Molecular Theory.

kind of action, there is another, depending on the evaporation from the surface of the little drops. The vapour of water is much rarer than air, and damp air is lighter than dry air at the same temperature and pressure. Hence the little drops make the air of the cloud damp, and if the mean density of the cloud is by this means made less than that of the surrounding air, the cloud will ascend.

CHAPTER XXII.

ON THE MOLECULAR THEORY OF THE CONSTITUTION OF BODIES.

WE have already shown that heat is a form of energy—that when a body is hot it possesses a store of energy, part at least of which can afterwards be exhibited in the form of visible work.

Now energy is known to us in two forms. One of these is Kinetic Energy, the energy of motion. A body in motion has kinetic energy, which it must communicate to some other body during the process of bringing it to rest. This is the fundamental form of energy. When we have acquired the notion of matter in motion, and know what is meant by the energy of that motion, we are unable to conceive that any possible addition to our knowledge could explain the energy of motion, or give us a more perfect knowledge of it than we have already.

There is another form of energy which a body may have, which depends, not on its own state, but on its position with respect to other bodies. This is called Potential Energy. The leaden weight of a clock, when it is wound up, has potential energy, which it loses as it descends. It is spent in driving the clock. This energy depends, not on the piece of lead considered in itself, but on the position of the lead with respect to another body-the earth-which attracts it.

In a watch, the mainspring, when wound up, has potential energy, which it spends in driving the wheels of the watch. This energy arises from the coiling up of the spring, which alters the relative position of its parts. In both cases, until the clock or watch is set agoing, the existence of potential energy, whether in the clock-weight or in the watch-spring, is not accompanied with any visible motion. We must therefore admit that potential energy can exist in a body or system all whose parts are at rest.

It is to be observed, however, that the progress of science is continually opening up new views of the forms and relations of different kinds of potential energy, and that men of science, so far from feeling that their knowledge of potential energy is perfect in kind, and incapable of essential change, are always endeavouring to explain the different forms of potential energy; and if these explanations are in any case condemned, it is because they fail to give a sufficient reason for the fact, and not because the fact requires no explanation.

We have now to determine to which of these forms of energy heat, as it exists in hot bodies, is to be referred. Is a hot body, like a coiled-up watch-spring, devoid of motion at present, but capable of exciting motion under proper conditions? or is it like a fly-wheel, which derives all its tremendous power from the visible motion with which it is animated?

It is manifest that a body may be hot without any motion being visible, either of the body as a whole, or of its parts relatively to each other. If, therefore, the body is hot in virtue of motion, the motion must be carried on by parts of the body too minute to be seen separately, and within limits so narrow that we cannot detect the absence of any part from its original place.

The evidence for a state of motion, the velocity of which

Heat is Motion.

72 mV = 3107

.nust far surpass that of a railway train, existing in bodies which we can place under the strongest microscope, and in which we can detect nothing but the most perfect repose, must be of a very cogent nature before we can admit that heat is essentially motion.

Let us therefore consider the alternative hypothesis—that the energy of a hot body is potential energy, or, in other words, that the hot body is in a state of rest, but that this state of rest depends on the antagonism of forces which are in equilibrium as long as all surrounding bodies are of the same temperature, but which as soon as this equilibrium is destroyed are capable of setting bodies in motion. With respect to a theory of this kind, it is to be observed that potential energy depends essentially on the relative position of the parts of the system in which it exists, and that potential energy cannot be transformed in any way without some change of the relative position of these parts. In every transformation of potential energy, therefore, motion of some kind is involved.

Now we know that whenever one body of a system is hotter than another, heat is transferred from the hotter to the colder body, either by conduction or by radiation. Let us suppose that the transfer takes place by radiation. Whatever theory we adopt about the kind of motion which constitutes radiation, it is manifest that radiation consists of motion of some kind, either the projection of the particles of a substance called caloric across the intervening space, or a wave-like motion propagated through a medium filling that space. In either case, during the interval between the time when the heat leaves the hot body and the time when it reaches the cold body, its energy exists in the intervening space in the form of the motion of matter.

