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XXX. *Of the Kinetic Theory of Gas, regarded as illustrating Nature.* By GEORGE JOHNSTONE STONEY, M.A., D.Sc., F.R.S., Vice-President, Royal Dublin Society*.

SCIENCE may be defined as the investigation of how nature works, of how and why events in nature occur.

This investigation is best carried on by employing the Physical Hypothesis, viz., that the objects of nature act on one another, either directly (action at a distance), or through intervening media (which by many is supposed to be an essentially different kind of action). Now, the objects of nature, in the more strict sense of that phrase, are syntheta of human perceptions and ultra-perceptions; and syntheta of perceptions cannot be what really act. Nevertheless, it is eminently useful to carry on our investigation under the physical hypothesis that it is they which act, and to confine our efforts to tracing out what effects this action must be supposed capable of producing, and under what laws it must operate, in order that it may account for what occurs in nature. This, however, is felt by many persons to be too abstract an attitude of mind; and to satisfy them, and create the plausibility which they demand, by relieving the fundamental conceptions of what is oppressively felt as the absurdity of supposing that syntheta of perceptions act, it is usual to supplement these syntheta by piling an aërial Pelion upon this solid Ossa, and by supposing that in addition to the *sensible object* which occupies any portion of space there is what is called *its material substance* occupying the same position, which, partly directly and partly by its motions, acts on other material substances [the æther being one of these material substances]. According to this, which is the prevalent hypothesis among both scientific and non-scientific men, it is these substances which travel about through space; and the sensible objects, which are what we see and feel, are supposed to accompany them in their wanderings by reason of the way in which they, the substances, act (usually through intermediate material agencies) upon our organs of sense †.

This is the usual point of view: but more careful thinkers

* From the Scientific Proceedings of the Royal Dublin Society of the 26th of June, 1895. Communicated by the Author.

† The author has endeavoured to trace out what it is that really occurs in all such cases. See his paper "On the Relation between Natural Science and Ontology," in the Scientific Proceedings of the Royal Dublin Society, vol. vi. (1890) p. 475.

will do well * to eschew this somewhat convenient, but by no means necessary, encumbrance upon the unadulterated process of physical investigation which treats the sensible objects themselves, the bare syntheta of perceptions and ultra-perceptions, as though they were what brought about the changes that occur in nature ; and which exclusively occupies itself in tracing out the laws that must, under this hypothesis, be in operation in order that the effects may be what they are.

Another and a very useful scaffolding which helps us in building up our investigation, is the introduction of forces between the physical cause (which is always the vicinity of some natural object) and the effect to be attributed to it under the physical hypothesis. We are thus enabled to speak of the acceleration of a stone in its fall towards the earth either as being due to the neighbourhood of the earth, or as being caused by a force of gravitation which acts on it, which force is, in its turn, regarded as brought into existence by the proximity of the earth to the stone. The introduction of this piece of intermediate scaffolding is of great service—

1. Because the force can be represented by a line whose length accurately represents the intensity, and whose direction accurately represents the direction of the effect upon the stone of the vicinity of the earth ;

2. Because the same effect upon the stone might have been due to other physical causes, as, for example, to a spring urging it forward, in which case the same piece of scaffolding, a force represented by the same line in the same position, would occupy its place between the cause and the effect ; and

3. Because the effect might have been different, while the physical cause remained the same—thus, if the stone lay on the ground, what the vicinity of the earth would have occasioned is stress between the stone and the ground.

Accordingly by referring effects in nature to the operation of forces, we are enabled in each case to indicate with accuracy the intensity and direction of the effect, without having to specify (*a*) which of several possible physical causes is the one in operation, or (*b*) which of the possible kinds of effect is that which is being produced : and this in practice is found to be an immense convenience.

* This course is much to be preferred, because it effectually avoids the risk of throwing dust in our own eyes. The justification of the Physical Hypothesis is its utility, not its truth—its incomparable efficiency as a means of investigating nature ; and it is better, though not essential, that students of Physics should make no mistake about a matter of this kind.

Such is an outline of the principles that underlie the dynamical investigation of nature, which is the form of investigation that penetrates most deeply into its secrets.

The dynamical investigation of nature being the most complete from the physicist's standpoint, is of course to be preferred to any other wherever it can be employed. Our present knowledge of astronomy, of rigid dynamics, of elasticity, of hydrodynamics, are among its great achievements. But there are other sciences in which we cannot penetrate so close to the origin of things, but which are, nevertheless, amenable to mathematical treatment onwards from a station less deep-seated. In these we begin with happily chosen equations, the truth of which we have not succeeded in tracing to their dynamical source in nature, but the consequences of which we can calculate and compare with what we observe to occur. Of this kind are the exquisite theory of light which was developed by M'Cullagh, and the enormous strides which our knowledge of electricity has made within the last half century, culminating in the marvellous electromagnetic theory of light.

In all such sciences we are greatly helped by mechanical illustrations, which may be regarded as working models, that, though they do not in the least profess to represent the unknown dynamical condition which exists in nature, furnish us with an apparatus which operates in ways that we can both compute and conceive, and which produces results that, in some important respects and within ascertainable limits, follow laws the same as or analogous to those that prevail in the part of nature which is illustrated by them. Of this kind is that most useful and simplest wave-theory of light which represents it by an undulation of mere transverse vibrations. Of the same kind are the various attempts to represent the "texture," which must prevail in the luminiferous æther*. And somewhat akin to these are those instructive analogies which can be traced out between different sciences, wherever in both the same differential equation governs the progress of events. Thus, when a current of electricity is turned on to a circuit, the current penetrates the wire from its surface towards its core, by the same law as that by which heat would, by conduction, be carried inwards from the surrounding dielectric—a process already familiar to us, and which, therefore, makes the sequence of events in the other case easily conceived.

