

forelimb is due to the humerus, which, like the clavicle, is so much reduced in length as to present the appearance of a flattened X-shaped bone, with prominent ridges and deep depressions for the attachments and origins of the powerful muscles connected with it. Its proximal extremity presents two rounded prominences: the smaller, the true head of the bone, articulates as usual with the scapula; the larger, which is really the external tuberosity rounded off, forms a separate synovial joint with the end of the clavicle. This double articulation gives to a naturally loose joint the rigidity necessary to support the great lateral pressure sustained by the forelimb in excavating. The forearm bones are normal, but those of the forefeet are much flattened and laterally expanded. The great width of the forefoot is also partly due to the presence of a peculiar falciform bone, lying on the inner side of the palm and articulating by its proximal extremity with the wrist. Into the radial side and under surface of this bone is inserted a tendon derived from that of the palmaris longus muscle, which, acting upon it as an abductor, separates it from the side of the palm, and so increases the width of the latter, at the same time rendering the palmar integument tense.

The muscles acting on these remarkably modified limbs are all homologous with those of the cursorial insectivora, differing only in their relative development. The tendon of the biceps traverses a long osseous tunnel, formed by the great expansion of the margin of the bicipital groove for the insertion of the large pectoralis major muscle; the anterior division of the latter muscle is unconnected with the sternum, extending across as a muscular band between the humeri, and co-ordinating the motions of the forelimbs. The *teres major* and *latissimus dorsi* muscles are of immense size, probably relatively larger than in any other mammal, and are inserted together into the prominent ridge below the pectoral attachment; they are the principal agents in the excavating action of the limb. The cervical muscles connecting the slender scapulae, and through them the forelimbs, with the centre line of the neck and with the occiput are large, and the ligamentum nuchae between them is ossified (as in all true moles); the latter condition appears to be

M O L E C U L E

IN the conception of the atom as opposed to the continuous and infinitely divisible constitution of matter, it is supposed that portions of matter called *atoms* exist, which are separated, or are capable of being separated, from each other by empty space. (See *ATOM*). It may be the case that each atom has unchangeable shape and volume as well as unchangeable mass, but such a conception of an atom is not essential to the hypothesis. It is not even necessary, as explained in the article *ATOM* (vol. iii., pp. 37, 38), to maintain that no part of space can be in two atoms at the same time. But one attribute of the atom upon which its permanence, or, so to speak, its personal identity, depends, is its constituent mass, and this remains the same, unchanged and unchangeable, through all time.

Boscovich, indeed, goes so far as to regard the atom as a mere centre of force, the result of whose existence is that no two atoms or centres can approach each other within a certain distance, while other physicists regard the atomic volume as a distinct portion of space occupied by that atom to the exclusion of every other, and comprising within it matter ideally infinitely divisible, but the parts of which in fact never have been, and never can be, separated from each other. In this latter mode of viewing the subject, all the conclusions of mechanics which are based on the conception of the continuity and infinite divisibility of matter may be applied to the equilibrium or motion of each individual atom, the atomic theory merely introducing the additional hypothesis that, in fact, these persistent entities called atoms do exist, and that out of them all substances which affect our senses are constructed. The theory of universal gravitation requires us to believe in the existence of forces or actions between every portion

pubis, whereas the true pubic bones are widely separated (as shown at *p*). In this mistake he has been followed by most comparative anatomists; and hence the mole is generally believed to present the unique peculiarity that the outlets of the urinary, generative, and digestive organs do not pass through the arch of the pelvis.

due to the prolongation forwards of the sternum (described above), preventing all flexion of the head downwards; and, accordingly, the normal office of the ligament being lost, it ossifies, and so affords a more fixed point for the origins of the superficial cervical muscles.