Hence, whether we consider the radiation of heat as effected by the projection of material caloric, or by the undulations of an intervening medium, the outer surface of a hot body must be in a state of motion, provided any cold X

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Molecular Theory.

body is in its neighbourhood to receive the radiations which it emits. But we have no reason to believe that the presence of a cold body is essential to the radiation of heat by a hot one. Whatever be the mode in which the hot body shoots forth its heat, it must depend on the state of the hot body alone, and not on the existence of a cold body at a distance, so that even if all the bodies in a closed region were equally hot, every one of them would be radiating heat; and the reason why each body remains of the same temperature is, that it receives from the other bodies exactly as much heat as it emits. This, in fact, is the foundation of Prevost's Theory of Exchanges. We must therefore admit that at every part of the surface of a hot body there is a radiation of heat, and therefore a state of motion of the superficial parts of the body. Now this motion is certainly invisible to us by any direct mode of observation, and therefore the mere fact of a body appearing to be at rest cannot be taken as a demonstration that its parts may not be in a state of motion.

Hence part, at least, of the energy of a hot body must be energy arising from the motion of its parts, or kinetic energy.

The conclusion at which we shall arrive, that a very considerable part of the energy of a hot body is in the form of motion, will become more evident when we consider the thermal energy of gases.

Every hot body, therefore, is in motion. We have next to enquire into the nature of this motion. It is evidently not a motion of the whole body in one direction, for however small we make the body by mechanical processes, each visible particle remains apparently in the same place, however hot it is. The motion which we call heat must therefore be a motion of parts too small to be observed separately ; the motions of different parts at the same instant must be in different directions ; and the motion of any one part must, at least in solid bodies, be such that, however fast it moves, it never reaches a sensible distance from the point from which it started.

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We have now arrived at the conception of a body as consisting of a great many small parts, each of which is in motion. We shall call any one of these parts a molecule of the substance. A molecule may therefore be defined as a small mass of matter the parts of which do not part company during the excursions which the molecule makes when the body to which it belongs is hot.

The doctrine that visible bodies consist of a determinate number of molecules is called the molecular theory of matter. The opposite doctrine is that, however small the parts may be into which we divide a body, each part retains all the properties of the substance. This is the theory of the infinite divisibility of bodies. We do not assert that there is an absolute limit to the divisibility of matter : what we assert is, that after we have divided a body into a certain finite number of constituent parts called molecules, then any further division of these molecules will deprive them of the properties which give rise to the phenomena observed in the substance.

The opinion that the observed properties of visible bodies apparently at rest are due to the action of invisible molecules in rapid motion is to be found in Lucretius.

- Daniel Bernoulli was the first to suggest that the pressure of air is due to the impact of its particles on the sides of the vessel containing it; but he made very little progress in the theory which he suggested.

Lesage and Prevost of Geneva, and afterwards Herapath in his 'Mathematical Physics,' made several important applications of the theory.

Dr. Joule in 1848 explained the pressure of gases by the impact of their molecules, and calculated the velocity which they must have to produce the observed pressure.

Krönig also directed attention to this explanation of the phenomena of gases.

It is to Professor Clausius, however, that we owe the recent development of the dynamical theory of gases. Since be Epianos

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took up the subject a great advance has been made by many enquirers. I shall now endeavour to give a sketch of the present state of the theory.

All bodies consist of a finite number of small parts called molecules. Every molecule consists of a definite quantity of matter, which is exactly the same for all the molecules of the same substance. The mode in which the molecule is bound together is also the same for all molecules of the same substance. A molecule may consist of several distinct portions of matter held together by chemical bonds, and may be set in vibration, rotation, or any other kind of relative motion, but so long as the different portions do not part company, but travel together in the excursions made by the molecule, our theory calls the whole connected mass a single molecule.

The molecules of all bodies are in a state of continual agitation. The hotter a body is, the more violently are its molecules agitated. In solid bodies, a molecule, though in continual motion, never gets beyond a certain very small distance from its original position in the body. The path which it describes is confined within a very small region of space.

In fluids, on the other hand, there is no such restriction to the excursions of a molecule. It is true that the molecule generally can travel but a very small distance before its path is disturbed by an encounter with some other molecule; but after this encounter there is nothing which determines the molecule rather to return towards the place from whence it came than to push its way into new regions. Hence in fluids the path of a molecule is not confined within a limited region, as in the case of solids, but may penetrate to any part of the space occupied by the fluid.

The actual phenomena of diffusion both in liquids and in gases furnish the strongest evidence that these bodies consist of molecules in a state of continual agitation.

But when we apply the methods of dynamics to the

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investigation of the properties of a system consisting of a great number of small bodies in motion the resemblance of such a system to a gaseous body becomes still more apparent.

I shall endeavour to give some account of what is known of such a system, avoiding all unnecessary mathematical calculations.

ON THE KINETIC THEORY OF GASES.

