

due to the enormous increase of the mortality among mere infants under one year of age; and this increase is due not only to deaths at one age, but to deaths from one class of diseases, viz., bowel complaints. If the deaths from bowel complaints be deducted from the deaths from all causes, there remains an excess of deaths in the cold months, and a deficiency in the warm months. In other words, the curve of mortality is regulated by the large number of deaths from diseases of the respiratory organs. The curve of mortality for London, if mere infants be excepted, has thus an inverse relation to the temperature, rising as the temperature falls, and falling as the temperature rises. On the other hand, in Victoria, Australia, where the summers are hotter and the winters milder, the curves of mortality and temperature are directly related to each other—mortality and temperature rising and falling

ATMOSPHERIC RAILWAY, a railway in which the pressure of air is used directly or indirectly to propel carriages, as a substitute for steam. It was devised at a time when the principles of propulsion were not so well understood as they are now, and when the dangers and inconveniences attendant on the use of locomotives were very much exaggerated. It had been long known that small objects could be propelled for great distances through tubes by air pressure, but a Mr Vallance, of Brighton, seems to have been the first to propose the application of this system to passenger traffic. He projected (about 1825) an atmospheric railway, consisting of a wooden tube about 6 feet 6 inches in diameter, with a carriage running inside it. A diaphragm fitting the tube, approximately air-tight, was attached to the carriage, and the air exhausted from the front of it by a stationary engine, so that the atmospheric pressure behind drove the carriage forward. Later inventors, commencing with Henry Pinkus (1835), for the most part kept the carriages altogether outside the tube, and connected them by a bar with a piston working inside it, this piston being moved by atmospheric pressure in the way just mentioned. The tube was generally provided with a slot upon its upper side, closed by a continuous valve or its equivalent, and arrangements were made by which this valve should be opened to allow the passage of the driving bar without permitting great leakage of air. About 1840, Messrs Clegg & Samuda made various experiments with an atmospheric tube constructed on this principle upon a portion of the West London Railway, near Wormwood Scrubs. The apparent success of these induced the Dublin

together; the reason being that in Victoria deaths from bowel complaints are much greater, and those from diseases of the respiratory organs much less than in London.

The curves show that the maximum annual mortality from the different diseases groups around certain specific conditions of temperature and moisture combined. Thus, *cold and moist weather* is accompanied with a high death-rate from rheumatism, heart diseases, diphtheria, and measles; *cold weather*, with a high death-rate from bronchitis, pneumonia, &c.; *cold and dry weather*, with a high death-rate from brain diseases, whooping-cough, convulsions; *warm and dry weather*, with a high death-rate from suicide and small-pox; *hot weather*, with a high death-rate from bowel complaints; and *warm moist weather* with a high death-rate from scarlet and typhoid fevers. (See CLIMATE.)

and Kingstown Railway to adopt Clegg & Samuda's scheme upon an extension of their line from Kingstown to Dalkey, where it was in operation in 1844. Later on, the same system was adopted on a part of the South Devon line and in several other places, and during the years 1844-1846 the English and French patent records show a very large number of more or less practicable and ingenious schemes for the tubes, valves, and driving gear of atmospheric railways. The atmospheric system was nowhere permanently successful, but in all cases was eventually superseded by locomotives, the last atmospheric line being probably that at St Germain, which was worked until 1862. Apart from difficulties in connection with the working of the valve, the maintenance of the vacuum, &c., other great practical difficulties, which had not been indicated by the experiments, soon made themselves known in the working of the lines. Above all, it was found that stationary engines, whether hauling a rope or exhausting a tube, could never work a railway with anything like the economy or the convenience of locomotives, a point which is now regarded as settled by engineers, but which was not so thoroughly understood thirty years ago. Lately, the principle of the atmospheric railway has been applied on a very large scale in London and elsewhere, under the name of "PNEUMATIC DESPATCH" (*q.v.*), to the transmission of small parcels in connection with postal and telegraph work, for which purpose it has proved admirably adapted. (See paper by Prof. Sternberg of Carlsruhe in Hensinger von Waldegg's *Handbuch für specielle Eisenbahntechnik*, vol. i. pt. 2, cap. xvii.)