The skull is long, with slender zygomatic arches; the nasal bones are strong and early become united, and in front of them the nostrils are continued forwards in tubes formed of thick cartilage, the septum between which becomes partially or wholly ossified beneath. There are 7 cervical, 13 dorsal, 6 lumbar, 6 sacral, and 10-12 caudal vertebrae; of the dorsal and lumbar there may be one vertebra more or less. The sacral vertebrae are united by their greatly expanded and laterally compressed spinous processes, and all the others, with the exception of the cervical, are very closely and solidly articulated together, so as to support the powerful propulsive and fossorial actions of the limbs. Dentition: 1 $\frac{3}{3}$, c. 1, pm. 1, m. 3, $\times 2 = 44$ teeth. The upper incisors are simple chisel-edged teeth; the canine is long and two-rooted; then follow three unequal conical premolars, and a fourth, much larger, and like a canine; these are succeeded by three molars with W-shaped cusps. In the lower jaw the three incisors on each side are slightly smaller, and slant more forwards; close behind them is a tooth which, though quite like them, must, from its position in front of the upper canines when the jaws are closed, be considered as the canine; behind it, but separated by an interval, is a large double-rooted conical tooth, the first premolar; the three following premolars are like the corresponding teeth above, but smaller, and are succeeded, as above, by three molars.

The geographical distribution of the common mole may be said to exceed that of all the other known species of the genus to which it belongs taken together. It extends from England to Japan, and from the Dovre-Fjeld Mountains in Scandinavia and the Middle Dwina region in Russia to southern Europe and the southern slopes of the Himalayas, where it occurs at an elevation of 10,000 feet. In Great Britain it is found as far north as Caithness, but in Ireland and in the Western Isles of Scotland (except Mull) it is altogether unknown. (G. E. D.)

of matter and every other portion, determinate in magnitude and direction, and such that, when on the infinitely divisible hypothesis the volumes of these portions are indefinitely diminished, these mutual forces are inversely proportional to the square of the distance between the portions (the distance between any two points, one in the volume of each portion, being in this case taken as the distance between the portions), and directly proportional to the products of the masses, or quantities of the two portions of matter,—such forces being regarded provisionally as ultimate facts, while inviting further analysis and explanation. Chemical and chemico-physical investigations indicate the existence of other actions between portions of matter, following other and for the most part unknown laws, and rapidly becoming inappreciable as the distance between the reacting portions is increased. All these hypotheses are to be retained on the hypothesis of discrete atoms as above enunciated, the mutual actions between atoms being the resultant of the actions between the various portions of their constituent matter. The volumes of the atoms are so small that, for any sensible distances apart, the line of the resultant mutual action between them may be taken as coincident with the line joining any point in the volume of one to any point in the volume of the other, but, for distances or parts comparable with the linear dimensions of the atoms, the size and shape of their bounding surfaces must be taken into consideration, and perhaps also the law of distribution of their constituent matter within that surface. In all respects, unless we accept the Boscovichian hypothesis, we simply regard the atom as made up, so to speak, of infinitely divisible matter, while substances, as we know them, are built up of indestructible and unchangeable atoms.

With this conception of an atom, as thus explained, we might be content to rest, confessing our total ignorance of the mode in which such atoms are built up into actual substances, being satisfied to regard such substances as

composed of these distinct portions of matter separated, or capable of being separated, by empty space from other portions. But the *molecular* hypothesis of the constitution of different kinds of substances aims at analysing this process by which such substances are built up out of their constituent atoms. The *molecule* of any substance is, by some chemists, defined as being the smallest portion of that substance to which can be attributed all the chemical properties of the substance; by others, as the smallest portion which, so long as the substance is chemically unchanged, keeps together without complete separation of its parts. In the language of Clausius's theorem, if the parts of the molecule have internal motion, the kinetic energy of such internal motion is equal to the virial of the mutual attractive forces of the parts. Thus the formation of the molecule of each particular substance is viewed as an essential step in the process of building up that substance out of its constituent atoms. The molecule is first built up out of atoms arranged in its formation according to a definite type, and then the substance itself is constituted of these molecules. Of course molecules may be, and in fact in many particular substances are, supposed to be monatomic; that is to say, the intermediate step of building up the molecule out of the atoms has, in these particular substances, been omitted, the atoms and molecules becoming then identical. The particular arrangement of the formed molecules in the building up of the substance determines the physical state of that substance,—that is, its fluid, solid, gaseous, crystalline, or amorphous state; but the chemical properties of the substance depend upon the constitution of the molecule. As the investigations and theories of chemistry appear to indicate irresistibly the existence of permanent atoms, so do they also lead almost as necessarily to the conception of the molecule as an entity which bears the same relation to special substances that the atoms bear to matter generally. So long as the molecule endures, the substance of which it is the molecule retains its chemical properties; with the dissolution of the molecule, the substance, as that special substance, perishes; the atoms alone continue, and are free to enter into other combinations. The permanence of the molecule is relative, that of the atom absolute. This conception of the molecular constitution of substances suggests physical questions of great interest, such as the shape, volume, and mass of the constituent molecules, and the relative motions of which their parts are susceptible; and the answers to these questions cannot fail to be of great value in chemical and chemico-physical investigations, as well as in the theories of light and electricity.