Again it must be remembered that in every dynamical

* See Scientific Proceedings of the Roy. Dubl. Soc. vol. vi. p. 392, or Philosophical Magazine for June 1890, p. 467.

investigation, what the mathematician really investigates is not the problem presented by nature, but some simplification of it. The legitimacy of this process and its value depend upon the important circumstance that, in dynamics, a slight change in the data leads only, at least for a time, to a slight change in the result. Thus in computing the mutual perturbations of the planets, the planets may be treated as though they were spheres, made up of untextured spherical shells each of a uniform density throughout; and it may be left out of account that they approach to being spheroids, with mountains on their surface, irregularities of a like kind at greater depths, rocks in those mountains, minerals in those rocks, a different molecular texture in each mineral, tidal strains, heat expansions by day, contractions by night, and so on—perhaps seas and an atmosphere, vegetation and animals, all in constant and complicated movement; with numberless other details. Now it is legitimate to omit all these from our calculation, for though every one of them produces its effect in actual nature, the difference between the outcome of their joint operation and that computed from the greatly simplified data of the mathematician is too small to make any approach to being perceived by any human agency. Hence, for any purpose which is of use to man, the approximation arrived at by the simpler problem is sufficient, wherever the errors are of such a nature that they are not cumulative. Nevertheless, it should be clearly recognized that it is a mechanism illustrating nature, and not nature itself, that has been mathematically investigated. So it is with all dynamical investigations: the data of nature have to be simplified to bring the task within the range of man's power over mathematical analysis; and the result is satisfactory because of the important fundamental principle referred to above, that in dynamics a slight modification of the data furnished by nature may be safely made, because it leads only to there being a small difference between the calculated result and that which occurs in nature—of course care being taken in each case that the approximation of the computed result to what occurs in nature shall be sufficiently close for the object we have in view.

These criticisms need to be pressed with special emphasis when we are examining investigations into the dynamical condition of gases. Here we have to substitute for the data of nature others which differ from them in undesirable ways and to an undesirable extent, in order to arrive at data simple enough to be available as a basis for mathematical deductions. Nevertheless, some of the results are not appreciably affected by this too great simplification of the data: for instance,

those which are consequences of such general facts as that the molecules spend most of their time in travelling about in straight lines like missiles, without a preponderance of the kinetic energy of the motions in any one direction ; and the further fact that the interchange of energy which occurs during the encounters, and the immense number of these encounters, lead to a rapid distribution to other motions of any excess of energy which any one motion of any one molecule may possess, and thus both equalize the pressure throughout the gas and establish the prevalence of a constant average ratio between that portion of the energy which manifests itself in the journeyings of the molecules, and that which is occupied in internal motions of the *Ba* class.

In order to make this language intelligible, it is necessary to explain that in treating of gases it is convenient to use the word *motions* in a generalized sense, so as to include both motions proper and all other events which are brought about by imparting energy to the gas, and which thereby become depositories of energy. These motions or events may be first divided into the two classes A and B, external and internal events. The A or external events are simply the motions of the centres of inertia of the molecules between their encounters ; the B events are rotations or other motions, or changes of configuration, of the parts of a molecule relatively to one another, or electrical or other events ; any events, in fact, which can be brought about by an expenditure of energy. These may all be spoken of either as motions or events, using the term motions in its generalized sense.

Again, the B events require to be subdivided into three classes : *Ba* events, which readily exchange energy with the A events, *i. e.*, which are affected by the speed with which two molecules plunge into one another when an encounter takes place, and which in turn contribute in a marked degree towards determining with what velocities they shall separate when the encounter is over. In contrast to these, the *Bc* events (if any such exist, as is perhaps probable if the vortex theory of matter is true) are such as are *completely* isolated from the A and *Ba* events, and therefore neither gain nor lose energy in the encounters. Between the *Ba* and *Bc* events stand *Bb* events, which seem to be a conspicuous part of what is actually going on in all the real gases of nature. These *Bb* events are not wholly unaffected by the encounters, but in any one encounter gain or lose but little energy ; while after millions of encounters, the transference of energy, perhaps chiefly in one direction—from them to other events—may be appreciable. Events of this kind may produce even

conspicuous effects in times which appear to us very short, since in the ordinary air about us each molecule meets with a million of encounters in something like the seventh part of the thousandth of one second of time. In attempting to interpret the results furnished by our dynamical investigations, the extraordinary* rapidity with which the molecular events succeed one another in the actual gases of nature must be fully allowed for.

Another matter to be kept carefully in mind is that most of the dynamical investigations go on the assumption that interaction between molecules, and the interaction within a molecule of one part of the molecule upon another *are the only forces that intervene*; whereas in all actual gases there is also a continuous interchange of energy going on between some of the internal events of the molecules and the ocean of unceasing ætherial undulations in which they are immersed.

One most remarkable and instructive dynamical theorem is due to the keen insight of Clerk Maxwell and of Professor Boltzmann.

Maxwell discovered the important theorem that if generalized coordinates be used to represent the motion of any system of bodies, and if the *vis viva* can be expressed as a sum of squares of momenta † of these coordinates, then the average energy will, if once equally divided among the terms of this series, continue to be so divided.

Boltzmann has extended this theorem into the following:—

If the *vis viva* can be expressed as a symmetrical function of the second order of the momenta (which may include both squares and products) then momentoids—linear functions of the momenta—can be so constructed that the *vis viva* shall be a sum of squares of these momentoids multiplied by functions of the coordinates; and the average energy, if at any time equally divided, will thenceforth continue to be equally divided between the terms of this expression.

Under the Maxwell Theorem it is between the momenta, under the Boltzmann-Maxwell Theorem it is between the momentoids, that the equal partition of energy takes place. The number of the momentoids is the same as of the momenta, and each of these latter is associated with a distinct degree of freedom in the system. Hence, when the Maxwell Theorem holds, the energy is equally divided among the degrees of

* See the description of an illustrative model in the last paragraph of this paper.