## A T O M

ATOM (*ἄτομος*) is a body which cannot be cut in two. The atomic theory is a theory of the constitution of bodies, which asserts that they are made up of atoms. The opposite theory is that of the homogeneity and continuity of bodies, and asserts, at least in the case of bodies having no apparent organisation, such, for instance, as water, that as we can divide a drop of water into two parts which are each of them drops of water, so we have reason to believe that these smaller drops can be divided again, and the theory goes on to assert that there is nothing in the nature of things to hinder this process of division from being repeated over and over again, times without end. This is the doctrine of the infinite divisibility of bodies, and it is in direct contradiction with the theory of atoms.

The atomists assert that after a certain number of such divisions the parts would be no longer divisible, because each of them would be an atom. The advocates of the

continuity of matter assert that the smallest conceivable body has parts, and that whatever has parts may be divided.

In ancient times Democritus was the founder of the atomic theory, while Anaxagoras propounded that of continuity, under the name of the doctrine of homœomeria (*ὁμοιομέρεια*), or of the similarity of the parts of a body to the whole. The arguments of the atomists, and their replies to the objections of Anaxagoras, are to be found in Lucretius.

In modern times the study of nature has brought to light many properties of bodies which appear to depend on the magnitude and motions of their ultimate constituents, and the question of the existence of atoms has once more become conspicuous among scientific inquiries.

We shall begin by stating the opposing doctrines of atoms and of continuity before giving an outline of the state of

molecular science as it now exists. In the earliest times the most ancient philosophers whose speculations are known to us seem to have discussed the ideas of number and of continuous magnitude, of space and time, of matter and motion, with a native power of thought which has probably never been surpassed. Their actual knowledge, however, and their scientific experience were necessarily limited, because in their days the records of human thought were only beginning to accumulate. It is probable that the first exact notions of quantity were founded on the consideration of number. It is by the help of numbers that concrete quantities are practically measured and calculated. Now, number is discontinuous. We pass from one number to the next *per saltum*. The magnitudes, on the other hand, which we meet with in geometry, are essentially continuous. The attempt to apply numerical methods to the comparison of geometrical quantities led to the doctrine of incommensurables, and to that of the infinite divisibility of space. Meanwhile, the same considerations had not been applied to time, so that in the days of Zeno of Elea time was still regarded as made up of a finite number of "moments," while space was confessed to be divisible without limit. This was the state of opinion when the celebrated arguments against the possibility of motion, of which that of Achilles and the tortoise is a specimen, were propounded by Zeno, and such, apparently, continued to be the state of opinion till Aristotle pointed out that time is divisible without limit, in precisely the same sense that space is. And the slowness of the development of scientific ideas may be estimated from the fact that Bayle does not see any force in this statement of Aristotle, but continues to admire the paradox of Zeno. (Bayle's *Dictionary*, art. "Zeno"). Thus the direction of true scientific progress was for many ages towards the recognition of the infinite divisibility of space and time.

It was easy to attempt to apply similar arguments to matter. If matter is extended and fills space, the same mental operation by which we recognise the divisibility of space may be applied, in imagination at least, to the matter which occupies space. From this point of view the atomic doctrine might be regarded as a relic of the old numerical way of conceiving magnitude, and the opposite doctrine of the infinite divisibility of matter might appear for a time the most scientific. The atomists, on the other hand, asserted very strongly the distinction between matter and space. The atoms, they said, do not fill up the universe; there are void spaces between them. If it were not so, Lucretius tells us, there could be no motion, for the atom which gives way first must have some empty place to move into.

"Quapropter locus est intactus, inane, vacansque  
Quod si non esset, nulla ratione moveri  
Res possent; namque, officium quod corporis exstat,  
Officere atque obstare, id in omni tempore adesset  
Omnibus: haud igitur quicquam procedere posset,  
Principium quoniam cedendi nulla daret res."  
*De Rerum Natura*, i. 335.

The opposite school maintained then, as they have always done, that there is no vacuum—that every part of space is full of matter, that there is a universal plenum, and that all motion is like that of a fish in the water, which yields in front of the fish because the fish leaves room for it behind.

"Cedere squamigeris latices nitentibus afont  
Et liquidas aperire vias, quia post loca pisces  
Lingunt, quo possint cedentes confluere unda."  
—i. 373.

In modern times Descartes held that, as it is of the essence of matter to be extended in length, breadth, and thickness, so it is of the essence of extension to be occu-

ped by matter, for extension cannot be an extension of nothing.