Now, whatever differences may exist between the properties of different substances in the solid and liquid states, there are certain properties which, in the gaseous state, manifest themselves with no variation whatever in all substances alike. Hence the explanation of these common properties—or gaseous laws, as they are called—has long possessed a peculiar fascination for physicists. The tendency to expand or fill all accessible space, manifested by all gases, proves that on the molecular hypothesis their compound atoms or molecules must be continually tending to fly apart. We must conceive gases as constituted of molecules, not only separable but actually separated by space void of the matter of which these gases consist; and it may be most reasonably expected, therefore, that any general laws to which substances in this state conform may afford us a valuable insight into the constitution of these separate molecules.

Now the general laws to which all gases conform are: (1) *Boyle's law*—that, in a given mass of any gas kept at constant temperature, the pressure per unit of area upon the containing surface increases in the same proportion as

the volume occupied by the gas is diminished, or at least with very slight deviation from exact proportionality; (2) *Charles's law*—that, if the temperature be varied while the pressure upon the gas remains the same, the gas increases by $\frac{1}{273}$ of its volume at zero centigrade for every degree of centigrade added to the temperature, or, which in combination with Boyle's law is the same thing, that if the density be constant, the pressure is directly proportional to the temperature measured from the point -273° centigrade, this point being called the zero of absolute temperature; (3) *Avogadro's law*—which asserts that all gases at the same temperature and pressure contain the same number of molecules in the same volume; and (4) *Dalton's law*—that in a mixture of different gases, when there is equilibrium, each gas behaves as a vacuum to all the rest.

It was at one time considered that these phenomena might be explained on the hypothesis of mutual repulsive forces between the parts of which the gas is composed, whether they were regarded as constituted of molecules or of infinitely divisible continuous matter,¹ but it has been shown in the article *ATOM* (vol. iii. p. 39 *sq.*) that there are at least two absolutely conclusive reasons why this explanation cannot be accepted. These objections, together with the experimental fact proved by Joule that gases, or at any rate atmospheric air, expand into vacuum with scarcely any appreciable change of temperature, must be considered fatal to any mutual-force theory of gaseous action, and, accordingly, physicists have been driven to seek for other methods of explaining these laws. The explanation which has been more developed than any other is that known as the kinetic theory of gases, which regards the intrinsic energy of a gaseous mass as residing, not in the potential energy of intermolecular forces, but mainly in the kinetic energy of the molecules themselves, which are assumed to be in a state of continual relative velocity, admitting at the same time a possible small intermolecular potential energy, and it may be also an interatomic energy, between the atoms of the individual molecules. That some such persistent relative motion does exist in every gaseous mass is evident from the rapidity with which odours penetrate the stillest air where no breath of wind—that is, of absolute motion of translation of the mass as a whole or any portion of finite size—is perceptible. It becomes an interesting question whether the laws of mechanics admit of a mass thus constituted ever arriving at a state of permanence; that is to say, whether, consistently with the hypothesis of infinite irregularities in the directions and magnitudes of velocities of individual molecules, there may be found any properties of the mass in the aggregate which remain

¹ An argument in favour of the molecular constitution of gases, to which attention was first called by Professor Osborne Reynolds (Memoir "On some Dimensional Properties of Matter in the Gaseous State," *Phil. Trans.*, 1879), is derived from certain phenomena observed in highly-rarefied gases, and in the transpiration of gases through porous plates. If, according to this argument, we had in a gas to do with a continuous plenum, such that every portion must possess the same properties, then these properties must exist independently of the amount of gas contained in any space, although their sensible effects might be increased or diminished by a variation in that amount. If, then, we can find properties of a gas depending on the size of the space in which it is enclosed, and on the quantity of gas enclosed in this space, we have proof that gas is not continuous—in other words, possesses dimensional structure. Such properties we do find in highly-rarefied gases, as, for instance, in the phenomena of Crooke's radiometer. The motion of the vanes when one side is heated by incident rays appears to depend on the distance between the vane and the containing walls of the vessel bearing some not very high ratio to the distance between the particles or molecules of the gas. At least no satisfactory explanation of the phenomena consistent with the gas being continuous has yet been suggested. Again, Professor O. Reynolds, from his experiments on the transpiration of gases through a porous plate, finds a relation between the gas and the coarseness or fineness of the plate, which would not exist were the gas continuous.