† A momentum may be defined as the differential coefficient of one of the coordinates with respect to time, multiplied by a coefficient which may be any function of the coordinates.

freedom ; but it is between certain quasi-groups of these degrees of freedom that the partition takes place under the Boltzmann-Maxwell Theorem. These quasi-groups, like the momentoids which define them, are of the same number as the degrees of freedom.

In most cases, where the only forces intervening are interactions between parts of the system, the energy can be expressed in the form required by the theorem. But this is not the case when certain external forces * come into operation, as, for example, when the æther acts on molecules as well as the molecules or parts of a molecule on one another.

Nevertheless, the theorem is of value in the interpretation of nature, because in many cases the æther intervenes somewhat as perturbing forces do in the case of the planets, modifying but not annulling the dynamical condition which would prevail if the sun's attraction alone exercised dominion over them.

On the other hand, it must be remembered that such a vast number of molecular events are crowded together within a duration that appears very short to us, that small effects have superabundant opportunity of gradually accumulating and becoming conspicuous, within a small fraction (*e. g.* within the thousandth part) of one second of time.

In estimating the average energy, the average may be struck either over a great succession of events happening to one molecule, or over what occurs simultaneously to a vast number of molecules †.

* Certain internal forces also : for example, such as manifest themselves in a change of state or in a chemical reaction. The theorem does not hold over intervals of time extending from an epoch before to an epoch after catastrophes of this kind.

† In Maxwell's and Boltzmann's investigations the averages have been struck only in the second way, *viz.*, over what occurs simultaneously to a vast number of molecules ; but general dynamical considerations seem to warrant our feeling sure that the average, if struck in the other way, *i. e.*, over a great succession of events happening to one molecule, would have the same value—on the understanding, of course, that the molecules are alike, and that the condition of the gas, in the respects with which the theorem is concerned, is a persistent condition.

In fact, it then seems safe to assume that in the course of a sufficiently long experience the coordinates and momenta of any one molecule will have approximately assumed all the combinations of values that the coordinates and momenta of any other molecule shall have had.

This is the same kind of assumption as the familiar assumption that if n dice (n being a sufficiently large number) were thrown simultaneously, sixes would turn up on a number of these dice which bears to the number of times sixes would turn up on one die thrown n times, a ratio which may be treated as a ratio of equality.

The importance and value of these results depend :—

1. On the small volume and the short time, as estimated by what are involved in human experiments, which suffice for the requisite averages—since each cube of a micron (the thousandth part of a millimetre) in the volume of the gas contains about 1000 millions of molecules* if it be under the same pressure and temperature as atmospheric air, and each of these molecules meets with about seven million encounters within the thousandth part of one second.

2. They also depend on the principle recited above, viz.—that if the data of a dynamical theorem be slightly altered, the conclusions are only disturbed to a small extent.

3. And they depend on the circumstance that the forces to be taken account of in applying the theorem may be confined to such forces as are concerned in those events which either directly or indirectly influence the motions of molecules in their journeys between their encounters. If, accordingly, there be any events of the kind which we have termed *Bc* events, they and the forces concerned in them may be kept outside the theorem, and may exist and involve any amount of energy ; which energy is, however, additional to that which in the theorem is regarded as the total energy, which is to be understood as the total of the energy of the events with which the theorem is concerned.

The following mechanical illustration, which is that usually employed, will enable us better to grasp the meaning and appreciate the value of these remarks. In it I will suppose the gas to be of one kind, with molecules that are all alike, and that the number of molecules and the average duration of a journey are what they are in atmospheric air at the surface of the earth.

The simplest way of fulfilling the condition that the expression for the energy shall be a sum of squares, is to provide a mechanical model in which the whole energy is kinetic; and the simplest way of securing this is to suppose each molecule to be a rigid elastic body, with a frictionless surface. The expression for the energy of the molecule will then take the familiar form :

$$T = \frac{1}{2} [M(u^2 + v^2 + w^2) + A\omega_1^2 + B\omega_2^2 + C\omega_3^2],$$

where the letters have their usual meanings. Here each term in the expression corresponds to one of the six degrees of freedom of the rigid body, and the theorem states that the

* See *Phil. Mag.* for August 1868, p. 141.

time-integrals of the several terms of this expression are equal, and that the average value of T is $1/N$ th of the total energy in the gas, N being the number of molecules; in other words, that the molecule exhibits one-sixth of its share of the total energy in each of the following ways, viz.:—1°, in its journeyings east and west; 2°, north and south; 3°, up and down; 4°, 5°, 6°, in spinning on each of its three principal axes. To simplify the conception as much as possible, we may suppose our model of a molecule to be a smooth ellipsoid of uniform density.

Let us next represent the molecules by ellipsoids of revolution. The full expression for the energy of such a body is—

$$T = \frac{1}{2} [M(u^2 + v^2 + w^2) + A\omega_1^2 + B(\omega_2^2 + \omega_3^2)], \quad (1)$$

but for the purposes of the theorem it may * be reduced to—

$$T' = \frac{1}{2} [M(u^2 + v^2 + w^2) + B(\omega_2^2 + \omega_3^2)], \quad (2)$$

since rotation round the axis of symmetry can neither be set going by the kinetic energy with which the molecules collide, nor if maintained in any other way can it in the least influence the values of u , v , and w .

The model when dealt with in this way is instructive, because it illustrates, as Mr. Bryan has pointed out (Proceedings of Cambridge Phil. Soc. of Nov. 26, 1894), how a motion may exist in a molecule which does not come under the theorem, and which therefore may be going on with any amount of energy.