"Ac proinde si quaeratur quid fiet, si Deus auferat omne corpus quod in aliquo vase continetur, et nullum aliud in ablati locum venire permittat? respondendum est, vasis latera sibi invicem hoc ipso fore contigua. Cum enim inter duo corpora nihil interjacet, necesse est ut se mutuo tangant, ac manifeste repugnat ut distent, sive ut inter ipsa sit distantia, et tamen ut ista distantia sit nihil; quia omnis distantia est modus extensionis, et ideo sine substantia extensa esse non potest."—*Principia*, ii. 18.

This identification of extension with substance runs through the whole of Descartes's works, and it forms one of the ultimate foundations of the system of Spinoza. Descartes, consistently with this doctrine, denied the existence of atoms as parts of matter, which by their own nature are indivisible. He seems to admit, however, that the Deity might make certain particles of matter indivisible in this sense, that no creature should be able to divide them. These particles, however, would be still divisible by their own nature, because the Deity cannot diminish his own power, and therefore must retain his power of dividing them. Leibnitz, on the other hand, regarded his monad as the ultimate element of everything.

There are thus two modes of thinking about the constitution of bodies, which have had their adherents both in ancient and in modern times. They correspond to the two methods of regarding quantity—the arithmetical and the geometrical. To the atomist the true method of estimating the quantity of matter in a body is to count the atoms in it. The void spaces between the atoms count for nothing. To those who identify matter with extension, the volume of space occupied by a body is the only measure of the quantity of matter in it.

Of the different forms of the atomic theory, that of Boscovich may be taken as an example of the purest monadism. According to Boscovich matter is made up of atoms. Each atom is an indivisible point, having position in space, capable of motion in a continuous path, and possessing a certain mass, whereby a certain amount of force is required to produce a given change of motion. Besides this the atom is endowed with potential force, that is to say, that any two atoms attract or repel each other with a force depending on their distance apart. The law of this force, for all distances greater than say the thousandth of an inch, is an attraction varying as the inverse square of the distance. For smaller distances the force is an attraction for one distance and a repulsion for another, according to some law not yet discovered. Boscovich himself, in order to obviate the possibility of two atoms ever being in the same place, asserts that the ultimate force is a repulsion which increases without limit as the distance diminishes without limit, so that two atoms can never coincide. But this seems an unwarrantable concession to the vulgar opinion that two bodies cannot co-exist in the same place. This opinion is deduced from our experience of the behaviour of bodies of sensible size, but we have no experimental evidence that two atoms may not sometimes coincide. For instance, if oxygen and hydrogen combine to form water, we have no experimental evidence that the molecule of oxygen is not in the very same place with the two molecules of hydrogen. Many persons cannot get rid of the opinion that all matter is extended in length, breadth, and depth. This is a prejudice of the same kind with the last, arising from our experience of bodies consisting of immense multitudes of atoms. The system of atoms, according to Boscovich, occupies a certain region of space in virtue of the forces acting between the component atoms of the system and any other atoms when brought near them. No other system of atoms can occupy the same region of space at the same time, because, before it could do so, the mutual

action of the atoms would have caused a repulsion between the two systems insuperable by any force which we can command. Thus, a number of soldiers with firearms may occupy an extensive region to the exclusion of the enemy's armies, though the space filled by their bodies is but small. In this way Boscovich explained the apparent extension of bodies consisting of atoms, each of which is devoid of extension. According to Boscovich's theory, all action between bodies is action at a distance. There is no such thing in nature as actual contact between two bodies. When two bodies are said in ordinary language to be in contact, all that is meant is that they are so near together that the repulsion between the nearest pairs of atoms belonging to the two bodies is very great.

Thus, in Boscovich's theory, the atom has continuity of existence in time and space. At any instant of time it is at some point of space, and it is never in more than one place at a time. It passes from one place to another along a continuous path. It has a definite mass which cannot be increased or diminished. Atoms are endowed with the power of acting on one another by attraction or repulsion, the amount of the force depending on the distance between them. On the other hand, the atom itself has no parts or dimensions. In its geometrical aspect it is a mere geometrical point. It has no extension in space. It has not the so-called property of impenetrability, for two atoms may exist in the same place. This we may regard as one extreme of the various opinions about the constitution of bodies.

