

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 Muir charged me with appropriating the work of Olszewski 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 unless it is answered. But as I can conceive nothing more uninteresting to your readers or myself, than a mere dialectical controversy with Mr. Muir, my reply to his letter published on the 21st will be brief.

"A careful study" of my previous letter has not enabled Mr. Muir 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 convicted me of dishonest appropriation of another man's work.

The third claim found in my reply by Mr. Muir, which is the all-important one, is, to use his own language, that in "1886 I liquefied oxygen by passing the gas through a long copper coil surrounded by liquid ethylene, and that my apparatus made it possible to transfer the liquid oxygen to a glass vessel wherein it could be used as a cooling agent." Well, the only question here is 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 Mr. Muir shirks.

Until Mr. Pattison Muir can declare that after trial an apparatus constructed according to the plan given in 1886 is essentially defective, and will not deliver liquid oxygen in a manner at all comparable to the Olszewski steel cylinder, described in the Cracow *Bulletin* of 1890, let him acknowledge at least that the case of Prof. Olszewski, 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 me to have made, Mr. Muir falls back upon a general attack upon the scientific work "that is attributed to the Fullerian Professor at 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, radiation at low temperatures, thermal transparency of liquid gases, refractive indices of oxygen, nitrogen, and air; spectroscopy of liquid oxygen and air, thermo-electric inversions, latent and specific heats, chemical action, magnetic properties, breaking stress of metals, solid matter and argon in liquid air, phosphorescence and photographic action, liquefaction of hydrogen, &c. The abstracts of the results of these investigations have been published, and if Mr. Pattison Muir would only take a little trouble he could find them. In due course, and when I think proper, fuller details will be published. Mr. Muir's case is, however, that my intellectual paper comes from Cracow, and that I have followed in the wake of the researches of his client. On referring to Prof. Olszewski's record of work since his alleged invention of the way to use liquid oxygen as a cooling agent in 1890, I find that with the exception of the refractive index of oxygen, which was anticipated by Prof. Liveing and myself, and an attempt to confirm the late Prof. Wroblewski's critical constants of hydrogen, the work carried on at the Royal Institution and at Cracow have had nothing in common. It is not my business to inquire why Prof. Olszewski should take five years over this work, any more than it is legitimate for Mr. Muir to complain that I ought to have done more with my apparatus of 1886, than cool a piece of meteorite or expand liquid oxygen into a vacuum. No doubt by implication Mr. Muir intends to convey that any success at the Royal Institution was due to the use of a steel cylinder instead of the copper coil of 1886, and that suggestion I have to emphatic-

ally contradict, seeing that a steel cylinder never was used in any part of the apparatus employed for the liquefaction of gases. Under the circumstances it will be for Mr. Pattison Muir to explain what new information I could derive from Prof. Olszewski's alleged invention of 1890 which had not been already involved in the construction and use of my 1886 apparatus. All this, however, does not relieve Mr. Muir from his embarrassment. He charged me with having attributed to myself work done by other men, and to this charge I pin him. Having failed in his first attack, he has changed his ground, ignored the evidence of dates and facts which he cannot overthrow, and made a second attack in a form chosen by himself. This also has failed ignominiously. It is to be hoped that in future, when scientific investigators enter on priority discussions, the real combatants will be left to their polemics without the interference of third persons.

Royal Institution, February 26.

JAMES DEWAR.

On Certain Questions of the Theory of Gases.

§ 1. I PROPOSE to answer two questions:—

(1) Is the Theory of Gases a true physical theory as valuable as any other physical theory?

(2) What can we demand from any physical theory?

The first question I answer in the affirmative, but the second belongs not so much to ordinary physics (let us call it ortho-physics) as to what we call in Germany metaphysics. For a long time the celebrated theory of Boscovich was the ideal of physicists. According to his theory, bodies as well as the ether are aggregates of material points, acting together with forces, which are simple functions of their distances. If this theory were to hold good for all phenomena, we should be still a long way off what Faust's *famulus* hoped to attain, viz. to know everything. But the difficulty of enumerating all the material points of the universe, and of determining the law of mutual force for each pair, would be only a quantitative one; nature would be a difficult problem, but not a mystery for the human mind.

When Lord Salisbury says that nature is a mystery,¹ he means, it seems to me, that this simple conception of Boscovich is refuted almost in every branch of science, the Theory of Gases not excepted. The assumption that the gas-molecules are aggregates of material points, in the sense of Boscovich, does not agree with the facts. But what else are they? And what is the ether through which they move? Let us again hear Lord Salisbury. He says:

"What the atom of each element is, whether it is a movement, or a thing, or a vortex, or a point having inertia, all these questions are surrounded by profound darkness. I dare not use any less pedantic word than entity to designate the ether, for it would be a great exaggeration of our knowledge if I were to speak of it as a body, or even as a substance."