constant, and in agreement with the accepted laws common to all gases. Now the physical theory of heat compels us to regard the intrinsic energy of any gaseous mass as dependent entirely or almost entirely upon the temperature. If, therefore, this intrinsic energy is to be sought for in the kinetic energy of the moving molecules, it follows that the average value of the kinetic energy of the molecules taken throughout the mass must be also a function of the temperature.

We will proceed to investigate the condition of permanence of a number of molecules moving about irregularly in any bounded space; and, for simplicity's sake, we shall first of all restrict ourselves to the case of monatomic molecules.

We know nothing of the size or shape of these atoms, except that the volume of each one must be incomparably smaller than that of the containing region. In shape we shall, as the simplest hypothesis, regard them as spherical. We shall suppose that there are no intermolecular forces between any two such atoms, except of such a nature as to be practically insensible when the atoms are not geometrically in contact, and similarly as regards the forces between the atoms and the material bounding surface, such forces being of the nature called "conservative." So that in point of fact we are investigating the mechanical properties of an infinitely large number of infinitely small and perfectly elastic spheres moving about in a given region and subject to frequent collisions.

PROBLEM.—A very large number of smooth elastic spheres, equal in every respect, are in motion within a region of space of given volume, and therefore occasionally impinge upon each other with various degrees of relative velocity and in various relative directions; required to find the law of distribution of velocities in order that such distribution may be permanent.

Let N be the total number of spheres, and let

$$\chi(u, v, w) du dv dw$$

be the number of spheres whose component velocities, parallel to the axes, are intermediate between u and $u + du$, v and $v + dv$, and w and $w + dw$ respectively.

If c be the resultant velocity of any of these last-mentioned spheres, and if θ be the inclination of c to the axis of z , and ϕ that of the plane xy to the plane xz , the last-mentioned expression will become, by changes of the independent variables from u, v, w to c, θ, ϕ , and σ

$$\chi(u, v, w) c^2 \sin \theta d\theta d\phi d\sigma.$$

Let a spherical surface of radius unity be described about any origin as centre, and let $d\sigma$ be written for the element $\sin \theta d\theta d\phi$ on this surface, then the last-written expression becomes

$$\chi(u, v, w) c^2 d\sigma d\sigma.$$

Since for the same magnitude of the resultant velocities all directions of motion must be equally probable, it follows that the coefficient of $d\sigma d\sigma$ in the last-written expression must be a function of c only, and therefore the number of spheres having component velocities between u and $u + du$, v and $v + dv$, w and $w + dw$, must be

$$\psi(c) du dv dw,$$

It is required to find the form of ψ in order that the value of this expression may be unaffected by collisions. The solution is, that the number of spheres with component velocities between the limits u and $u + du$, v and $v + dv$, w and $w + dw$ must be

$$Ae^{-hu^2} du dv dw;$$

or

$$Ae^{-hc^2} c^2 d\sigma d\sigma,$$

employing the notation already used.

Integrating with respect to $d\sigma$ from 0 to 4π , we find for the number of spheres with velocities between c and $c + dc$ the expression

$$4\pi Ae^{-hc^2} dc.$$

Again, since the number with component velocities between u and $u + du$, v and $v + dv$, w and $w + dw$ is

$$Ae^{-h(u^2+v^2+w^2)} du dv dw,$$

it follows that the number of spheres having velocities intermediate between u and $u + du$ parallel to the x axis is

$$\left(\sqrt{\frac{2}{\pi}} Ae^{-hu^2} du\right) \left(\sqrt{\frac{2}{\pi}} Ae^{-hv^2} dv\right) \left(\sqrt{\frac{2}{\pi}} Ae^{-hw^2} dw\right),$$

$$Ae^{-hu^2} du \int_0^\infty e^{-hv^2} dv \int_0^\infty e^{-hw^2} dw;$$

that is,

$$\frac{\pi}{h} Ae^{-hu^2} du,$$

where A is to be determined by the equations

$$\frac{\pi}{h} A \int_0^\infty e^{-hu^2} du = N,$$

or

$$A \frac{\pi^{\frac{3}{2}}}{h^{\frac{3}{2}}} = N;$$

therefore

$$A = \frac{N h^{\frac{3}{2}}}{\pi^{\frac{3}{2}}};$$

that is to say, the number of spheres having velocities between c and $c + dc$ is