The opposite extreme, that of Anaxagoras—the theory that bodies apparently homogeneous and continuous are so in reality—is, in its extreme form, a theory incapable of development. To explain the properties of any substance by this theory is impossible. We can only admit the observed properties of such substance as ultimate facts. There is a certain stage, however, of scientific progress in which a method corresponding to this theory is of service. In hydrostatics, for instance, we define a fluid by means of one of its known properties, and from this definition we make the system of deductions which constitutes the science of hydrostatics. In this way the science of hydrostatics may be built upon an experimental basis, without any consideration of the constitution of a fluid as to whether it is molecular or continuous. In like manner, after the French mathematicians had attempted, with more or less ingenuity, to construct a theory of elastic solids from the hypothesis that they consist of atoms in equilibrium under the action of their mutual forces, Stokes and others showed that all the results of this hypothesis, so far at least as they agreed with facts, might be deduced from the postulate that elastic bodies exist, and from the hypothesis that the smallest portions into which we can divide them are sensibly homogeneous. In this way the principle of continuity, which is the basis of the method of Fluxions and the whole of modern mathematics, may be applied to the analysis of problems connected with material bodies by assuming them, for the purpose of this analysis, to be homogeneous. All that is required to make the results applicable to the real case is that the smallest portions of the substance of which we take any notice shall be sensibly of the same kind. Thus, if a railway contractor has to make a tunnel through a hill of gravel, and if one cubic yard of the gravel is so like another cubic yard that for the purposes of the contract they may be taken as equivalent, then, in estimating the work required to remove the gravel from the tunnel, he may, without fear of error, make his calculations as if the gravel were a continuous substance. But if a worm has to make his way through the gravel, it makes the greatest possible difference to him whether he tries to push right against a piece of gravel, or directs his course through

one of the intervals between the pieces; to him, therefore, the gravel is by no means a homogeneous and continuous substance.

In the same way, a theory that some particular substance, say water, is homogeneous and continuous may be a good working theory up to a certain point, but may fail when we come to deal with quantities so minute or so attenuated that their heterogeneity of structure comes into prominence. Whether this heterogeneity of structure is or is not consistent with homogeneity and continuity of substance is another question.

The extreme form of the doctrine of continuity is that stated by Descartes, who maintains that the whole universe is equally full of matter, and that this matter is all of one kind, having no essential property besides that of extension. All the properties which we perceive in matter he reduces to its parts being movable among one another, and so capable of all the varieties which we can perceive to follow from the motion of its parts (*Principia*, ii. 23). Descartes's own attempts to deduce the different qualities and actions of bodies in this way are not of much value. More than a century was required to invent methods of investigating the conditions of the motion of systems of bodies such as Descartes imagined. But the hydrodynamical discovery of Helmholtz that a vortex in a perfect liquid possesses certain permanent characteristics, has been applied by Sir W. Thomson to form a theory of vortex atoms in a homogeneous, incompressible, and frictionless liquid, to which we shall return at the proper time.

#### OUTLINE OF MODERN MOLECULAR SCIENCE, AND IN PARTICULAR OF THE MOLECULAR THEORY OF GASES.

We begin by assuming that bodies are made up of parts, each of which is capable of motion, and that these parts act on each other in a manner consistent with the principle of the conservation of energy. In making these assumptions, we are justified by the facts that bodies may be divided into smaller parts, and that all bodies with which we are acquainted are conservative systems, which would not be the case unless their parts were also conservative systems.

We may also assume that these small parts are in motion. This is the most general assumption we can make, for it includes, as a particular case, the theory that the small parts are at rest. The phenomena of the diffusion of gases and liquids through each other show that there may be a motion of the small parts of a body which is not perceptible to us.

We make no assumption with respect to the nature of the small parts—whether they are all of one magnitude. We do not even assume them to have extension and figure. Each of them must be measured by its mass, and any two of them must, like visible bodies, have the power of acting on one another when they come near enough to do so. The properties of the body, or medium, are determined by the configuration and motion of its small parts.

The first step in the investigation is to determine the amount of motion which exists among the small parts, independent of the visible motion of the medium as a whole. For this purpose it is convenient to make use of a general theorem in dynamics due to Clausius.

When the motion of a material system is such that the time average of the quantity  $\Sigma(mx^2)$  remains constant, the state of the system is said to be that of stationary motion. When the motion of a material system is such that the sum of the moments of inertia of the system, about three axes at right angles through its centre of mass, never varies by more than small quantities from a constant value, the system is said to be in a state of stationary motion.