To describe the situation in other and very convenient language, the motions of translation of the ellipsoids of revolution between their encounters are A events, and the energy of these events, viz.:—

$$\text{Average value of } \Sigma \frac{1}{2} M(u^2 + v^2 + w^2)$$

* It is very necessary to bear in mind that, so far as the theorem is concerned, it is optional with us whether we make this reduction from 6 to 5 terms or not. But if we retain the term $\frac{1}{2} A\omega_1^2$, we must remember that the theorem only deals with motion subsequent to an initial condition *in which an equal partition of energy had been made* among the terms. It states that *if* this condition existed initially, it will continue subsequently; and this is evident so far as the rotation round the axis of symmetry is concerned, since, if this rotation were once set up, it would continue unchanged. For some purposes we must retain the six terms, *e.g.* in order to see how the transition from the case of a solid of revolution to the case of a solid which differs but little from a solid of revolution, takes place without an abrupt change in the effect predicted by the theorem, so as to comply with the general principle of continuity in dynamics.

is $3/5$ of the whole of that energy of the mechanical model which comes under the notice of the theorem. The rotations ω_2 and ω_3 are *Ba* events, and their energy, viz. :—

$$\text{Average value of } \Sigma \frac{1}{2} B(\omega_2^2 + \omega_3^2)$$

is $2/5$ of the energy dealt with by the theorem. The rotation ω_1 is a *Bc* event, which can be kept outside the theorem. In it, accordingly, any amount of energy may reside.

Another instructive mechanical illustration is constructed by considering each molecule as a rigid ellipsoid of one uniform density surrounded by a rigid envelope of another uniform density, extending from the surface of the ellipsoid to the smooth surface of an outer concentric sphere (see Bryan, *loc. cit.*). Such a complex molecule may represent a diatomic molecule with only three of its degrees of freedom operated upon during collisions. Here the energy of the molecule is

$$T = \frac{1}{2} [M(u^2 + v^2 + w^2) + A\omega_1^2 + B\omega_2^2 + C\omega_3^2],$$

whereas the part concerned in the theorem is only

$$T' = \frac{1}{2} M(u^2 + v^2 + w^2),$$

since the external surface being a smooth rigid sphere round the centre of inertia, the collisions cannot set up rotations.

In this case u , v , and w are *A* events ; and, on the average, divide equally among themselves the share of energy coming to this molecule under the theorem. At the same time the rotations ω_1 , ω_2 , ω_3 are *Bc* events, and may be going forward, subject only to the equations of the rotation of a rigid body round its centre of inertia, viz. :—

$$T'' = \frac{1}{2} (A\omega_1^2 + B\omega_2^2 + C\omega_3^2),$$

$$G = A^2\omega_1^2 + B^2\omega_2^2 + C^2\omega_3^2.$$

Their energy T'' may, accordingly, be of any amount in each molecule separately.

We have hitherto had only *A*, *Ba*, and *Bc* motions in our illustrative models. *Bc* events are of little practical interest ; whereas the study of *Bb* events is of much use, since they are probably present in large amount in actual gases. It is easy to modify our mechanical illustration so as to introduce events of this class. It may be done in either of the models we have employed by imagining the surface to be roughened (either by a small amount of friction or in the sense of being covered with slight frictionless elevations and depressions), and by

supposing electrons (the charges of electricity which are associated with chemical bonds, and which, so long as they are undisguised, are acted on by the disturbance perpetually going on in the surrounding æther) to be carried about by the internal or B events of the molecule. To complete the picture we may suppose most of these electrons to be so connected with the internal economy of the molecule that they can only perform evolutions that are resolvable into partials that have definite periods.

Before this change the internal events were Ba and Bc events, but, owing to the introduction of the slight roughness, the Bc events have become Bb events; *i.e.* they have acquired the power of very slowly, and through a great number of collisions, affecting *u*, *v*, and *w*, which are the A events. But even if the roughness be so slight that they require a million of collisions to impart a sensible proportion of their energy to the A events, they will accomplish a protracted task of this kind in about the seventh part of the thousandth of one second, if, as we have supposed, the rapidity of events in our model is as great as it is in gases at atmospheric pressures and temperatures. Now, observations with the phosphoroscope indicate that the persistence of Bb events, when once excited, is in all the observed cases much greater; so that the outer surfaces of our model molecules should be *very* nearly, though not quite, smooth. Other experiments which are in progress seem to show that, in some instances at least, the energy radiated away from phosphorescent events is much less than that which they lose by conduction, *i.e.* by imparting energy to A or Ba events. Now an excessively small defect in smoothness, such as we have supposed, would not prevent the Boltzmann-Maxwell distribution of energy from being nearly the actual distribution among A and Ba events, wherever the other conditions of the theorem are, or are nearly, fulfilled; while side by side with them any amount of energy may be maintained in Bb events by the electromagnetic waves which unremittingly traverse the surrounding æther, or may be set up by chemical reaction*.

* It is easy to contrive other useful models, and to treat them like those in the text. Of this kind are models with spherical, spheroidal, or ellipsoidal outer surfaces, but with centres of inertia, either displaced from the centre of figure, or moving about it under definable conditions; or with more than one body inside the outer surface, and either concentric or not concentric with it, and with viscous or other connexions which would provide for various kinds of interaction; or with the rigid outer surface discarded, and central forces put in its place—a substitution which either need not, or need not more than a little, alter the condition that the average energy shall be a sum of squares; and many others. Each

Another important matter to be referred to is that in the cases in which the theorem holds good, γ , the ratio of the two specific heats (at constant pressure and at constant volume) has the following value—

$$\gamma = 1 + \frac{2}{m},$$

where m is the number of terms—each the square of a momentoid multiplied by a selected coefficient—in the expression for the energy. Now observation gives γ in many cases, and we thus arrive, by the foregoing equation, at m , the number of the terms in the expression of T , which is the same as the number of degrees of freedom in the molecule of those events with which the theorem is concerned, if the constitution of the gas be such that the theorem approximately applies to it. To what motions these degrees of freedom are to be supposed to correspond will depend on what experiment has been made use of in determining γ . If the experiment is one that lasts a long time—for instance a whole second or more—then the Bb motions as well as the A and the Ba motions will usually have had abundant time to operate; but if it depends on rapidly changing events, as where the velocity of sound in the gas is the fact that is ascertained, then we may expect that some of the Bb events will be unable to influence the result. It is very convenient to distinguish the internal events into Ba motions and Bb motions; but it must be remembered that this distinction is one of degree, and that, although in most gases they appear as different as is the chin from the cheek, it would nevertheless be quite as impossible to indicate precisely where the one ends and the other begins.