A gaseous body is supposed to consist of a great number of molecules moving with great velocity. During the greater part of their course these molecules are not acted on by any sensible force, and therefore move in straight lines with uniform velocity. When two molecules come within a certain distance of each other, a mutual action takes place between them, which may be compared to the collision of two billiard balls. Each molecule has its course changed, and starts on a new path. I have concluded from some experiments of my own that the collision between two hard spherical balls is not an accurate representation of what takes place during the encounter of two molecules. A better representation of such an encounter will be obtained by supposing the molecules to act on one another in a more gradual manner, so that the action between them goes on for a finite time, during which the centres of the molecules first approach each other and then separate.

We shall refer to this mutual action as an Encounter between two molecules, and we shall call the course of a molecule between one encounter and another the Free Path of the molecule. In ordinary gases the free motion of a molecule takes up much more time than that occupied by an encounter. As the density of the gas increases, the free path diminishes, and in liquids no part of the course of a molecule can be spoken of as its free path.

In an encounter between two molecules we know that, since the force of the impact acts between the two bodies, the motion of the centre of gravity of the two molecules remains the same after the encounter as it was before. We also know by the principle of the conservation of energy that the velocity of each molecule relatively to the centre of gravity remains the same in magnitude, and is only changed in direction.

Let us next suppose a number of molecules in motion contained in a vessel whose sides are such that if any energy is communicated to the vessel by the encounters of molecules against its sides, the vessel communicates as much energy to other molecules during their encounters with it, so as to preserve the total energy of the enclosed system. The first thing we must notice about this moving system is that even if all the molecules have the same velocity originally, their encounters will produce an inequality of velocity, and that this distribution of velocity will go on continually. Every molecule will then change both its direction and its velocity at every encounter; and, as we are not supposed to keep a record of the exact particulars of every encounter, these changes of motion must appear to us very irregular if we follow the course of a single molecule. If, however, we adopt a statistical view of the system, and distribute the molecules into groups, according to the velocity with which at a given instant they happen to be moving, we shall observe a regularity of a new kind in the proportions of the whole number of molecules which fall into each of these groups.

And here I wish to point out that, in adopting this statistical method of considering the average number of groups of molecules selected according to their velocities, we have abandoned the strict kinetic method of tracing the exact circumstances of each individual molecule in all its encounters. It is therefore possible that we may arrive at results which, though they fairly represent the facts as long as we are supposed to deal with a gas in mass, would cease to be applicable if our faculties and instruments were so

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Distribution of Energy.

sharpened that we could detect and lay hold of each molecule and trace it through all its course.

For the same reason, a theory of the effects of education deduced from a study of the returns of registrars, in which no names of individuals are given, might be found not to be applicable to the experience of a schoolmaster who is able to trace the progress of each individual pupil.

The distribution of the molecules according to their velocities is found to be of exactly the same mathematical form as the distribution of observations according to the magnitude of their errors, as described in the theory of errors of observation. The distribution of bullet-holes in a target according to their distances from the point aimed at is found to be of the same form, provided a great many shots are fired by persons of the same degree of skill.

We have already met with the same form in the case of heat diffused from a hot stratum by conduction. Whenever in physical phenomena some cause exists over which we have no control, and which produces a scattering of the particles of matter, a deviation of observations from the truth, or a diffusion of velocity or of heat, mathematical expressions of this exponential form are sure to make their appearance.

It appears then that of the molecules composing the system some are moving very slowly, a very few are moving with enormous velocities, and the greater number with intermediate velocities. To compare one such system with another, the best method is to take the mean of the squares of all the velocities. This quantity is called the Mean Square of the velocity. The square root of this quantity is called the Velocity of Mean Square.

DISTRIBUTION OF KINETIC ENERGY BETWEEN TWO DIFFERENT SETS OF MOLECULES.

If two sets of molecules whose mass is different are in motion in the same vessel, they will by their encounters

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be considered as depending on the coefficient of diffusion of the components through each other.

MOLECULAR THEORY OF RADIATION.