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

When an attraction or repulsion exists between two points, half the product of this stress into the distance between the two points is called the *virial* of the stress, and is reckoned positive when the stress is an attraction, and negative when it is a repulsion. The virial of a system is the sum of the virials of the stresses which exist in it. If the system is subjected to the external stress of the pressure of the sides of a vessel in which it is contained, this stress will introduce an amount of virial  $\frac{2}{3}pV$ , where  $p$  is the pressure on unit of area and  $V$  is the volume of the vessel.

The theorem of Clausius may now be stated as follows:—In a material system in a state of stationary motion the time-average of the kinetic energy is equal to the time-average of the virial. In the case of a fluid enclosed in a vessel

$$\frac{1}{2}\Sigma(mv^2) = \frac{2}{3}pV + \frac{1}{2}\Sigma\Sigma(Rr)$$

where the first term denotes the kinetic energy, and is half the sum of the product of each mass into the mean square of its velocity. In the second term,  $p$  is the pressure on unit of surface of the vessel, whose volume is  $V$ , and the third term expresses the virial due to the internal actions between the parts of the system. A double symbol of summation is used, because every pair of parts between which any action exists must be taken into account. We have next to show that in gases the principal part of the pressure arises from the motion of the small parts of the medium, and not from a repulsion between them.

In the first place, if the pressure of a gas arises from the repulsion of its parts, the law of repulsion must be inversely as the distance. For, consider a cube filled with the gas at pressure  $p$ , and let the cube expand till each side is  $n$  times its former length. The pressure on unit of surface according to Boyle's law is now  $\frac{p}{n^2}$ , and since the area of a face of the cube is  $n^2$  times what it was, the whole pressure on the face of the cube is  $\frac{1}{n}$  of its original value. But since everything has been expanded symmetrically, the distance between corresponding parts of the air is now  $n$  times what it was, and the force is  $n$  times less than it was. Hence the force must vary inversely as the distance.

But Newton has shown (*Principia*, bk. i. prop. 93) that this law is inadmissible, as it makes the effect of the distant parts of the medium on a particle greater than that of the neighbouring parts. Indeed, we should arrive at the conclusion that the pressure depends not only on the density of the air but on the form and dimensions of the vessel which contains it, which we know not to be the case.

If, on the other hand, we suppose the pressure to arise entirely from the motion of the molecules of the gas, the interpretation of Boyle's law becomes very simple. For, in this case

$$pV = \frac{1}{3}\Sigma(mv^2).$$

The first term is the product of the pressure and the volume, which according to Boyle's law is constant for the same quantity of gas at the same temperature. The second term is two-thirds of the kinetic energy of the system, and we have every reason to believe that in gases when the temperature is constant the kinetic energy of unit of mass is also constant. If we admit that the kinetic energy of unit of mass is in a given gas proportional to the absolute temperature, this equation is the expression of the law of Charles as well as of that of Boyle, and may be written—

$$pV = R\theta.$$

where  $\theta$  is the temperature reckoned from absolute zero, and  $R$  is a constant. The fact that this equation expresses with considerable accuracy the relation between the volume, pressure, and temperature of a gas when in an extremely rarified state, and that as the gas is more and more compressed the deviation from this equation becomes more apparent, shows that the pressure of a gas is due almost entirely to the motion of its molecules when the gas is rare, and that it is only when the density of the gas is considerably increased that the effect of direct action between the molecules becomes apparent.

The effect of the direct action of the molecules on each other depends on the number of pairs of molecules which at a given instant are near enough to act on one another. The number of such pairs is proportional to the square of the number of molecules in unit of volume, that is, to the square of the density of the gas. Hence, as long as the medium is so rare that the encounter between two molecules is not affected by the presence of others, the deviation from Boyle's law will be proportional to the square of the density. If the action between the molecules is on the whole repulsive, the pressure will be greater than that given by Boyle's law. If it is, on the whole, attractive, the pressure will be less than that given by Boyle's law. It appears, by the experiments of Regnault and others, that the pressure does deviate from Boyle's law when the density of the gas is increased. In the case of carbonic acid and other gases which are easily liquefied, this deviation is very great. In all cases, however, except that of hydrogen, the pressure is less than that given by Boyle's law, showing that the virial is on the whole due to attractive forces between the molecules.