The following table of the best determinations of γ is given by Mr. Capstick in 'Science Progress' for June 1895. I have added the last two columns in which are given the values of m which the determinations would suggest, if the Boltzmann-Maxwell theorem could be regarded as holding good for the gas.

In this table, γ is the ratio of the two Specific Heats, as given by observation; m is the number of degrees of freedom of each molecule; and $m-3$ is the number of degrees of freedom of its B , or internal, motions: according to the Boltzmann-Maxwell theorem.

may be in its way instructive if we use it to enable us to picture modes of action that occur in gases, and if we are careful not to be misled into fancying that any of our models can be accepted as even in a remote degree resembling the state of things that does prevail within the molecules of matter.

Name of Gas.	Chemical Formula of Molecule.	Atomicity of Molecule.	Observed Value of γ .	Computed Value of	
				m .	$m-3$.
Mercury	Hg	1	1.67	3.0	0.0
Argon	Not yet known.		1.65	3.1	0.1
Transparent Gases.	Hydrogen.....	2	1.41	4.9	1.9
	Nitrogen		1.41	4.9	1.9
	Carbon monoxide ..		1.40	5.0	2.0
	Hydrochloric acid ..		1.39	5.1	2.1
	Hydrobromic acid ..		1.42	4.8	1.8
	Hydriodic acid ...		1.40	5.0	2.0
Coloured Gases.	Chlorine		1.32	6.2	3.2
	Bromine		1.29	6.9	3.9
	Iodine		1.29	6.9	3.9
	Iodine chloride ...		1.31	6.5	3.5
Carbon dioxide.....	CO ₂	3	1.308	6.5	3.5
Nitrous oxide	N ₂ O		1.310	6.5	3.5
Sulphuretted hydrogen ...	SH ₂		1.340	5.9	2.9
Carbon bisulphide	CS ₂		1.239	8.4	5.4
Ammonia	NH ₃	4	1.30	6.7	3.7
Methane	CH ₄	5	1.313	6.4	3.4
Methyl chloride	CH ₃ Cl		1.279	7.2	4.2
Methyl bromide	CH ₃ Br		1.274	7.3	4.3
Methyl iodide	CH ₃ I		1.286	7.0	4.0
Methylene chloride	CH ₂ Cl ₂		1.219	9.2	6.2
Chloroform	CHCl ₃		1.154	13.0	10.0
Carbon tetrachloride	CCl ₄		1.130	15.4	12.4
Silicon tetrachloride	SiCl ₄		1.129	15.6	12.6
Ethylene	C ₂ H ₄	6	1.260	7.7	4.7
Vinyl bromide	C ₂ H ₃ Br		1.198	10.1	7.1
Ethane	C ₂ H ₆	8	1.180	11.1	8.1
Ethyl chloride	C ₂ H ₅ Cl		1.187	10.7	7.7
Ethyl bromide	C ₂ H ₅ Br		1.188	10.6	7.6
Ethylene chloride.....	C ₂ H ₄ Cl ₂		1.137	14.7	11.7
Ethylidene chloride	C ₂ H ₄ Cl ₂		1.134	14.9	11.9
Allyl chloride	C ₃ H ₅ Cl	9	1.137	14.7	11.7
Allyl bromide	C ₃ H ₅ Br		1.145	13.9	10.9
Alcohol	C ₂ H ₅ OH		1.133	15.1	12.1
Propane	C ₃ H ₈	11	1.130	15.4	12.4
Normal propyl chloride ...	C ₃ H ₇ Cl		1.126	15.9	12.9
Isopropyl chloride	C ₃ H ₇ Cl		1.127	15.9	12.9
Isopropyl bromide	C ₃ H ₇ Br		1.131	15.4	12.4
Ethyl formate	HCO·OC ₂ H ₅		1.124	16.1	13.1
Methyl acetate	CH ₃ CO·OCH ₃		1.137	14.7	11.7

Postponing for the present the observations which the details of this table suggest, and taking a general survey of it, it was difficult to see how the small number of degrees of freedom suggested by the Boltzmann-Maxwell Theorem, as shown in the last column of this table, could be reconciled with the known great complexity of the molecules of which real gases consist, until Professor FitzGerald pointed out (Proceedings of the Royal Society for February 14, 1895, p. 312) that the æther, acting on the electrons, which in turn are intimately connected with the ponderable matter of the molecule, must perform the function of a more or less perfect linkage between molecules, compelling them, so far as some of their motions are concerned, to move together in swarms. This follows at once from the circumstance that the electromagnetic waves, in which radiant heat and light consist, are hundreds of times longer than the average intervals between molecules in gases at the pressures and temperatures at which the gases in the table were when experimented on to determine the value of γ .

There may be a hundred degrees of freedom in a molecule. Of these the three which are concerned in its power of travelling about between its encounters are not affected by what goes on in the æther, and are therefore inalienably associated with that molecule; but as regards the 97 others, the linkage through the æther may be such that millions of molecules are, as it were, held in one grasp, either firmly or more or less loosely. Accordingly, as regards any one molecule, these 97 may make no appreciable increase, or may make but a moderate increase to the three which in all cases must attach to the molecule. These three are A events, and along with them we should class the few Ba events which have no electrons associated with them, of which there seem to be two in several of the transparent diatomic gases.