The phenomena already described are explained on the molecular theory by the motion of agitation of the molecules, a motion which is exceedingly irregular, the intervals between successive encounters and the velocities of a molecule during successive free paths not being subject to any law which we can express. The internal motion of a single molecule is of a very different kind. If the parts of the molecule are capable of relative motion without being altogether torn asunder, this relative motion will be some kind of vibration. The small vibrations of a connected system may be resolved into a number of simple vibrations, the law of each of which is similar to that of a pendulum. It is probable that in gases the molecules may execute many of such vibrations in the interval between successive encounters. At each encounter the whole molecule is roughly shaken. During its free path it vibrates according to its own laws, the amplitudes of the different simple vibrations being determined by the nature of the collision, but their periods depending only on the constitution of the molecule itself. If the molecule is capable of communicating these vibrations to the medium in which radiations are propagated, it will send forth radiations of certain definite kinds, and if these belong to the luminous part of the spectrum, they will be visible as light of definite refrangibility. This, then, is the explanation, on the molecular theory, of the bright lines observed in the spectra of incandescent gases. They represent the disturbance communicated to the luminiferous medium by molecules vibrating in a regular and periodic manner during their free paths. If the free path is long, the molecule, by communicating its vibrations to the ether, will cease to vibrate till it encounters some other molecule.

By raising the temperature we increase the velocity of

the motion of agitation and the force of each encounter. The higher the temperature the greater will be the amplitude of the internal vibrations of all kinds, and the more likelihood will there be that vibrations of short period will be excited, as well as those fundamental vibrations which are most easily produced. By increasing the density we diminish the length of the free path of each molecule, and thus allow less time for the vibrations excited at each encounter to subside, and, since each fresh encounter disturbs the regularity of the series of vibrations, the radiation will no longer be capable of complete resolution into a series of vibrations of regular periods, but will be analysed into a spectrum showing the bright bands due to the regular vibrations, along with a ground of diffused light, forming a continuous spectrum due to the irregular motion introduced at each encounter.

Hence when a gas is rare the bright lines of its spectrum are narrow and distinct, and the spaces between them are dark. As the density of the gas increases, the bright lines become broader and the spaces between them more luminous.

There is another reason for the broadening of the bright lines and the luminosity of the whole spectrum in dense gases, which we have already stated at p. 245. There is this difference, however, between the effect there mentioned and that described here. At p. 245 the light from a certain stratum of incandescent gas was supposed to penetrate through other strata, which absorbed the brighter rays faster than the less luminous ones. This effect depends only on the total quantity of gas through which the rays pass, and will be the same whether it is a mile of gas at thirty inches pressure, or thirty miles at one inch pressure. The effect which we are now considering depends on the absolute density, so that it is by no means the same whether a stratum containing a given quantity of gas is one mile or thirty miles thick. When the gas is so far condensed that it assumes the liquid or solid form, then, as the molecules have no free path, they have no regular vibrations, and no bright lines are commonly observed in incandescent liquids or solids. Mr. Huggins, however, has observed bright lines in the spectrum of incandescent erbia and lime, which appear to be due to the solid matter, and not to its vapour.

LIMITATION OF THE SECOND LAW OF THERMODYNAMICS.

Before I conclude, I wish to direct attention to an aspect of the molecular theory which deserves consideration.

One of the best established facts in thermodynamics is that it is impossible in a system enclosed in an envelope which permits neither change of volume nor passage of heat, and in which both the temperature and the pressure are everywhere the same, to produce any inequality of temperature or of pressure without the expenditure of work. This is the second law of thermodynamics, and it is undoubtedly true as long as we can deal with bodies only in mass, and have no power of perceiving or handling the separate molecules of which they are made up. But if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is at present impossible to us. For we have seen that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower ones to pass from B to A. He will thus, without expenditure of work, raise the tem-

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Statistical Knowledge of Bodies.

perature of B and lower that of A, in contradiction to the second law of thermodynamics.

This is only one of the instances in which conclusions which we have drawn from our experience of bodies consisting of an immense number of molecules may be found not to be applicable to the more delicate observations and experiments which we may suppose made by one who can perceive and handle the individual molecules which we deal with only in large masses.

In dealing with masses of matter, while we do not perceive the individual molecules, we are compelled to adopt what I have described as the statistical method of calculation, and to abandon the strict dynamical method, in which we follow every motion by the calculus.

It would be interesting to enquire how far those ideas about the nature and methods of science which have been derived from examples of scientific investigation in which the dynamical method is followed are applicable to our actual knowledge of concrete things, which, as we have seen, is of an essentially statistical nature, because no one has yet discovered any practical method of tracing the path of a molecule, or of identifying it at different times.

I do not think, however, that the perfect identity which we observe between different portions of the same kind of matter can be explained on the statistical principle of the stability of the averages of large numbers of quantities each of which may differ from the mean. For if of the molecules of some substance such as hydrogen, some were of sensibly greater mass than others, we have the means of producing a separation between molecules of different masses, and in this way we should be able to produce two kinds of hydrogen, one of which would be somewhat denser than the other. As this cannot be done, we must admit that the equality which we assert to exist between the molecules of hydrogen applies to each individual molecule, and not merely to the average of groups of millions of molecules.

