy rests.

Take however another case, in which the probability may be

readily calculated. Let a hermetically sealed glass jar of air contain 2,000,000,000,000 molecules of oxygen, and 8,000,000,000,000 molecules of nitrogen. If examined any time in the infinitely distant future, what is the number of chances against one that all the molecules of oxygen and none of nitrogen shall be found in one stated part of the vessel equal in volume to $\frac{1}{5}$th of the whole? The number expressing the answer in the Arabic notation has about 2,173,220,000,000 of places of whole numbers. On the other hand, the chance against their being exactly $\frac{2}{10}$ths of the whole number of particles of nitrogen, and at the same time exactly $\frac{2}{10}$ths of the whole number of particles of oxygen in the first specified part of the vessel, is only 4021×10^9 to 1.

APPENDIX.

Calculation of probability respecting Diffusion of Gases.

For simplicity, I suppose the sphere of action of each molecule to be infinitely small in comparison with its average distance from its nearest neighbour; thus, the sum of the volumes of the spheres of action of all the molecules will be infinitely small in proportion to the whole volume of the containing vessel. For brevity, space external to the sphere of action of every molecule will be called free space: and a molecule will be said to be in free space at any time when its sphere of action is wholly in free space; that is to say, when its sphere of action does not overlap the sphere of action of any other molecule. Let A, B, denote any two particular portions of the whole containing vessel, and let a, b, be the volumes of those portions. The chance that at any instant one individual molecule of whichever gas shall be in A is $\dfrac{a}{a+b}$, however many or few other molecules there may be in A at the same time; because its chances of being in any specified portions of free space are proportional to their volumes; and, according to our supposition, even if all the other molecules were in A, the volume of free space in it would not be sensibly diminished by their presence. The chance that of n molecules in the whole

space there shall be i stated individuals in A, and that the other $n-i$ molecules shall be at the same time in B, is

$$\left(\frac{a}{a+b}\right)^{i}\left(\frac{b}{a+b}\right)^{n-i}, \text{ or } \frac{a^{i} b^{n-i}}{(a+b)^{n}}.$$

Hence the probability of the number of molecules in A being exactly i, and in B exactly $n-i$, irrespectively of individuals, is a fraction having for denominator $(a+b)^{n}$, and for numerator the term involving $a^{i} b^{n-i}$ in the expansion of this binomial; that is to say, it is—

$$\frac{n(n-1)\ldots\ldots(n-i+1)}{1.2\quad\ldots\ldots\quad i}\left(\frac{a}{a+b}\right)^{i}\left(\frac{b}{a+b}\right)^{n-i}$$

If we call this T_i, we have

$$T_{i+1}=\frac{n-i}{i+1}\frac{a}{b}\,T_i.$$

Hence T_i is the greatest term if i is the smallest integer, which makes

$$\frac{n-i}{i+1}<\frac{b}{a};$$

this is to say, if i is the smallest integer which exceeds

$$n\frac{a}{a+b}-\frac{b}{a+b}.$$

Hence if a and b are commensurable, the greatest term is that for which

$$i=n\frac{a}{a+b}.$$

To apply these results to the cases considered in the preceding article, put in the first place

$$n = 2 \times 10^{12},$$

this being the number of particles of oxygen; and let $i = n$. Thus, for the probability that all the particles of oxygen shall be in A, we find

$$\left(\frac{a}{a+b}\right)^{8 \times 10^{12}}$$

Similarly, for the probability that all the particles of nitrogen are in the space B, we find

$$\left(\frac{b}{a+b}\right)^{2 \times 10^{12}}$$

Hence the probability that all the oxygen is in A and all the nitrogen in B is

$$\left(\frac{a}{a+b}\right)^{2 \times 10^{12}} \times \left(\frac{b}{a+b}\right)^{8 \times 10^{12}}$$

Now by hypothesis

$$\frac{a}{a+b} = \frac{2}{10},$$

and therefore

$$\frac{b}{a+b} = \frac{8}{10};$$

hence the required probability is

$$\frac{2^{26 \times 10^{12}}}{10^{10^{13}}} \ .$$

Call this $\frac{1}{N}$, and let log denote common logarithm. We have

$$\log \ N = 10^{13} - 26 \times 10^{12} \times \log \ 2 = (10 - 26 \ \log \ 2) \times 10^{12} = 2173220$$

$\times 10^6$. This is equivalent to the result stated in the text above. The logarithm of so great a number, unless given to more than thirteen significant places, cannot indicate more than the number of places of whole numbers in answer to the proposed question, expressed according to the Arabic notation.

The calculation of T_i, when i and $n-i$ are very large numbers, is practicable by Stirling's theorem, according to which we have approximately

$$1.2. \cdots \cdot i = i^{i + \frac{1}{2}} \epsilon^{-i} \sqrt{2\pi} \ ,$$

and therefore

$$\frac{n(n-1) \ldots (n-i+1)}{1.2 \quad \ldots \quad i} = \frac{n^{n + \frac{1}{2}}}{\sqrt{2\pi} \, i^{i + \frac{1}{2}} (n-i)^{n - i + \frac{1}{2}}}.$$

Hence for the case

$$i = n \, \frac{a}{a + b},$$

which, according to the preceding formulæ, gives T_i its greatest value, we have

$$T_i = \frac{1}{\sqrt{2 \pi n e f}},$$

where

$$e = \frac{a}{a + b} \text{ and } f = \frac{b}{a + b}.$$

Thus, for example, let $n = 2 \times 10^{12}$;

$$e = \cdot 2, \ f = \cdot 8,$$

we have

$$T_i = \frac{1}{800000 \sqrt{\pi}} = \frac{1}{1418000}.$$

This expresses the chance of there being 4×10^{11} molecules of oxygen in A, and 16×10^{11} in B. Just half this fraction expresses the probability that the molecules of nitrogen are distributed in exactly the same proportion between A and B, because the number of molecules of nitrogen is four times greater than of oxygen.

If n denote the molecules of one gas, and n' that of the molecules of another, the probability that each shall be distributed between A and B in the exact proportion of the volume, is

$$\frac{1}{2 \pi e f \sqrt{n n'}}.$$

The value for the supposed case of oxygen and nitrogen is

$$\frac{1}{2 \pi \times \cdot 16 \times 4 \times 10^{12}} = \frac{1}{4021 \times 10^{9}},$$

which is the result stated at the conclusion of the text above.