If this be so—and hardly any physicist will contradict this—then neither the Theory of Gases nor any other physical theory can be quite a congruent account of facts, and I cannot hope with Mr. Burbury, that Mr. Bryan will be able to deduce all the phenomena of spectroscopy from the electromagnetic theory of light. Certainly, therefore, Hertz is right when he says:² "The rigour of science requires, that we distinguish well the undraped figure of nature itself from the gay-coloured vesture with which we clothe it at our pleasure." But I think the predilection for nudity would be carried too far if we were to forego every hypothesis. Only we must not demand too much from hypotheses.

It is curious to see that in Germany, where till lately the theory of action at a distance was much more cultivated than in Newton's native land itself, where Maxwell's theory of electricity was not accepted, because it does not start from quite a precise hypothesis, at present every special theory is old-fashioned, while in England interest in the Theory of Gases is still active; *vide*, among others, the excellent papers of Mr. Tait, of whose ingenious results I cannot speak too highly, though I have been forced to oppose them in certain points.

Every hypothesis must derive indubitable results from mechanically well-defined assumptions by mathematically correct methods. If the results agree with a large series of facts, we must be content, even if the true nature of facts is not

¹ Presidential Address to the British Association at Oxford.

² Hertz, "Untersuchungen über die Ausbreitung der elektrischen Kraft," p. 31. (Barth, Leipzig, 1892.)

revealed in every respect. No one hypothesis has hitherto attained this last end, the Theory of Gases not excepted. But this theory agrees in so many respects with the facts, that we can hardly doubt that in gases certain entities, the number and size of which can roughly be determined, fly about pell-mell. Can it be seriously expected that they will behave exactly as aggregates of Newtonian centres of force, or as the rigid bodies of our Mechanics? And how awkward is the human mind in divining the nature of things, when forsaken by the analogy of what we see and touch directly?

The following assumptions, 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 Boscovich's standpoint.

Let 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 Kelvin's vortex rings move through a frictionless liquid in ordinary hydrodynamics. If we were to take a vessel filled with one gram of gas kept during an infinitely long time always at 0° C. and containing always the same portion of ether, every atom of ether and every atom of our gas molecules would reach the same average *vis viva*. If then we were to raise the temperature to 1° C. and to wait till every ponderable and every ether atom was in thermal equilibrium, the total energy would be augmented by what we may call the ideal specific heat. 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 is not at all 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 quite 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 vibrations of the ether can transfer sensible energy from one ponderable body to another, and therefore a correction for radiant heat must be applied to observations of specific heats. 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 Hertzian waves are not caused by vibrations of the ponderable matter of the brass balls, the form of which only 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 *vis viva* 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 were enclosed for an infinitely long time in the same vessel with the molecules of the gas.

But how can the molecules of a gas behave as rigid bodies? Are they not composed of smaller atoms? Probably they are; but the *vis viva* 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 *vis viva* of their internal vibrations corresponding to the original temperature. This transference of energy, in fact, takes place so slowly that it cannot be perceived amid the fluctuations of temperature of the surrounding bodies. The possibility of the transference of energy being so gradual cannot be denied, if we also attribute to the ether so little friction that the Earth is not sensibly retarded by moving through it for many hundreds of years.

If the ether be 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 electric 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 differ in their motions of approach and separation, 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 Gassiot's tubes 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. For then I have shown that the problem is not insoluble, and nature will have found a better solution 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, "Bemerkungen über einige Probleme der mechanischen Wärmetheorie," *Sitz. ber. der k. Wien. Acad.* vol. lxxv. 1877. 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 dynamics alone.

Let us compare 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

$$\int \frac{dQ}{T} < 0,$$

then for the second we must have

$$\int \frac{dQ}{T} > 0.$$

That is, if under certain conditions

$$\int \frac{dQ}{T} < 0,$$

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

$$\int \frac{dQ}{T} > 0.$$

In the same manner, Mr. Culverwell wishes to refute my Minimum Theorem. Mr. Culverwell's reasoning is suspicious, 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 diffusion 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.

Though interesting and striking at the first moment, Mr. Culverwell's arguments rest, 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 H must always decrease. It can only be deduced from the laws of probability, that if the initial state is not specially arranged for a certain purpose, but haphazard governs freely, the probability that H decreases is always greater than that it increases. It is well known that the theory of probability is as exact as any other mathematical theory, if properly understood. If we make 6000 throws with dice, we cannot prove that we shall throw any particular number exactly 1000 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 $1/6$ the oftener 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 abscissæ and draw the curve, whose ordinates are the corresponding values of H . The greater 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 certain, though very few, summits or maximum ordinates which rise to a greater height than H (min.).

We will 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 in a part of the curve ascending to or descending from a higher summit. Then the ordinates on the one side of H_1 will be greater, and on the other less than H_1 . But because higher summits are so extremely improbable, the first case will be the most probable, and if we choose an ordinate of given magnitude H_1 guided by haphazard in the curve, it will be not certain, but very probable, that the ordinate decreases if we go in either direction.