We here seem to be led to another conclusion. If the æther were a mere linkage, and not at the same time an agency which excites simultaneous motions within swarms of molecules, it would appear from the Boltzmann-Maxwell theorem that none such would in any appreciable degree be brought into existence by the encounters between molecules. If, for example, the expression for T contains two B terms instead of 97, then only $\frac{2}{97}$ of the energy which is taken account of in the theorem would be available for distribution among 97 distinct kinds of motion, and therefore too little for any but a very few of them to be able to exhibit an observable effect. The rest, the Bb events, would all depend for their activity upon energy reaching the molecules as radiant heat

or in some other form through the æther, or in some other way, as, for example, from a disruption of chemical bonds. But though the encounters would be unequal to the task of arousing them from a state of quiescence, they, on their side, if brought into a state of activity by some other agency may be able to impart energy to A and Ba events, which are the proximate dynamical cause of the ordinary gaseous laws. This peculiar behaviour, whereby energy passes more freely one way than in the opposite direction, is a dynamical consequence of the linkage between molecules to which Professor FitzGerald has called attention. Owing to this linkage the encounters may have to produce an effect on a platoon of molecules in order to affect the Bb motions of any one of them; and as these encounters are many and irregular their aggregate effect can be but small wherever the linkage is effective; while, as regards the reaction, the body of linked Bb motions act in each encounter on the A or Ba motions of a single molecule and may produce a considerable effect on them. The dynamical relation is analogous to what would prevail between a number of light pellets bombarding a massive body on all sides. Their effect on the motion of the massive body is small, while its effect on their motions is large. It seems to be in this way that radiant heat can warm a gas through the lines in its spectrum, very slowly in the more transparent gases, less slowly in coloured gases.

An electron within a molecule may be associated with either its Ba or its Bb motions. Thus, when a phosphorescent body has been exposed to suitable light, it is an electron associated with Bb motions that is primarily acted on by the æther. Now phosphorescence is a very prevalent property of bodies, inasmuch as it has been ascertained by the phosphoroscope that a large proportion of the substances about us are phosphorescent. And although most of them, after being stimulated, retain their power of radiating light for but the fraction of a second, there are some phosphorescent substances in which it lasts for hours. It must be remembered that any fraction of a second which the phosphoroscope can detect is an immense duration as regards the rapidity of molecular events. Accordingly it is with Bb events that we are here dealing. All Bb events are sluggish from the molecular standpoint in handing over any excess of energy they may possess, either directly or indirectly, to the motions of translation of the molecule. But viewing the matter from our human standpoint, it is convenient to distinguish those which can accomplish this in a small fraction of a second from those which take so much longer a time that we can

easily perceive it. We may call the first Bb_1 events. These are they which can effect the transfer through some few millions of encounters. And we may call the still more isolated events Bb_2 events. These latter, for example, manifest their existence when phosphorescence lasts for a whole second or more—truly enormous durations as regards molecular activities.

When an electron is associated with Ba events it will promptly transfer over any excess of energy it receives from the æther to u , v , and w , the translational velocities of the molecule. Accordingly, on the one hand, the temperature and pressure of the gas will increase, on the other the ætherial undulations that acted on the electron will have ceased—in other words, the gas is one that has an absorption-spectrum.

If, at the other extreme, the electron is associated with Bc , or absolutely isolated events, a beam of light passing through the gas will, if it contain certain rays, set these electrons moving. They, however, will not impart any of their acquired energy to other events going on in the gas, but will continue swinging in all the molecules in coincidence with the electromagnetic wave as it sweeps past them in the æther; thus restoring to the latter the same amount of energy which they received, and in the form of an undulation travelling at the same rate, and in the same direction, and oscillating in the same periodic time. Thus, so far as regards the motion of this electron, the gas is transparent.

Between these extremes electrons associated with Bb events will lie, and may produce any intermediate event.

It is very instructive to glance over the determinations of γ in the table on p. 374. Take, for example, the diatomic gases. Six of them are transparent, and the other four are coloured. The transparent gases furnish values for γ which all lie in the neighbourhood of 1.4, which is the value which would correspond to a molecule having five degrees of freedom if the conditions of Boltzmann's theorem were completely fulfilled. In transparent gases they are probably not much interfered with, since in them the electrons are associated with Bb_2 events, and it is only after *many* millions of encounters that the æther can, through them, sensibly affect the A and Ba events with which the theorem is concerned. On the other hand, in the coloured gases one or more electrons (in these special gases probably something like six or eight electrons, judging from their spectra) are associated with Bb_1 events, and largely affect the events with which the theorem is concerned. They accordingly cause γ to be different from what it would be if the dynamical interactions stood alone,

which, judging from the transparent gases, we may conclude would be 1.4, furnished by 5 degrees of freedom. The B β motions in question would probably add something like three times 6 or 8 more degrees of freedom if the molecule stood alone, but by reason of the linkage only some fraction of this addition has to be made. It appears from the table that in chlorine, which is the least deeply-coloured gas, that is, the gas in which the linkage is most effective, the addition to be made is of 1.2 degrees of freedom; while in bromine and iodine an addition of 1.9 degrees of freedom has to be made, indicating that the linkage is more lax in these gases.

Since in so many bodies the electrons seem to be associated with events which are very much isolated from those that are chiefly affected by the encounters, the modification of the dynamical condition which is introduced through them may be regarded as a perturbation. It would perhaps not be impracticable to discover in what way perturbing forces, not obeying the conditions of the Boltzmann-Maxwell theorem, can influence the results of that theorem. This would be of much value; and if it can be made out, will perhaps explain why in some transparent diatomic gases the value of γ is above 1.4, while it is less than that value in others. The reason probably is that in hydrogen, nitrogen, and hydrobromic acid the motions associated with their two B α degrees of freedom are able to rouse a certain amount of activity in adjoining B β events, and that thus a part of their energy gets to be exposed to linkage.

