

LETTERS TO THE EDITOR.

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Liquefaction of Gases.

In a long letter which you published in Nature of February 14, Mr. Pattison Mair charged me with appropriating the work of Osiwetzki and passing it off as my own. I replied at some length, not on account of the intrinsic importance of the attack, but because there are always persons ready to assume that a charge of this kind, by whomsoever made, must be unanswerable and unanswerably true. But I can conceive nothing more unseemly than to urge readers on, or myself, to a mere dialectical controversy with Mr. Mair, my reply to his letter published on the previous page.

"A careful study" of my previous letter has not enabled Mr. Mair to substantiate his original charge of wilful piracy. On the contrary, he entirely shifts his ground. He extracts four clauses from my reply and proceeds to deal with them, ignoring altogether the only question of the smallest importance, namely, the one claim made by himself to have connected me, disinterestedly, with Osiwetzki. He has nothing to say about that.

The third claim found in my reply by Mr. Mair, which is the only important one, is, to use his own language, that in "1885 I liquefied oxygen by passing the gas through a long column of water, arranged in such a manner as to prevent the liquid oxygen in a glass vessel wherein it was cooled by submerging the outside of the vessel in liquid ethylene, and that I have made it possible to transfer the liquid oxygen to a glass vessel wherein it could be used as a cooling agent.

We have here whether I did or did not do what I claim to have done in a public lecture delivered and published in the year 1886, and this question he wholly disregards.

Until Mr. Pattison Mair can declare that after trial an apparatus constructed according to the plan given in 1885 is exquisitely defective, and will not deliver liquid oxygen in a manner at all comparable to the Osiwetzki steel cylinder, described in the Crazow Bulletin of 1890, let him acknowledge at least that the case of Mr. Mair, which he championed in his last letter, will have to be abandoned.

Having failed to overthrow a single one of the claims which he himself after "careful study" holds to have made mine, Mr. Mair falls back upon a general attack upon the scientific work that is attributed to the Fellows Prose or the Royal Institution. "With what is attributed to me by others, I have no concern. The low temperature work that has been commenced and so far developed in the laboratory of the Royal Institution comprises the following subjects: Construction of apparatus for the production of liquid air and other gases in quantity, improving high vacuum, vacuum vessels for storage and manipulation of liquid gases, solid air, radiators at low temperatures, thermal transparencies of liquid gases, reflective indices of oxygen, nitrogen, and air, spectrophotometry of liquid oxygen and air, the absorption of light of various colors in specific heats, chemical action, magnetic properties, breaking strong metal, solid matter and argon in liquid air, phosphorescence, and phosphorescence, the interaction of nitrogen, etc...."

The absence of these results of these investigations have been published, and if Mr. Pattison Mair would only take a little trouble he could find the date, course and when I have made it. Proper, fuller details will have to be sent to Mr. Mair's care, but, that my intellectual input comes from Crazow, and that I have not seen the wake of the researchers of his client. On referring to Prof. Osiwetzki's record of work since his alleged invention of the waas to设计理念 oxygen as a cooling agent in 1895, I find that with the exception of the relative index of oxygen, which was anticipated by Prof. Long in 1889, and myself, and an attempt to convey the late Prof. Willaume, is a critical concept of hydrogen, the work carried on at the Royal Institution and at Crazow has been done without the least connection of 1895, than cool a piece of meteorite or expand liquid oxygen into a vacuum. No doubt by implication Mr. Mair intends to convey the use of a steel cylinder instead of the copper still of 1886, and that suggestion, I have to emphasize-

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revealed in every respect. No one hypothesis has hitherto attempted at this last end, the Theory of Gases excepted. But this theory agrees in so many respects with the facts, that we can hardly doubt that in gases certain velocities, the number and size of which can roughly be determined, by what is called the law of the virial. Can it be seriously expected that they will behave exactly as aggregates of Newtonian centers of force, or as the rigid bodies of our Mechanic's Art, and how awkward is the human mind in dividing the nature of things, when forced by the analogy of what we see and touch directly?

The following experiment, while not professing to explain the mysteries to which Lord Salisbury alluded, nevertheless show that it is possible to explain the spectra of gases while ascribing 5 degrees of freedom to the molecules, and without departing from Boscovitch's standpoint.

