

ON THE DYNAMICAL EVIDENCE OF THE MOLECULAR CONSTITUTION OF BODIES*

WHEN any phenomenon can be described as an example of some general principle which is applicable to other phenomena, that phenomenon is said to be explained. Explanations, however, are of very various orders, according to the degree of generality of the principle which is made use of. Thus the person who first observed the effect of throwing water into a fire would feel a certain amount of mental satisfaction when he found that the results were always similar, and that they did not depend on any temporary and capricious antipathy between the water and the fire. This is an explanation of the lowest order, in which the class to which the phenomenon is referred consists of other phenomena which can only be distinguished from it by the place and time of their occurrence, and the principle involved is the very general one that place and time are not among the conditions which determine natural processes. On the other hand, when a physical phenomenon can be completely described as a change in the configuration and motion of a material system, the dynamical explanation of that phenomenon is said to be complete. We cannot conceive any further explanation to be either necessary, desirable, or possible, for as soon as we know what is meant by the words configuration, motion, mass, and force, we see that the ideas which they represent are so elementary that they cannot be explained by means of anything else.

The phenomena studied by chemists are, for the most part, such as have not received a complete dynamical explanation.

Many diagrams and models of compound molecules have been constructed. These are the records of the efforts of chemists to imagine configurations of material systems by the geometrical relations of which chemical phenomena may be illustrated or explained. No chemist, however, professes to see in these diagrams anything more than symbolic representations of the various degrees of closeness with which the different components of the molecule are bound together.

In astronomy, on the other hand, the configurations and motions of the heavenly bodies are on such a scale that we can ascertain them by direct observation. Newton proved that the observed motions indicate a continual tendency of all bodies to approach each other, and the doctrine of universal gravitation which he established not only explains the observed motions of our system, but enables us to calculate the motions of a system in which the astronomical elements may have any values whatever.

When we pass from astronomical to electrical science, we can still observe the configuration and motion of electrified bodies, and thence, following the strict Newtonian path, deduce the forces with which they act on each other; but these forces are found to depend on the distribution of what we call electricity. To form what Gauss called a "construirbar Vorstellung" of the invisible process of electric action is the great desideratum in this part of science.

In attempting the extension of dynamical methods to the explanation of chemical phenomena, we have to form an idea of the configuration and motion of a number of material systems, each of which is so small that it cannot be directly observed. We have, in fact, to determine, from the observed external actions of an unseen piece of machinery, its internal construction.

The method which has been for the most part employed in conducting such inquiries is that of forming an hypothesis, and calculating what would happen if the hypothesis were true. If these results agree with the actual phenomena, the hypothesis is said to be verified, so long, at least, as some one else does not invent another hypothesis which agrees still better with the phenomena.

The reason why so many of our physical theories have been built up by the method of hypothesis is that the speculators have not been provided with methods and terms sufficiently general to express the results of their induction in its early stages. They were thus compelled either to leave their ideas vague and therefore useless, or to present them in a form the details of which could be supplied only by the illegitimate use of the imagination.

In the meantime the mathematicians, guided by that instinct which teaches them to store up for others the irrepressible secretions of their own minds, had developed with the utmost generality the dynamical theory of a material system.

* A lecture delivered at the Chemical Society, Feb. 18, by Prof. Clerk-Maxwell, F.R.S.

Of all hypotheses as to the constitution of bodies, that is surely the most warrantable which assumes no more than that they are material systems, and proposes to deduce from the observed phenomena just as much information about the conditions and connections of the material system as these phenomena can legitimately furnish.

When examples of this method of physical speculation have been properly set forth and explained, we shall hear fewer complaints of the looseness of the reasoning of men of science, and the method of inductive philosophy will no longer be derided as mere guess-work.

It is only a small part of the theory of the constitution of bodies which has as yet been reduced to the form of accurate deductions from known facts. To conduct the operations of science in a perfectly legitimate manner, by means of methodised experiment and strict demonstration, requires a strategic skill which we must not look for, even among those to whom science is most indebted for original observations and fertile suggestions. It does not detract from the merit of the pioneers of science that their advances, being made on unknown ground, are often cut off, for a time, from that system of communications with an established base of operations, which is the only security for any permanent extension of science.