$$\frac{4h^{\frac{3}{2}}}{\sqrt{\pi}} Ne^{-hc^2} dc.$$

Multiplying this expression by c , and integrating the product with regard to c from 0 to ∞ , and dividing by N , the mean velocity for all the spheres becomes

$$\frac{2}{\sqrt{\pi h}};$$

and multiplying by c^2 instead of by c , we find the mean square of all the velocities to be

$$\frac{3}{2h}.$$

In the preceding investigation no account has been taken of collisions between the spheres and the enclosing boundary of the region in which they are contained, because in every such collision the magnitude of the velocity of each sphere is unaltered and its direction is changed according to the ordinary law of reflexion, whence it is evident that the distribution is unaffected by such collisions. Also, the investigation has been confined to the cases of spheres colliding in pairs, but since there need be no limit to the smallness of the interval between any pair of collisions the result really embraces the cases of simultaneous collisions between three or more spheres; for if a sphere A collides with another B , and immediately afterwards with a third C , the resultant velocity of A after this second collision must be the same as if it had collided with B and C simultaneously.

The foregoing investigation has been given in some detail because the principles upon which it proceeds are essentially the same as those by which all questions of the distribution of energy among a great number of moving bodies are determined, although it may be found, as well as the detailed investigations of the results immediately following, in published memoirs and systematic treatises on the kinetic theory of gases.

If the spheres be not all of equal mass, but if there be within the region N spheres of mass m , N' of mass m' , and so on, then it may be proved, by reasoning exactly similar to the foregoing, that when the permanent or stable state of motion has been attained the number of spheres of the N set with component velocities between u and $u + du$, v and $v + dv$, w and $w + dw$ is

$$Ae^{-\frac{hmc^2}{2}} du dv dw,$$

and the number of the N' set having component velocities between u' and $u' + du'$, v' and $v' + dv'$, w' and $w' + dw'$, is

$$A'e^{-\frac{h'mc'^2}{2}} du' dv' dw',$$

where $c^2 = u^2 + v^2 + w^2$, $c'^2 = u'^2 + v'^2 + w'^2$, h is a constant the same for both sets, and

$$A = \frac{N}{\pi^{\frac{3}{2}}} \cdot \left(\frac{mh}{2}\right)^{\frac{3}{2}}, \quad A' = \frac{N'}{\pi^{\frac{3}{2}}} \cdot \left(\frac{m'h}{2}\right)^{\frac{3}{2}},$$

and so on if there be any other sets.

The mean velocity and mean square velocity of each sphere of the N set are

$$\frac{2}{\sqrt{\pi}} \sqrt{\frac{2}{mh}} \text{ and } \frac{3}{mh} \text{ respectively,}$$

and the mean kinetic energy of each of such spheres is

$$\frac{3}{2h}.$$

the last result being common to all the sets.

If the spheres in the given region be acted on by any given forces tending to fixed centres, and functions of the distances of the centres of the spheres from the centres of force, we may not in such case assume, a priori, that the chances of velocities in all directions are the same; but we may assume that the number of spheres of any set (N) with coordinates of their centres intermediate between

x and $x + dx$, y and $y + dy$, z and $z + dz$, and component velocities intermediate between u and $u + du$, v and $v + dv$, w and $w + dw$, is

$$\psi(x, y, z, u, v, w) dx dy dz du dv dw.$$

In the state of permanence the form of ψ must be independent of the time (t), so long as the sphere is moving free from collisions with any other.

From the last-mentioned condition it must follow that, if $\phi_1 = \phi_1$, $\phi_2 = \phi_2$, &c., be any equations among the variables determining the position and motion of any sphere obtained by the elimination of t from the equations of motion of that sphere, then ψ must be of the form $\psi(\phi_1, \phi_2, \text{&c.})$. With the assumption, then, that the number of spheres of the given set with variables between the above-mentioned limits is

$$\psi(\phi_1, \phi_2, \dots) dx \dots dw,$$

we find for the form of ψ , by reasoning like the foregoing,

$Ae^{-h(\chi + \frac{mc^2}{2})}$, where χ is the potential energy of the sphere in the position x, y, z , and $c^2 = u^2 + v^2 + w^2$, and h is a constant, the same for all the sets.