The molecules of certain gases behave as rigid bodies. The molecules of the gas and of the enclosing vessel move through the ether without loss of energy, as rigid bodies, or, as Lord Kewin's vortex rings move through a frictionless liquid in ordinary hydrodynamics. If we were to take a vessel filled with one gram of gas and put it in an infinitely long time always at 0°C, and containing always the same portion of ether, every atom of ether and every atom of gas molecules would reach the same average size at once. If then we were to raise the temperature to 1°C, and to wait till every ponderable and every atom of ether was in thermal equilibrium, the total energy would be augmented almost beyond belief. But in actually heating one gram of gas, the ether always flows freely through the walls of the vessel. It comes from the universe, and there is no question of the ether being in thermal equilibrium with the molecules of the gas. It is true that it always carries off energy, if the outside space is colder than the gas; but this energy may be so small as to be altogether negligible in comparison with the energy which the gas loses by heat-conduction, and which must be experimentally determined and subtracted in measuring the specific heat. Only certain transverse waves can transfer sensible energy from one ponderable body to another, and therefore a convection for radiant heat must be applied to obtain the proper results. These transverse vibrations are not produced (as in the older theories of light) by simple atomic vibrations, but their pitch depends on the shape of the hollow space which the molecule forms in the ether, just as Huygen's waves are not caused by vibrations of the ponderable matter of the brass ball, the form of which determines the pitch. The unknown electric action accompanying a chemical process augments these transverse vibrations enormously. The generalised coordinates of the ether, on which these vibrations depend, have not the same virial as the coordinates which determine the position of a molecule, because the entire ether has not had time to come into thermal equilibrium with the gas molecules, and has in no respect attained the state which it would have if it had been filled for an infinitely long time in the same vessel with the molecules of the gas.

How can the molecules of a gas behave as rigid bodies? Are they not composed of smaller atoms? Probably they are; but the distribution of their internal vibrations is transformed into progressive and rotatory motion so slowly, that when a gas is brought to a lower temperature the molecules may retain for days, or even for years, the higher virial of their internal vibrations corresponding to the original temperature. This transformation of energy is so slow that it can not affect the observed fluctuations of temperature of the surrounding bodies. The possibility of the transformation of energy being so gradual cannot be denied, if we also attribute to the ether so slight friction that the Earth is not sensibly retarded by moving through it for many hundreds of years. If the ether bear an external medium which flows freely through the gas, we might find a difficulty in explaining how it is that the source of radiant heat seems to be in the energy of the gas itself. But I still think it possible that the source of energy of the transverse vibrations caused by the impact of two gas molecules in the surrounding ether, may be in the progressive and rotatory energy of the molecule. If the electric states of two molecules are different, the states of their application of appropriate transposition, the energy of progressive motion may be transformed into electric energy.

Moreover, it is doubtful whether emission of rays of visible light takes place in simple gases without chemical action. Certainly the light of sodium and that of Gass's tube do not come from gases whose molecules are in thermal equilibrium.

It may be objected that the above is nothing more than a series of imperfectly proved hypotheses. But granting its improbability, it suffices that this explanation is not impossible, and nature will have found a solution of the question more than mine.

§ 2. Mr. Culverwell's objections against my Minimum Theorem bear the closest connection to what I pointed out in the second part of my paper, "Probleme der mechanischen Wissenschaft," "[4] Hauernich the more direct Problem der Mechanik der Wissenschaft," "Jahrh. der Wiss. Acad. vol. xx the 1857. There I pointed out that my Minimum Theorem, as well as the so-called Second Law of Thermodynamics, are only theorems of probability. The Second Law can never be proved mathematically by means of the equations of motion, but may be taken as a postulate, just as the law of gravity is taken as a postulate for the motion of celestial bodies.

Let us compute two motions of a dynamical system. At the beginning of the second motion, let the coordinates specifying the position of every part of the moving system, and the magnitudes of all the corresponding velocities, be the same as they were at the end of the first motion, but let the direction of every velocity be exactly reversed. Then in the second motion the system moves exactly in the opposite way to what it does in the first; hence, if for the first motion we have

$$\frac{d\mathbf{v}}{dt} < 0$$

then for the second we must have

$$\frac{d\mathbf{v}}{dt} > 0$$

That is, if under certain conditions

$$\frac{d\mathbf{v}}{dt} < 0$$

we can always find other initial conditions which give for the same system with the same equations of motion,

$$\frac{d\mathbf{v}}{dt} > 0$$

In the same manner, Mr. Culverwell wishes to relate my Minimum Theorem to his Second Law of Thermodynamics, because by the same reasoning we could prove that oxygen and nitrogen do not diffuse. Suppose that initially one half of a closed vessel contains pure oxygen, and in the other half pure nitrogen; when the vessel has advanced for a certain time, reverse the directions of all velocities, then the gases separate again, and, according to Mr. Culverwell's argument, we could believe that the probability that oxygen and nitrogen separate, is as great as the probability that they mix.