Hitherto we have regarded molecules as acted on in two ways only—by dynamical interactions between or within the molecules, and by the effect of electromagnetic waves on such of the electrons as are undisguised charges of electricity. But there are other ways in which molecules may be acted on, of which the most conspicuous intervenes energetically on those critical occasions when chemical reaction takes place. Here it is the electrons that are primarily concerned, as is manifest from Faraday's law of electrolysis. In cases of friction also, or of disruption of a crystal, it is manifest that some of the electrons are started into activity. In fact it may be presumed that the intermolecular bonds within a crystal are fundamentally of the same kind as the interatomic bonds within a molecule, and that in both it is interaction between electrons that is principally called into play. It should also be noted that the number of electrons within an atom may be greater than its place in Mendeléeff's table would seem to suggest, as is, for example, evidenced by the chemical behaviour of potassium.

In chemical reactions, if the product is gaseous, and if the electrons which are set swinging are associated with Ba events, the most obvious effect is a sudden increase of temperature and pressure; if associated with Bb_2 events the most obvious effect is a flash of light; and if associated with Bb_1 events both effects will be conspicuous: and this, in accordance with what we learn through the phosphoroscope, would seem to be what most frequently happens.

It seems probable that it is when excited by chemical reactions that electrons produce their most conspicuous luminous effects, whether in flames or in so-called incandescent spectra. It should be remembered that as electrons are for the most part associated with Bb motions within the molecule, it may happen that they but slowly influence the temperature of the gas as indicated by the thermometer, and that accordingly the luminous effects may be greatly in excess of what a mere incandescent body at the same moderate temperature could produce. Hence the phrase incandescent spectrum is not always appropriate, since the supposition that the temperature inside a Plücker tube must be high is erroneous.

These inferences are entirely borne out by the recently published observations of Professor Lewes upon gas-flames (see Proceedings of the Royal Society for March 7 and March 21, 1895). He finds that the first group of chemical changes which the issuing gas undergoes are brought about by *radiant* heat; in other words, by electromagnetic waves in the æther acting on those electrons which are concerned in the chemical changes, and which, from their not being affected by convected heat, must be associated with Bb , and not with Ba events. In this way

are produced. Of these, acetylene is the one that, on decomposition, emits almost all the light. Professor Lewes finds that, on attaining a situation where the temperature is sufficient, the acetylene resolves into carbon and hydrogen, which subsequently combine with oxygen; and that in the brief interval one or both of them emit *more light than belongs to the temperature of that situation*; in other words, that one or more electrons associated with Bb motions have been roused into great activity by the decomposition, and have time to radiate abundantly, probably a long time from the molecular standpoint, before either they have expended their

excess of energy, or the combination with oxygen takes place, whichever event comes first.

The summary of the results of this recent investigation have been here translated into molecular language, to serve as an example of the additional insight which we may already hope to gain into the chemistry of nature by adopting the molecular standpoint; and whenever the secret of the motions of electrons within molecules becomes known this insight will doubtless be vastly increased. Through the spectroscope we seem to be on the borderland of this great discovery.

Reference has been made to chemical reaction, friction, and the disruption of a crystal, as events which may bring into a state of activity some of the electrons associated with *Bb* motions. Another event which seems to have this effect is the gaseous encounter between two molecules of the same kind. A suggestive experiment was made in the laboratory of the Royal Dublin Society, when Professor Emerson Reynolds, F.R.S., and the present author were engaged in examining the spectra of coloured vapours (*Philosophical Magazine*, July 1871, p. 41). We had examined the splendid absorption-spectrum of chlorochromic anhydride mixed with air. Here the encounters that the molecules of the vapour met with were most of them encounters with molecules of air, the minority only being encounters between molecules of the vapour. If the vessel containing the vapour be freed from air, the encounters between molecules of the vapour will be present in the same number as before, while all encounters between air and vapour will be absent. Hence we argued (for at that time we supposed the motions in the molecules to have been evoked by the undulation in the æther)*, that the molecules being less knocked about should produce a spectrum of lines that would be less diffuse. On trying the experiment, however, we found that the spectrum was sensibly the same as before. From this observation it would appear that the motions to which the spectrum is due are affected by the encounters between molecules of the

* The amplitude of the *Bb* motions which the undulation in the æther, if acting alone, can develop is apparently too small; and this is probably because, at this small amplitude, the transference of energy from *Bb* motions to *Ba* and *A* motions is inconspicuous. Where this is the case the ætherial undulation acting alone upon the gas cannot suffer any sensible amount of absorption. But the conditions are altogether different if some other agency produces an amplitude which can freely part with its energy by conduction, and which at the same time can be acted on by the æther in the direction which tends to keep the amplitude up. Under these circumstances there will be active withdrawal of energy from the æther, and an absorption-spectrum will result. This seems to be what happens in coloured gases.

[*Added September 1895.*—What seems a simpler and therefore more

vapour, and are uninfluenced by encounters between air molecules and vapour molecules. Hence they are due to something different from the mere kinetic energy of the collisions; and this something may be, and probably is, that during the struggle between molecules of the same kind, a struggle which is a protracted struggle from the molecular standpoint, there occurs either always, or now and then, an interchange of some of the chemical atoms constituting the molecules. This, which is equivalent to two chemical decompositions, followed by two equivalent chemical combinations, must set the electrons concerned into a state of more or less activity.

This interchange of atoms during the encounters is presumably the source, not only of such absorption-spectra as that of chlorochromic anhydride, but also of the bright spectra seen in Plücker's tubes.