In studying the constitution of bodies we are forced from the very beginning to deal with particles which we cannot observe. For whatever may be our ultimate conclusions as to molecules and atoms, we have experimental proof that bodies may be divided into parts so small that we cannot perceive them.

Hence, if we are careful to remember that the word particle means a small part of a body, and that it does not involve any hypothesis as to the ultimate divisibility of matter, we may consider a body as made up of particles, and we may also assert that in bodies or parts of bodies of measurable dimensions, the number of particles is very great indeed.

The next thing required is a dynamical method of studying a material system consisting of an immense number of particles, by forming an idea of their configuration and motion, and of the forces acting on the particles, and deducing from the dynamical theory those phenomena which, though depending on the configuration and motion of the invisible particles, are capable of being observed in visible portions of the system.

The dynamical principles necessary for this study were developed by the fathers of dynamics, from Galileo and Newton to Lagrange and Laplace; but the special adaptation of these principles to molecular studies has been to a great extent the work of Prof. Clausius of Bonn, who has recently laid us under still deeper obligations by giving us, in addition to the results of his elaborate calculations, a new dynamical idea, by the aid of which I hope we shall be able to establish several important conclusions without much symbolical calculation.

The equation of Clausius, to which I must now call your attention, is of the following form:—

$$pV = \frac{2}{3} T - \frac{2}{3} \sum \sum (\frac{1}{2} Rr).$$

Here p denotes the pressure of a fluid, and V the volume of the vessel which contains it. The product pV , in the case of gases at constant temperature, remains, as Boyle's Law tells us, nearly constant for different volumes and pressures. This member of the equation, therefore, is the product of two quantities, each of which can be directly measured.

The other member of the equation consists of two terms, the first depending on the motion of the particles, and the second on the forces with which they act on each other.

The quantity T is the kinetic energy of the system, or, in other words, that part of the energy which is due to the motion of the parts of the system.

The kinetic energy of a particle is half the product of its mass into the square of its velocity, and the kinetic energy of the system is the sum of the kinetic energy of its parts.

In the second term, r is the distance between any two particles, and R is the attraction between them. (If the force is a repulsion or a pressure, R is to be reckoned negative.)

The quantity $\frac{1}{2} Rr$, or half the product of the attraction into the distance across which the attraction is exerted, is defined by Clausius as the virial of the attraction. (In the case of pressure or repulsion, the virial is negative.)

The importance of this quantity was first pointed out by Clausius, who, by giving it a name, has greatly facilitated the application of his method to physical exposition.

The virial of the system is the sum of the virials belonging to every pair of particles which exist in the system. This is ex-

pressed by the double sum $\sum \sum (\frac{1}{2} Rr)$, which indicates that the value of $\frac{1}{2} Rr$ is to be found for every pair of particles, and the results added together.

Clausius has established this equation by a very simple mathematical process, with which I need not trouble you, as we are not studying mathematics to-night. We may see, however, that it indicates two causes which may affect the pressure of the fluid on the vessel which contains it: the motion of its particles, which tends to increase the pressure, and the attraction of its particles, which tends to diminish the pressure.

We may therefore attribute the pressure of a fluid either to the motion of its particles or to a repulsion between them.

Let us test by means of this result of Clausius the theory that the pressure of a gas arises entirely from the repulsion which one particle exerts on another, these particles, in the case of gas in a fixed vessel, being really at rest.

In this case the virial must be negative, and since by Boyle's Law the product of pressure and volume is constant, the virial also must be constant, whatever the volume, in the same quantity of gas at constant temperature. It follows from this that Rr , the product of the repulsion of two particles into the distance between them, must be constant, or in other words that the repulsion must be inversely as the distance, a law which Newton has shown to be inadmissible in the case of molecular forces, as it would make the action of the distant parts of bodies greater than that of contiguous parts. In fact, we have only to observe that if Rr is constant, the virial of every pair of particles must be the same, so that the virial of the system must be proportional to the number of pairs of particles in the system—that is, to the square of the number of particles, or in other words to the square of the quantity of gas in the vessel. The pressure, according to this law, would not be the same in different vessels of gas at the same density, but would be greater in a large vessel than in a small one, and greater in the open air than in any ordinary vessel.