But interesting and striking at the first moment, Mr. Culverwell's argument rests, as I think, only upon a mistake of my assumptions: it can never be proved from the equations of motion alone, that the minimum function $M$ must always decrease. It can only be deduced from the laws of probability, that the initial state is not specially arranged for a certain purpose, but haphazard governs freely, the probability that $M$ decreases is always less than the probability that it increases. It will therefore be necessary to consider the problem of probability as exact as any other mathematical theory, if properly understood. If we make space throws with dice, we cannot prove that we shall throw any particular number exactly 100 times; but we can prove that the ratio of the number of throws in which that number turns up to the whole number of throws, approaches the more to 50 the faster we throw.

Let us now take a given rigid vessel with perfectly smooth and perfectly elastic walls containing a given number of gas-molecules moving for an indefinitely long time. All regular motions (e.g. one where all the molecules move in one plane) shall be excluded. During the greater part of this time $H$ will be very nearly equal to its minimum value $H_{(min)}$. Let us construct the $H$-curve, i.e. let us take the time as axis of abscissae and draw the curve, whose ordinates are the corresponding values of $H$. The greater the majority of the ordinates of this curve are very nearly equal to $H_{(min)}$. But because greater values of $H$ are not mathematically impossible, but only very improbable, the curve has usually than very few, summits or maximum ordinates which rise to a greater height than $H_{(min)}$.

We now consider a certain ordinate $H_{(1)}$; $H_{(min)}$. Two cases are possible. $H_{(1)}$ may be very near the top of a summit, so that $H$ decreases if we go either in the positive or negative direction along the axis representing time. The second case is, that $H_{(1)}$ lies considerably on the one side $H$, but be the first and ordinate of $H$ curve, it will decrease.

We will next state whether $H$ is in a certain, but not exactly 1 true at all indefinite system, cases where again.

But (theorem, 0 shows that it zero, only ex. Hence Mr is not as much wrong, if it is taking all variations which configuration average, of shape $g$, whether whether I What I proton probable the probability, it to it decreases value for $d$ element $d$, the number of which for which $t$ I will not only show the case of dice, with the die, number $i$, an throwing $i$, (6, i) in a plane, ti

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we refer to the figures given in my papers; I will only show that just the same takes place in the much simpler case of three of dice. We will make an indefinitely long series of throws with only one die, Let us count the number of times of throwing the number 1, among the first 60 throws, A the number in an interval of 1, among all the throws the second and the third and so on. Let us construct a series of points n a plane, the successive abscissæ of which are

$$\begin{align*}
\rho = \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{5} + \frac{1}{6} + \frac{1}{7} + \frac{1}{8} + \frac{1}{9} + \frac{1}{10} + \frac{1}{11} + \frac{1}{12} + \ldots
\end{align*}$$

The ordinate of which are

$$\begin{align*}
y = \left(\frac{1}{1} - \frac{1}{2}, \frac{1}{2} - \frac{1}{3}, \frac{1}{3} - \frac{1}{4}, \frac{1}{4} - \frac{1}{5}, \frac{1}{5} - \frac{1}{6}, \frac{1}{6} - \frac{1}{7}, \frac{1}{7} - \frac{1}{8}, \frac{1}{8} - \frac{1}{9}, \frac{1}{9} - \frac{1}{10}, \frac{1}{10} - \frac{1}{11}, \frac{1}{11} - \frac{1}{12}, \ldots\right)
\end{align*}$$

Let us count this series of points the "P-curve." If we take a large number, the greater proportion of the ordinate of this curve will be very small. But the P-curve (like the aforementioned H-curve) has summits which are higher than the ordinary course of the curve. Let us now consider all the points of the P-curve, whose ordinates are exactly $1$. We will call these points the "points of the white." Since for each point $n = (\rho - \frac{1}{2})$, for the points B we have $A = 2n$; these points mark, therefore, the case where, by chance, we have thrown the number 1 in 2 throws out of 60. If $n$ is at all large, that is extremely improbable, but never absolutely impossible. Let 2 be a much number smaller than $n$, and let us go forward from the abscissa of each point $n$ through a distance of $60/n$ in the direction of $x$ positive. We shall probably meet a point, the ordinate of which $<1$. The probability that we meet an ordinate $>1$ is extremely small, but not zero. By reasoning in the same manner as Mr. Culverwell, we might believe that if we take backward (i.e. in the direction of $x$ negative) from the abscissa of each point $n$ through a distance of $60/n$, it would be probable that in 2 throws out of 60, we have thrown the number 1. But this inference is not correct. Whether we go to the positive or in the negative direction the ordinate will probably decrease. We can even calculate the probable diminution of $y$. We have seen that for every point B we have $A = 2n$ (i.e. 60 throws of $x$ turning up $n$). If we move in the positive or negative direction along the axis of $x$ through the distance $\delta x$, we include one of the 60 throws, and we include a new one. When we move forward through the distance $60/n$, we have excluded 60 of the original throws, and included 60 others. Among the excluded throws we have probably $2n$, among the included ones $n$ rows of the number 1. Therefore the probable diminution of $A$ is $2n$ and the probable diminution of $y$ is $2n/60$. Approximately. Because the variation of $x$ was $60/n$, we may write