If we integrate the expression $Ae^{-h(\chi + \frac{mc^2}{2})} dx dy dz du dv dw$ for all values of x, y, z within the given region, we find for the number of spheres of any set with component velocities between u and $u + du$, v and $v + dv$, w and $w + dw$,

$$Be^{-\frac{hmc^2}{2}} du dv dw,$$

whence we easily see that the chances of velocities in all directions are the same, and that the mean velocity and mean square velocity of any sphere of this set are $\frac{2\sqrt{2\pi}}{\sqrt{mh}}$ and $\frac{3}{mh}$ respectively, and the mean

kinetic energy of any such sphere is $\frac{3}{2h}$, and therefore the same for all the sets.

Furthermore, if we integrate the expression

$$Ae^{-h(\chi + \frac{mc^2}{2})} dx dy dz du dv dw$$

for all values of u, v , and w from $-\infty$ to $+\infty$ respectively, we obtain a result of the form $Ce^{-h\chi} dx dy dz$, and therefore the number of spheres of the set in question with centres within the elementary volume $dx dy dz$, or, what is the same thing with the exception of a constant factor, the chance of the centre of any sphere of that set being within that elementary volume, is $Ce^{-h\chi} dx dy dz$, so that the density of the N set of matter in the neighbourhood of the point x, y, z is $mCe^{-h\chi}$.

We are now in a position to compare the physical properties of a medium composed of monatomic molecules in motion, and free from any intermolecular or interatomic forces with those of ordinary gases, so long at least as the atoms are spherical.

Consider two contiguous portions of such a medium separated by any plane parallel to that of yz , and, since the distribution and motion of each set of spheres is independent of all the other sets, let us confine our attention to the spheres of the N set. Suppose that there are N such spheres per unit volume in the neighbourhood of the point x, y, z , whose component velocities parallel to the axis of x are between u and $u + du$. The number of these spheres which cross the elementary area $dy dz$ in time dt will be the same as the number of the dN spheres whose centres are situated within the elementary parallelepiped $dx dy dz$, in which dx is equal to $u dt$, and this number is

$$Nu dy dz dt.$$

Each of these spheres carries across with it a momentum parallel to x equal to mu ; the total momentum parallel to x transferred across $dy dz$ in time dt is therefore

$$mNu^2 dy dz dt.$$

If u be positive, this is positive momentum transferred from the negative to the positive side of the plane yz ; and if u be negative, this is negative momentum similarly transferred from the positive to the negative side of that plane. In either case it follows that by the mere motion of these spheres across the area $dy dz$ the positive momentum parallel to the axis of x is diminished by the quantity $mNu^2 dy dz dt$ on the negative side of the plane yz , and increased by the same quantity on the positive side of that plane in the time dt ; m being, as before, the mass of each sphere. Hence, on the whole, there is a transference of positive x momentum in the time dt across the area $dy dz$ equal to $m dy dz dt \int_{-\infty}^{\infty} u^2 N$; that is, equal to

$$dy dz dt \rho \bar{v}^2,$$

where ρ is the density of the N matter at the point x, y, z , and \bar{v}^2 is the mean square of the v velocities.

But either by integration or general reasoning it is easily seen

that $\bar{v}^2 = \frac{\bar{v}^2}{3}$, where \bar{v}^2 is the mean square of the resultant velocities of the N spheres, and is equal, as we have proved, to

$$\frac{3}{mh}.$$

Therefore, there is a transference of positive momentum from the negative to the positive side of the plane yz across the area $dy dz$ in time dt equal to

$$\frac{\rho dy dz dt}{mh}.$$

Each separate sphere whose component velocities are u, v , and w carries across the same area y and z momenta equal to mv and mw respectively, so that in the time dt there are carried across the area $dy dz$ y and z momenta equal to $\sum muv dy dz dt$ and $\sum mwv dy dz dt$, respectively. By symmetry it is clear that $\sum muv$ and $\sum mwv$ are separately zero. Therefore, the resultant mutual actions of the two portions of the medium under consideration in the time dt is the transference across the elementary area $dy dz$ of a quantity of x

momentum equal to $\rho dy dz dt \frac{\bar{v}^2}{3}$ from the negative to the positive side of the bounding plane. If this mutual action, or, as it is generally called, "pressure" when referred to unit of surface, be denoted by the symbol p , we get the equation

$$p dy dz dt = \rho dy dz dt \frac{\bar{v}^2}{3},$$

or

$$p = \rho \frac{\bar{v}^2}{3} = \frac{\rho}{mh}.$$

Since the momenta parallel to y and z remain unaltered, it follows that the mutual action or pressure between contiguous portions of the medium in the neighbourhood of any point is normal to the bounding surface at that point. Since also the expression for p or $\frac{\rho}{mh}$ is independent of the direction of the x axis, it follows that the pressure at any point of the medium is the same in all directions.