The pressure of a gas cannot therefore be explained by assuming repulsive forces between the particles.

It must therefore depend, in whole or in part, on the motion of the particles.

If we suppose the particles not to act on each other at all, there will be no virial, and the equation will be reduced to the form

$$Vp = \frac{2}{3} T.$$

If M is the mass of the whole quantity of gas, and c is the mean square of the velocity of a particle, we may write the equation—

$$Vp = \frac{1}{3} Mc^2$$

or in words, the product of the volume and the pressure is one-third of the mass multiplied by the mean square of the velocity. If we now assume, what we shall afterwards prove by an independent process, that the mean square of the velocity depends only on the temperature, this equation exactly represents Boyle's Law.

But we know that most ordinary gases deviate from Boyle's Law, especially at low temperatures and great densities. Let us see whether the hypothesis of forces between the particles, which we rejected when brought forward as the sole cause of gaseous pressure, may not be consistent with experiment when considered as the cause of this deviation from Boyle's Law.

When a gas is in an extremely rarefied condition, the number of particles within a given distance of any one particle will be proportional to the density of the gas. Hence the virial arising from the action of one particle on the rest will vary as the density, and the whole virial in unit of volume will vary as the square of the density.

Calling the density ρ , and dividing the equation by V , we get—

$$p = \pi \rho c^2 - \frac{2}{3} A \rho^2$$

where A is a quantity which is nearly constant for small densities.

Now, the experiments of Regnault show that in most gases, as the density increases the pressure falls below the value calculated by Boyle's Law. Hence the virial must be positive; that is to say, the mutual action of the particles must be in the main attractive, and the effect of this action in diminishing the pressure must be at first very nearly as the square of the density.

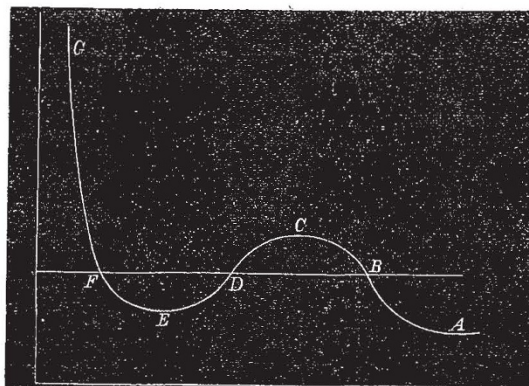
On the other hand, when the pressure is made still greater the substance at length reaches a state in which an enormous increase of pressure produces but a very small increase of density.

This indicates that the virial is now negative, or, in other words, the action between the particles is now, in the main, repulsive. We may therefore conclude that the action between two particles at any sensible distance is quite insensible. As the particles approach each other the action first shows itself as an attraction, which reaches a maximum, then diminishes, and at length becomes a repulsion so great that no attainable force can reduce the distance of the particles to zero.

The relation between pressure and density arising from such an action between the particles is of this kind.

As the density increases from zero, the pressure at first depends almost entirely on the motion of the particles, and therefore varies almost exactly as the pressure, according to Boyle's Law. As the density continues to increase, the effect of the mutual attraction of the particles becomes sensible, and this causes the rise of pressure to be less than that given by Boyle's Law. If the temperature is low, the effect of attraction may become so large in proportion to the effect of motion that the pressure, instead of always rising as the density increases, may reach a maximum, and then begin to diminish.

At length, however, as the average distance of the particles is still further diminished, the effect of repulsion will prevail over that of attraction, and the pressure will increase so as not only to be greater than that given by Boyle's Law, but so that an exceedingly small increase of density will produce an enormous increase of pressure.



Hence the relation between pressure and volume may be represented by the curve $ABCD EFG$, where the horizontal ordinate represents the volume, and the vertical ordinate represents the pressure.

As the volume diminishes, the pressure increases up to the point C , then diminishes to the point E , and finally increases without limit as the volume diminishes.