Another kind of evidence as to the nature of the action between the molecules is furnished by an experiment made by Dr Joule. Of two vessels, one was exhausted and the other filled with a gas at a pressure of 20 atmospheres; and both were placed side by side in a vessel of water, which was constantly stirred. The temperature of the whole was observed. Then a communication was opened between the vessels, the compressed gas expanded to twice its volume, and the work of expansion, which at first produced a strong current in the gas, was soon converted into heat by the internal friction of the gas. When all was again at rest, and the temperature uniform, the temperature was again observed. In Dr Joule's original experiments the observed temperature was the same as before. In a series of experiments, conducted by Dr Joule and Sir W. Thomson on a different plan, by which the thermal effect of free expansion can be more accurately measured, a slight cooling effect was observed in all the gases examined except hydrogen. Since the temperature depends on the velocity of agitation of the molecules, it appears that when a gas expands without doing external work the velocity of agitation is not much affected, but that in most cases it is slightly diminished. Now, if the molecules during their mutual separation act on each other, their velocity will increase or diminish according as the force is repulsive or attractive. It appears, therefore, from the experiments on the free expansion of gases, that the force between the molecules is small but, on the whole, attractive.

Having thus justified the hypothesis that a gas consists of molecules in motion, which act on each other only when they come very close together during an encounter, but which, during the intervals between their encounters which constitute the greater part of their existence, are describing free paths, and are not acted on by any molecular force, we proceed to investigate the motion of such a system.

The mathematical investigation of the properties of such

a system of molecules in motion is the foundation of molecular science. Clausius was the first to express the relation between the density of the gas, the length of the free paths of its molecules, and the distance at which they encounter each other. He assumed, however, at least in his earlier investigations, that the velocities of all the molecules are equal. The mode in which the velocities are distributed was first investigated by the present writer, who showed that in the moving system the velocities of the molecules range from zero to infinity, but that the number of molecules whose velocities lie within given limits can be expressed by a formula identical with that which expresses in the theory of errors the number of errors of observation lying within corresponding limits. The proof of this theorem has been carefully investigated by Boltzmann,<sup>1</sup> who has strengthened it where it appeared weak, and to whom the method of taking into account the action of external forces is entirely due.

The mean kinetic energy of a molecule, however, has a definite value, which is easily expressed in terms of the quantities which enter into the expression for the distribution of velocities. The most important result of this investigation is that when several kinds of molecules are in motion and acting on one another, the mean kinetic energy of a molecule is the same whatever be its mass, the molecules of greater mass having smaller mean velocities. Now, when gases are mixed their temperatures become equal. Hence we conclude that the physical condition which determines that the temperature of two gases shall be the same is that the mean kinetic energies of agitation of the individual molecules of the two gases are equal. This result is of great importance in the theory of heat, though we are not yet able to establish any similar result for bodies in the liquid or solid state.

In the next place, we know that in the case in which the whole pressure of the medium is due to the motion of its molecules, the pressure on unit of area is numerically equal to two-thirds of the kinetic energy in unit of volume. Hence, if equal volumes of two gases are at equal pressures the kinetic energy is the same in each. If they are also at equal temperatures the mean kinetic energy of each molecule is the same in each. If, therefore, equal volumes of two gases are at equal temperatures and pressures, the number of molecules in each is the same, and therefore, the masses of the two kinds of molecules are in the same ratio as the densities of the gases to which they belong.

This statement has been believed by chemists since the time of Gay-Lussac, who first established that the weights of the chemical equivalents of different substances are proportional to the densities of these substances when in the form of gas. The definition of the word molecule, however, as employed in the statement of Gay-Lussac's law is by no means identical with the definition of the same word as in the kinetic theory of gases. The chemists ascertain by experiment the ratios of the masses of the different substances in a compound. From these they deduce the chemical equivalents of the different substances, that of a particular substance, say hydrogen, being taken as unity. The only evidence made use of is that furnished by chemical combinations. It is also assumed, in order to account for the facts of combination, that the reason why substances combine in definite ratios is that the molecules of the substances are in the ratio of their chemical equivalents, and that what we call combination is an action which takes place by a union of a molecule of one substance to a molecule of the other.

This kind of reasoning, when presented in a proper form and sustained by proper evidence, has a high degree of

coagency. But it is purely chemical reasoning; it is not dynamical reasoning. It is founded on chemical experience, not on the laws of motion.