$$\frac{\delta y}{\delta x} = \frac{2n}{60}.$$

We have now, with Mr. Culverwell, a gas in a given state. If in this state H is greater than $H_{\text{min}}$ it will be certain, but very probable, that H decreases and finally reaches a given value $H_{\text{min}}$, and the same is true at all subsequent instants of time. If in an intermediate state we reverse all velocities, we get an exceptional case, where H increases for a certain time and then decreases again. But the existence of such cases does not disprove our theorem. On the contrary, the contrary, the theory of probability itself shows that the probability of such cases is not extremely zero, only extremely small. Hence Mr. Barbour is wrong, if he concedes that H increases in as many cases as it decreases, and Mr. Culverwell is also wrong, if he says that all that any proof can show is, that taking all values of $dH/dt$ got from taking all the configurations which approach towards a permanent state, and all the configurations which approach towards, and then striking some average, $dH/dt$ would be negative. On the contrary, we have shown the possibility that H may have a tendency to decrease, whether we pass to the right or to the left of the latter configuration. What I proved in my paper is as follows: It is extremely probable that H is very near to its minimum value; if it is greater, it may be nearly so, but it cannot be so unless its probability that it decreases is always greater. Thus, if I obtain a certain value for $dH/dt$, this result does not hold for every time- element, but it is only an average value. But the greater the number of molecules, the smaller is the time-interval $dt$ for which the result holds good.

If Mr. Culverwell says that my theorem cannot be true because if it were true every atom of the universe would have the same average $\bar{v} \bar{v}$, and all energy would be dissipated. I find, on the contrary, that this argument only tends to confirm my theorem, which requires only that in the course of time the universe must tend to a state where the average $\bar{v} \bar{v}$ of every molecule is the same and all energy is dissipated, and that is indeed the case. Let us ask how far the universe has not yet reached, we again come to a "Selfisharian mystery." I will end this paper with an idea of my old assistant, Dr. Schaets. We assume that the whole universe is, and rests for ever, in thermal equilibrium. The probability that one (only one) part of the universe is in a certain state, is the smaller the further this state is from thermal equilibrium; but this probability in greater, the greater is the universe itself. If we assume the universe great enough, the probability that some relatively small part being in any given state (however far from the state of thermal equilibrium), as great as we please, that is, we cannot imagine the improbability of such a state. But can we imagine, on the other side, how small a part of the whole universe this is? Assuming the universe great enough, the probability that such a small part of it as our world should be in its present state, is no longer small.

If this assumption were correct, our world would return more and more to thermal equilibrium; but because the whole universe is so great, it might be probable that at some future time another other-world might deviate as far from thermal equilibrium as our world does at present. Then the above-mentioned H-curve would form a representation of what takes place in the universe. The summits of the curve would represent the worlds which viable motion and life exist, the flat parts of the curve the worlds which have only the barycenter, the lowest point of the curve the worlds which have no motion or life at all. If we imagine the barycenter at the origin, the axis $x$ would be the time axis, the axis $y$ would be the axis of energy. The value of $y$ would represent the energy, or the inverses of the absolute temperatures of the worlds. The value of $x$ would represent the age of these worlds. If we imagine the axis $y$ to be divided into parts $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, $\frac{1}{5}$, $\frac{1}{6}$, $\frac{1}{7}$, $\frac{1}{8}$, $\frac{1}{9}$, $\frac{1}{10}$, $\frac{1}{11}$, $\frac{1}{12}$, $\ldots$ marks, we find the " changed worlds" which have lost all the energy they had at birth, and so on up to the "unchanged worlds" which have not yet lost any energy. The plane of the two axes would represent the universe of all possible worlds. The axis $x$ would be the time axis, the axis $y$ the axis of energy. The value of $y$ would represent the energy, or the inverses of the absolute temperatures of the worlds. The value of $x$ would represent the age of these worlds. If we imagine the axis $y$ to be divided into parts $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, $\frac{1}{5}$, $\frac{1}{6}$, $\frac{1}{7}$, $\frac{1}{8}$, $\frac{1}{9}$, $\frac{1}{10}$, $\frac{1}{11}$, $\frac{1}{12}$, $\ldots$ marks, we find the " changed worlds" which have lost all the energy they had at birth, and so on up to the "unchanged worlds" which have not yet lost any energy. The plane of the two axes would represent the universe of all possible worlds.