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Molecular Theory.

NATURE AND ORIGIN OF MOLECULES.

We have thus been led by our study of visible things to a theory that they are made up of a finite number of parts or molecules, each of which has a definite mass, and possesses other properties. The molecules of the same substance are all exactly alike, but different from those of other substances. There is not a regular gradation in the mass of molecules from that of hydrogen, which is the least of those known to us, to that of bismuth ; but they all fall into a limited number of classes or species, the individuals of each species being exactly similar to each other, and no intermediate links are found to connect one species with another by a uniform gradation.

We are here reminded of certain speculations concerning the relations between the species of living things. We find that in these also the individuals are naturally grouped into species, and that intermediate links between the species are wanting. But in each species variations occur, and there is a perpetual generation and destruction of the individuals of which the species consist.

Hence it is possible to frame a theory to account for the present state of things by means of generation, variation, and discriminative destruction.

In the case of the molecules, however, each individual is permanent; there is no generation or destruction, and no variation, or rather no difference, between the individuals of each species.

Hence the kind of speculation with which we have become so familiar under the name of theories of evolution is quite inapplicable to the case of molecules.

It is true that Descartes, whose inventiveness knew no bounds, has given a theory of the evolution of molecules. He supposes that the molecules with which the heavens are nearly filled have received a spherical form from the long-continued grinding of their projecting parts, so that,

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Equality and Permanence of Molecules.

like marbles in a mill, they have 'rubbed each other's angles down.' The result of this attrition forms the finest kind of molecules, with which the interstices between the globular molecules are filled. But, besides these, he describes another elongated kind of molecules, the *particula striata*, which have received their form from their often threading the interstices between three spheres in contact. They have thus acquired three longitudinal ridges, and, since some of them during their passage are rotating on their axes, these ridges are not in general parallel to the axis, but are twisted like the threads of a screw. By means of these little screws he most ingeniously attempts to explain the phenomena of magnetism.

But it is evident that his molecules are very different from ours. His seem to be produced by some general break-up of his solid space, and to be ground down in the course of ages, and, though their relative magnitude is in some degree determinate, there is nothing to determine the absolute magnitude of any of them.

Our molecules, on the other hand, are unalterable by any of the processes which go on in the present state of things, and every individual of each species is of exactly the same magnitude, as though they had all been cast in the same mould, like bullets, and not merely selected and grouped according to their size, like small shot.

The individuals of each species also agree in the nature of the light which they emit—that is, in their natural periods of vibration. They are therefore like tuning-forks all tuned to concert pitch, or like watches regulated to solar time.

In speculating on the cause of this equality we are debarred from imagining any cause of equalization, on account of the immutability of each individual molecule. It is difficult, on the other hand, to conceive of selection and elimination of intermediate varieties, for where can these eliminated molecules have gone to if, as we have reason to believe, the hydrogen, &c., of the fixed stars is composed of molecules identical in 17

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all respects with our own? The time required to eliminate from the whole of the visible universe every molecule whose mass differs from that of some one of our so-called elements, by processes similar to Graham's method of dialysis, which is the only method we can conceive of at present, would exceed the utmost limits ever demanded by evolutionists as many times as these exceed the period of vibration of a molecule.

But if we suppose the molecules to be made at all, or if we suppose them to consist of something previously made, why should we expect any irregularity to exist among them? If they are, as we believe, the only material things which still remain in the precise condition in which they first began to exist, why should we not rather look for some indication of that spirit of order, our scientific confidence in which is never shaken by the difficulty which we experience in tracing it in the complex arrangements of visible things, and of which our moral estimation is shown in all our attempts to think and speak the truth, and to ascertain the exact principles of distributive justice?

APPENDIX.

Table of the Coefficients of Interdiffusion of Gases, from the Memoir of Professor Loschmidt (see p. 279), in square centimètres per second

				D
Carbonic acid		Air		•1423
a sola s <u>m</u> aalos e		Hydrogen		.5614
deditional and set of		Oxygen .	1.0	•1409
o interestion		Marsh gas		.1586
e deater Manual all		Carbonic oxide		.1406
and an an internation		Nitrous oxide		.0982
Oxygen .		Hydrogen		.7214
_		Carbonic oxide		.1802
Carbonic oxide		Hydrogen		.6422
Sulphurous acid	0.0.	Hydrogen		.4800

cf. 6077

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