We will now assume, with Mr. Culverwell, a gas in a given state. If in this state H is greater than H (min.) it will be not certain, but very probable, that H decreases and finally reaches not exactly but very nearly the value H (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 theory of probability itself shows that the probability of such cases is not mathematically zero, only extremely small.

Hence Mr. Burbury 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 recede from it, 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 former or to the latter configurations. What I proved in my papers is as follows: It is extremely probable that H is very near to its minimum value; if it is greater, it may increase or decrease, but the 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 dt , but 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.

I will not here repeat the proofs given in my papers; I will only show that just the same takes place in the much simpler case of dice. We will make an indefinitely long series of throws with a die. Let A_1 be the number of times of throwing the number 1, among the first $6n$ throws, A_2 the number of times of throwing 1, among all the throws between the second and the $(6n+1)$ th inclusive, and so on. Let us construct a series of points in a plane, the successive abscissæ of which are

$$0, \frac{1}{n}, \frac{2}{n}, \frac{3}{n}, \dots$$

the ordinates of which are

$$y_1 = \left(\frac{A_1}{n} - 1\right)^2, y_2 = \left(\frac{A_2}{n} - 1\right)^2 \dots$$

let us call this series of points the "P-curve." If n is a large number, the greater proportion of the ordinates of this new 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 B." Since for each point $y = (A/n - 1)^2$, therefore for the points B we have $A = 2n$; these points mark, therefore, the case where, by chance, we have thrown the number 1 in $2n$ out of $6n$ throws. If n is at all large, that is extremely improbable, but never absolutely impossible. Let v be a number much smaller than n , and let us go forward from the abscissa of each point B through a distance = $6v/n$ 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 go backward (i.e. in the direction of x negative) from the abscissa of each point B through a distance = $6v/n$, it would be probable that we should meet ordinates > 1. But this inference is not correct. Whether we go in the positive or in the negative direction the ordinates 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. $2n$ throws out of $6n$ turning up 1). If we move in the positive or negative direction along the axis of x through the distance $1/n$, we exclude one of the $6n$ throws, and we include a new one. When we move forward through the distance $6v/n$, we have excluded $6v$

of the original throws, and included $6v$ others. Among the excluded throws we have probably $2v$, among the included ones v throws of the number 1. Therefore the probable diminution of A is v , the probable diminution of y is $2v/n$ approximately. Because the variation of x was $6v/n$, we may write

$$\frac{dy}{dx} = -\frac{1}{3}$$

But this is not an ordinary differential coefficient. It is only the average ratio of the increase of y to the corresponding increase of x for all points, whose ordinates are = 1. The P-curve belongs to the large class of curves which have nowhere a uniquely defined tangent. Even at the top of each summit the tangent is not parallel to the x -axis, but is undefined. In other words, the chord joining two points on the curve does not tend towards a definite limiting position when one of the two points approaches and ultimately coincides with the other.¹ The same applies to the H-curve in the Theory of Gases. If I find a certain negative value for dH/dt , that does not define the tangent of the curve in the ordinary sense, but it is only an average value.

§ 3. Mr. Culverwell says that my theorem cannot be true because if it were true every atom of the universe would have the same average *vis viva*, 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 *vis viva* of every atom is the same and all energy is dissipated, and that is indeed the case. But if we ask why this state is not yet reached, we again come to a "Salisbury mystery."

I will conclude this paper with an idea of my old assistant, Dr. Schuetz.

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 is greater, the greater is the universe itself. If we assume the universe great enough, we can make the probability of one relatively small part being in any given state (however far from the state of thermal equilibrium), as great as we please. We can also make the probability great that, though the whole universe is in thermal equilibrium, our world is in its present state. It may be said that the world is so far from thermal equilibrium that 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 world 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 some other world might deviate as far from thermal equilibrium as our world does at present. Then the afore-mentioned H-curve would form a representation of what takes place in the universe. The summits of the curve would represent the worlds where visible motion and life exist.

LUDWIG BOLTZMANN.

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Oysters and Typhoid.

WITH reference to the article "Oysters and Typhoid," which appeared in your last issue, it may interest your readers to know that De Giaxa investigated some years ago the behaviour of the typhoid bacillus in sea-water, both in its natural and sterilised condition. He found that in ordinary sea-water the typhoid bacillus suffered very considerably in the competition with the numerous other water bacteria present, but it was still identified on the ninth day after it was first introduced. In sea-water in which all other bacteria had been destroyed, the typhoid bacillus was detected in very appreciable numbers on the twenty-fifth day. More recently, however, the existence of typhoid bacilli in sterilised sea-water has been examined by Cassedebat, and his results are not in accord with those obtained by Giaxa. Cassedebat found that whilst many pathogenic

¹ See Ulisse Dini, "Grundlagen für eine Theorie der Functionen einer reellen Veränderlichen" (Teubner, 1892, § 126), or Weierstrass, *Journal für die Mathematik*, Band 79, p. 23.