We have hitherto supposed the experiment to be conducted in such a way that the density is the same in every part of the medium. This, however, is impossible in practice, as the only condition we can impose on the medium from without is that the whole of the medium shall be contained within a certain vessel. Hence, if it is possible for the medium to arrange itself so that part has one density and part another, we cannot prevent it from doing so.

Now the points B and F represent two states of the medium in which the pressure is the same but the density very different. The whole of the medium may pass from the state B to the state F , not through the intermediate states CDE , but by small successive portions passing directly from the state B to the state F . In this way the successive states of the medium as a whole will be represented by points on the straight line BF , the point B representing it when entirely in the rarified state, and F representing it when entirely condensed. This is what takes place when a gas or vapour is liquefied.

Under ordinary circumstances, therefore, the relation between pressure and volume at constant temperature is represented by the broken line $ABFG$. If, however, the medium when liquefied is carefully kept from contact with vapour, it may be preserved in the liquid condition and brought into states represented by the portion of the curve between F and E . It is also possible that methods may be devised whereby the vapour may be prevented from condensing, and brought into states represented by points in BC .

The portion of the hypothetical curve from *C* to *E* represents states which are essentially unstable, and which cannot therefore be realised.

Now let us suppose the medium to pass from *B* to *F* along the hypothetical curve *BCDEF* in a state always homogeneous, and to return along the straight line *FB* in the form of a mixture of liquid and vapour. Since the temperature has been constant throughout, no heat can have been transformed into work. Now the heat transformed into work is represented by the excess of the area *FDE* over *BCD*. Hence the condition which determines the maximum pressure of the vapour at given temperature is that the line *BF* cuts off equal areas from the curve above and below.

The higher the temperature, the greater the part of the pressure which depends on motion, as compared with that which depends on forces between the particles. Hence, as the temperature rises, the dip in the curve becomes less marked, and at a certain temperature the curve, instead of dipping, merely becomes horizontal at a certain point, and then slopes upward as before. This point is called the critical point. It has been determined for carbonic acid by the masterly researches of Andrews. It corresponds to a definite temperature, pressure and density.

At higher temperatures the curve slopes upwards throughout, and there is nothing corresponding to liquefaction in passing from the rarest to the densest state.

The molecular theory of the continuity of the liquid and gaseous states forms the subject of an exceedingly ingenious thesis by Mr. Johannes Diderik van der Waals, a graduate of Leyden. There are certain points in which I think he has fallen into mathematical errors, and his final result is certainly not a complete expression for the interaction of real molecules, but his attack on this difficult question is so able and so brave, that it cannot fail to give a notable impulse to molecular science. It has certainly directed the attention of more than one inquirer to the study of the Low-Dutch language in which it is written.

The purely thermodynamical relations of the different states of matter do not belong to our subject, as they are independent of particular theories about molecules. I must not, however, omit to mention a most important American contribution to this part of thermodynamics by Prof. Willard Gibbs,† of Yale College, U.S., who has given us a remarkably simple and thoroughly satisfactory method of representing the relations of the different states of matter by means of a model. By means of this model, problems which had long resisted the efforts of myself and others may be solved at once.

J. CLERK-MAXWELL

(To be continued.)

SOCIETIES AND ACADEMIES

LONDON

Geological Society, Feb. 19.—Annual General Meeting.—Mr. John Evans, V.P.R.S., president, in the chair.—The Secretary read the reports of the Council and of the Library and Museum Committee. The general position of the Society was described as satisfactory, although, owing to extraordinary expenses during the year, the excess of income over expenditure was but small in comparison with former years. The Society was said to be prosperous, and the number of Fellows to be rapidly increasing.

In presenting the Wollaston Gold Medal to Prof. de Koninck, of Liège, F.M.G.S., the President addressed him as follows:—"Monsieur le Docteur de Koninck, it is my pleasing duty to place in your hands the Wollaston Medal, which has been awarded to you by the Council of this Society in recognition of your extensive and valuable researches and numerous geological publications, especially in Carboniferous Palæontology. These researches are so well known, and have gained you so world-wide a reputation, that I need say no more than that your palæontological works must of necessity be almost daily consulted by all who are interested in the fauna of the Carboniferous period. Already in 1853 the numerous and able Palæontological works which you had published in the preceding twenty years had attracted the grateful notice of the Council of this