Our definition of a molecule is purely dynamical. A molecule is that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas. The result of the kinetic theory, therefore, is to give us information about the relative masses of molecules considered as moving bodies. The consistency of this information with the deductions of chemists from the phenomena of combination, greatly strengthens the evidence in favour of the actual existence and motion of gaseous molecules.

Another confirmation of the theory of molecules is derived from the experiments of Dulong and Petit on the specific heat of gases, from which they deduced the law which bears their name, and which asserts that the specific heats of equal weights of gases are inversely as their combining weights, or, in other words, that the capacities for heat of the chemical equivalents of different gases are equal. We have seen that the temperature is determined by the kinetic energy of agitation of each molecule. The molecule has also a certain amount of energy of internal motion, whether of rotation or of vibration, but the hypothesis of Clausius, that the mean value of the internal energy always bears a proportion fixed for each gas to the energy of agitation, seems highly probable and consistent with experiment. The whole kinetic energy is therefore equal to the energy of agitation multiplied by a certain factor. Thus the energy communicated to a gas by heating it is divided in a certain proportion between the energy of agitation and that of the internal motion of each molecule. For a given rise of temperature the energy of agitation, say of a million molecules, is increased by the same amount whatever be the gas. The heat spent in raising the temperature is measured by the increase of the whole kinetic energy. The thermal capacities, therefore, of equal numbers of molecules of different gases are in the ratio of the factors by which the energy of agitation must be multiplied to obtain the whole energy. As this factor appears to be nearly the same for all gases of the same degree of atomicity, Dulong and Petit's law is true for such gases.

Another result of this investigation is of considerable importance in relation to certain theories,<sup>2</sup> which assume the existence of aethers or rare media consisting of molecules very much smaller than those of ordinary gases. According to our result, such a medium would be neither more nor less than a gas. Supposing its molecules so small that they can penetrate between the molecules of solid substances such as glass, a so-called vacuum would be full of this rare gas at the observed temperature, and at the pressure, whatever it may be, of the ætherial medium in space. The specific heat, therefore, of the medium in the so-called vacuum will be equal to that of the same volume of any other gas at the same temperature and pressure. Now, the purpose for which this molecular æther is assumed in these theories is to act on bodies by its pressure, and for this purpose the pressure is generally assumed to be very great. Hence, according to these theories, we should find the specific heat of a so-called vacuum very considerable compared with that of a quantity of air filling the same space.

We have now made a certain definite amount of progress towards a complete molecular theory of gases. We know the mean velocity of the molecules of each gas in metres per second, and we know the relative masses of the molecules of different gases. We also know that the molecules of one and the same gas are all equal in mass. For, if they

<sup>2</sup> See Gustav Hansemann, *Die Atome und ihre Bewegungen* 1871. (H. G. Mayer.)

are not, the method of dialysis, as employed by Graham, would enable us to separate the molecules of smaller mass from those of greater, as they would stream through porous substances with greater velocity. We should thus be able to separate a gas, say hydrogen, into two portions, having different densities and other physical properties, different combining weights, and probably different chemical properties of other kinds. As no chemist has yet obtained specimens of hydrogen differing in this way from other specimens, we conclude that all the molecules of hydrogen are of sensibly the same mass, and not merely that their mean mass is a statistical constant of great stability.