If the gas be monatomic, the spectrum is probably emitted only when the circumstances are such that two molecules can temporarily coalesce into a diatomic molecule during the encounter, and become dissociated when the encounter is over; but in all cases where there is no ultimate change in the chemical constitution of the gas, its spectrum seems to be due to some event which is equivalent to equal and opposite chemical reactions having taken place during either all or some of the encounters.

An excellent way of helping us to appreciate the events with which we have to deal in molecular physics, is to conceive a model of them in which the durations shall all be enlarged 600 billions of times (6×10^{14}). This particular magnification is found to have special convenience attached to it*. If prolonged to this extent, the most rapidly recurring motions in nature that are *as yet* known to us, viz., those periodic events in a gas which give rise to the lines in its spectrum, would swing at rates comparable with the motions

probable explanation has been suggested to me by Professor FitzGerald. It is that the electrons are sufficiently linked together through the æther to be but little affected by the A and Ba events while on their side competent to influence such events, in the way described on p. 376. Under these circumstances the number of encounters might be increased by adding air, or otherwise, without perceptible effect on them; while they, if susceptible of being excited by light in the way that phosphorescent bodies are, would act as carriers of energy from the æther to the A and Ba events, thus causing absorption of light. It ought not to be impracticable to devise experiments which will determine with certainty which of the possible explanations is the real one.]

* Wave-lengths of rays of light are usually expressed as fractions of a micron, and pendulums beating the same fractions of a second represent the corresponding ætherial vibrations on the scale employed in the text.

of the limbs of animals, and would have about as great a range from the swiftest of them to the slowest. On the same immense time-scale the duration of the journeys of the molecules of ordinary air would average about one day each, while the encounter which closes each journey may last some 20 minutes*. The motions of the limbs of animals are able to accomplish a good deal in a struggle lasting 20 minutes. On the same scale, the ten-thousandth of a second of time grows to be an immense duration, extending to 1900 years. The number of struggles to be encountered by each molecule in the ten-thousandth of a second is accordingly the same as the number of days in the whole Christian Era, from the birth of Christ down to the end of the present century. If something can be done during the 20 minutes that one of the struggles may last, how great a task might be accomplished by such an enormous succession of them. It must be borne in mind, too, that these encounters are not mere repetitions of one another, but that each has its own definite incidents. Moreover, all this is what occurs in the experience of one individual molecule, so that we must multiply it by something like a thousand

* We may fill in this picture by combining a lengthening of distances with the prolongation of the times. A cubic millimetre, the volume of a small pin's head, if each of its edges were magnified 10^{10} times, would become almost as huge as the earth. Under the same circumstances molecules of air would be spaced at intervals averaging ten metres; and 700 metres would have become the mean distance to which they would travel between their encounters. On this great scale it would not be inappropriate to use men or other animals to represent the individual molecules—their hearts beating, their chests heaving, their limbs in vigorous motion to represent the B or internal events. And as to the motions with which the molecules of a gas dart about amongst one another, these as they exist in common air would have become journeys as long and of as various lengths as the streets of a great city, while the widths of the streets may stand for the intervals at which the representatives of the molecules are to be spaced asunder at starting.

In this model we have applied so much more magnification to time than to space that all the velocities come out 60,000 times slower than in nature. Accordingly our animated molecules must be conceived of as quietly gliding along the journeys they have to make between their encounters; for the mean duration of a journey is to be a day, and the average speed must accordingly be only half a metre per minute—on the supposition that our model is to represent what occurs in gas as dense as air and at its temperature and pressure. It thus appears that we must conceive them as requiring on the average about a quarter of an hour to get past each house in the streets along which they have so slowly to make their way.

A model of this kind is not without its use, if it were only as a means by which we can gain a lively perception of how considerable the events going on *within* the molecules may be when compared with the motions of translation of the molecules.

millions, in order to sum up what may be accomplished by all the encounters of all the molecules within one cubic micron* of gas in the ten-thousandth part of a second, and that we may in some degree understand how it comes to pass that opportunity is afforded in nature for accomplishing work which requires rare collocations of conditions that can but seldom emerge. Such is Nature's real laboratory—events in inconceivable numbers, the whole phantasmagoria of these innumerable events changing every instant down to its minutest details with inconceivable rapidity, the changes in most cases kept within limits, but in some exploring every part of a wide range: it is thus that those wonderful operations are carried on, which issue in the astonishing results that lie everywhere in such profusion around us. We seem almost to get an obscure and partial glimpse of how, in organic nature, tasks of the most unlikely kind are accomplished, through the needful opportunities now and then turning up within each tiny speck of so Protean a material as protoplasm, a body of which the mutations have probably time-relations of the same order as those we have been endeavouring to illustrate, and whose activities are therefore more incessant, more various, and more complex, within every thousandth of a second, in every speck and corner of each living cell, than the mind can even conceive. It is very little man yet knows of what is going on abundantly about him in every stick and stone.

XXXI. *On the Cryoscopic Relations of Dilute Solutions of Cane-Sugar and Ethyl Alcohol.* By HARRY C. JONES†.

THAT the van't Hoff‡ equation $t = 0.02 \frac{T^2}{W}$ does not hold for the lowering of the freezing-point of water produced by the presence of a very small amount of such a non-electrolyte as cane-sugar, is indicated by the work of Arrhenius§, Raoult||, Loomis¶, myself**, and others. While the molecular lowerings for dilute solutions of several non-electrolytes as found by Loomis are less than the calculated, the

* There are 70 or 80 cubic microns in the volume of each of the small disks in human blood.

† Communicated by the Author.

‡ *Zeit. f. phys. Chem.* i. p. 497.

§ *Ibid.* ii. p. 495.

|| *Ibid.* ix. p. 343.

¶ *Ber. d. deutsch. chem. Gesell.* xxvi. p. 797.

** *Phil. Mag.* xxxvi. p. 465 (1893); *Zeit. f. phys. Chem.* xii. p. 642.