Society, who in that year begged you to accept the balance of the proceeds of the Wollaston Fund, in aid of the publication of your work on Encrinites, then in progress. It was in the same year that the Society had the satisfaction of electing you a Foreign Member of their body; and now, after a second period of rather more than twenty years devoted to the study not only of geology and palæontology, but also of chemical analysis, I have the pleasure of conferring upon you the highest additional honour it lies in the power of this Society to bestow, by presenting you with the medal founded by the illustrious Wollaston, who was himself also a chemist as well as a geologist. If anything could add to the satisfaction we feel in thus bestowing the medal, it is your presence among us this day, which will enable you more fully to appreciate our unanimous sense of the high value of your labours in the cause which we all have at heart."

The President then presented the balance of the proceeds of the Wollaston Donation Fund to Mr. L. C. Miall, of Leeds, and addressed him in the following terms:—"Mr. Miall, I have much pleasure in presenting you with the balance of the proceeds of the Wollaston Fund, which has been awarded you by the Council of this Society to assist you in your researches on Fossil Reptilia. Those who had the good fortune to be present at the meeting of the British Association at Bradford in 1873, and to hear the masterly report of the Committee on the Labyrinthodonts of the Coal-measures, drawn up by yourself, and those also who have studied the papers which you have communicated to this Society on the Remains of Labyrinthodonta from the Keuper Sandstone of Warwick, must be well aware of the thorough and careful nature of your researches, carried on, I believe, in a somewhat isolated position, and remote from those aids which are so readily accessible in the metropolis and some of our larger towns. I trust that the proceeds of this fund which I have now placed in your hands will be regarded as a testimony of the interest which this Society takes in your labours, and may also prove of some assistance to you in still further prosecuting them."

Mr. Miall, in reply, said that he felt that his sincere thanks were due to the Geological Society for awarding him the balance of the proceeds of the Wollaston Donation Fund as a token of appreciation of the little work that he had been able to do, and also to the President for the terms in which he had been kind enough to speak of him. He should regard this donation, not only as an honour received by him, but also as a trust to be expended to the best of his power in accordance with the intentions with which it had been conferred upon him by the Society.

The President next handed the Murchison Medal to Mr. David Forbes for transmission to Mr. W. J. Henwood, F.R.S., and spoke as follows:—"Mr. David Forbes, in placing the Murchison Medal and the accompanying cheque in your hands, to be conveyed to our distinguished Fellow, Mr. William Jory Henwood, I must request you to express to him our great regret that he is unable to attend personally to receive it. His researches on the metalliferous deposits, not only of Cornwall and Devonshire, but of Ireland, Wales, North-western India, North America, Chili, and Brazil, extending as they do to questions of subterranean temperature, electric currents, and the quantities of water present in mines, are recorded in memoirs which form text-books for mining students. They have for the most part been contributed to the Royal Geological Society of Cornwall, which has taken a pride in publishing them; but I trust that it will be a source of satisfaction to Mr. Henwood, after fifty years of laborious research, and amidst the physical suffering caused by a protracted illness, to receive this token of appreciation at the hands of another Society which takes no less interest in the subjects of his investigations."

Mr. David Forbes said that in receiving the Murchison Medal, on behalf of Mr. W. J. Henwood, he was commissioned by that gentleman to express his great regret that the bad state of his health and his advanced age prevented his appearing in person to thank the Council for the high honour they had conferred upon him, and the extreme gratification he felt in finding that the results of his labours in the investigation of the phenomena of mineral veins, which had extended over more than fifty years, had thus been recognised by the Geological Society of London.

The President then presented to Prof. H. G. Seeley the balance of the Murchison Geological Fund, and said:—"Mr. Seeley, your researches in geology and on fossil osteology have already extended over a period of upwards of sixteen years, and the numerous and valuable essays which you have contributed to the Annals and Magazine of Natural History, as well

* Over de continuïteit van den gas en vloeïstof toestand. Leiden: A. W. Sijthoff, 1873.

† "A method of geometrical representation of the thermodynamic properties of substances by means of surfaces." Transactions of the Connecticut Academy of Arts and Sciences, Vol. ii. Part 2.