But as yet we have not considered the phenomena which enable us to form an estimate of the actual mass and dimensions of a molecule. It is to Clausius that we owe the first definite conception of the free path of a molecule and of the mean distance travelled by a molecule between successive encounters. He showed that the number of encounters of a molecule in a given time is proportional to the velocity, to the number of molecules in unit of volume, and to the square of the distance between the centres of two molecules when they act on one another so as to have an encounter. From this it appears that if we call this distance of the centres the diameter of a molecule, and the volume of a sphere having this diameter the volume of a molecule, and the sum of the volumes of all the molecules the molecular volume of the gas, then the diameter of a molecule is a certain multiple of the quantity obtained by diminishing the free path in the ratio of the molecular volume of the gas to the whole volume of the gas. The numerical value of this multiple differs slightly, according to the hypothesis we assume about the law of distribution of velocities. It also depends on the definition of an encounter. When the molecules are regarded as elastic spheres we know what is meant by an encounter, but if they act on each other at a distance by attractive or repulsive forces of finite magnitude, the distance of their centres varies during an encounter, and is not a definite quantity. Nevertheless, the above statement of Clausius enables us, if we know the length of the mean path and the molecular volume of a gas, to form a tolerably near estimate of the diameter of the sphere of the intense action of a molecule, and thence of the number of molecules in unit of volume and the actual mass of each molecule. To complete the investigation we have, therefore, to determine the mean path and the molecular volume. The first numerical estimate of the mean path of a gaseous molecule was made by the present writer from data derived from the internal friction of air. There are three phenomena which depend on the length of the free path of the molecules of a gas. It is evident that the greater the free path the more rapidly will the molecules travel from one part of the medium to another, because their direction will not be so often altered by encounters with other molecules. If the molecules in different parts of the medium are of different kinds, their progress from one part of the medium to another can be easily traced by analysing portions of the medium taken from different places. The rate of diffusion thus found furnishes one method of estimating the length of the free path of a molecule. This kind of diffusion goes on not only between the molecules of different gases, but among the molecules of the same gas, only in the latter case the results of the diffusion cannot be traced by analysis. But the diffusing molecules carry with them in their free paths the momentum and the energy which they happen at a given instant to have. The diffusion of momentum tends to equalise the apparent motion of different parts of the medium, and constitutes the phenomenon called the internal friction or viscosity of gases. The diffusion of energy tends to equalise the

temperature of different parts of the medium, and constitutes the phenomenon of the conduction of heat in gases.

These three phenomena—the diffusion of matter, of motion, and of heat in gases—have been experimentally investigated,—the diffusion of matter by Graham and Loschmidt, the diffusion of motion by Oscar Meyer and Clerk Maxwell, and that of heat by Stefan.

These three kinds of experiments give results which in the present imperfect state of the theory and the extreme difficulty of the experiments, especially those on the conduction of heat, may be regarded as tolerably consistent with each other. At the pressure of our atmosphere, and at the temperature of melting ice, the mean path of a molecule of hydrogen is about the 10,000th of a millimetre, or about the fifth part of a wave-length of green light. The mean path of the molecules of other gases is shorter than that of hydrogen.

The determination of the molecular volume of a gas is subject as yet to considerable uncertainty. The most obvious method is that of compressing the gas till it assumes the liquid form. It seems probable, from the great resistance of liquids to compression, that their molecules are at about the same distance from each other as that at which two molecules of the same substance in the gaseous form act on each other during an encounter. If this is the case, the molecular volume of a gas is somewhat less than the volume of the liquid into which it would be condensed by pressure, or, in other words, the density of the molecules is somewhat greater than that of the liquid.

Now, we know the relative weights of different molecules with great accuracy, and, from a knowledge of the mean path, we can calculate their relative diameters approximately. From these we can deduce the relative densities of different kinds of molecules. The relative densities so calculated have been compared by Lorenz Meyer with the observed densities of the liquids into which the gases may be condensed, and he finds a remarkable correspondence between them. There is considerable doubt, however, as to the relation between the molecules of a liquid and those of its vapour, so that till a larger number of comparisons have been made, we must not place too much reliance on the calculated densities of molecules. Another, and perhaps a more refined, method is that adopted by M. Van der Waals, who deduces the molecular volume from the deviations of the pressure from Boyle's law as the gas is compressed.

The first numerical estimate of the diameter of a molecule was that made by Loschmidt in 1865 from the mean path and the molecular volume. Independently of him and of each other, Mr Stoney, in 1868, and Sir W. Thomson, in 1870, published results of a similar kind—those of Thomson being deduced not only in this way, but from considerations derived from the thickness of soap bubbles, and from the electric action between zinc and copper.

The diameter and the mass of a molecule, as estimated by these methods, are, of course, very small, but by no means infinitely so. About two millions of molecules of hydrogen in a row would occupy a millimetre, and about two hundred million million million of them would weigh a milligramme. These numbers must be considered as exceedingly rough guesses; they must be corrected by more extensive and accurate experiments as science advances; but the main result, which appears to be well-established, is that the determination of the mass of a molecule is a legitimate object of scientific research, and that this mass is by no means immeasurably small.

Loschmidt illustrates these molecular measurements by a comparison with the smallest magnitudes visible by means of a microscope. Nobert, he tells us, can draw 4000 lines in the breadth of a millimetre. The intervals between

<sup>1</sup> *Sitzungsberichte der K. K. Akad. Wien*, 8th Oct. 1868