If the contiguous portions of the medium be separated by a material instead of an ideal plane, it will be necessary for the maintenance of equilibrium that there should be an action between this plane and the adjacent medium, equivalent to the transference of momentum estimated above; but action measured by the rate per unit of time at which momentum is generated constitutes moving force or statical pressure. Hence the force or pressure between the plane and medium is normal to the plane, independent of the direction of the plane through the point, and equal to the value of $\frac{\rho}{mh}$ at the point.

When several sets of spheres are present together in the region under consideration, the distribution of the centres and of the velocities of each set is, as we have seen, independent of the co-existence of the other sets. If therefore ρ_1, ρ_2 , &c., be the densities of the matter of the different sets in the neighbourhood of the point x, y, z , and if p_1, p_2 , &c., be the pressures at that point defined as above, and if m_1, m_2 , &c., be the masses of the spheres of each of the sets, and p the total pressure, we get

$$p = p_1 + p_2 + \text{&c.} \\ = \frac{\rho_1}{m_1 h} + \frac{\rho_2}{m_2 h} + \text{&c.}$$

Hence we arrive at the following conclusions:—(1) there is one physical quantity having the same value for every set of spheres—namely, the mean kinetic energy of each sphere, or $\frac{3}{2h}$; let this quantity be called τ ; (2) the distribution of the positions and velocities of the spheres of each set is independent of the co-existence of the remaining sets, and is in all respects the same as if that particular set existed alone in the region considered; (3) the pressure at any point referred to unit of surface at any point of the medium arising from the action of any one of the sets is $\frac{2}{3m} \rho \tau$, where ρ is the density of that particular set at the point in question, and τ is the physical quantity above referred to as common to all the sets.

This third inference may be expanded into the following three laws:—(a) if τ be kept constant, then the pressure arising from each set varies as the density of that set; (b) if ρ be kept constant, then the pressure from each set varies as τ ; (c) if the pressures for all the sets be the same, then $\frac{\rho}{m}$ is also the same, or the number of spheres per unit volume is the same.

Now suppose there is a mixture of any number of gases in any region; when there is equilibrium there is one physical quantity, namely, temperature, which is the same for all; the intrinsic

energy of this mixture depends, as we know, upon its temperature, and the energy of these moving spheres is entirely kinetic, and may be conceived, therefore, to be a function of the mean *vis viva*. Let us then assume that in this medium of moving spheres we have a representation of a mass of gases, and that what is called the temperature of the gaseous mass is nothing else than the τ or mean kinetic energy of each moving sphere. Then, with this assumption, the three parts (α , β , γ) of inference (3) above correspond to the gaseous laws connected with the names of Boyle, Charles, and Avogadro respectively, and inference (2) corresponds with the law of Dalton concerning gaseous mixtures.

We may also deduce the ordinary hydrostatical equations of equilibrium from the formulae which we have obtained.

For, since these equations give us
$$p = \frac{p}{m\bar{h}}, \text{ and } \rho = mBe^{-hX},$$

we get

$$\frac{dp}{dx} = -\rho \frac{dX}{dx} = \rho X, \text{ and } \frac{dX}{dx} = -\tau X,$$

and similarly

$$\frac{dp}{dy} = \rho Y, \frac{dp}{dz} = \rho Z,$$

where X , Y , and Z are the component impressed forces, or the negatives of the space variations of χ along the coordinate axes.

So far, therefore, the physical properties of a perfect gas or mixture of such gases correspond, in all respects, with the physical properties of a medium consisting of a set of elastic spheres, or of a mixture of sets of such spheres, with the sole assumption that the physical property termed temperature, in the case of the gas, corresponds to, or is represented by, the mean kinetic energy of each of the spheres, and that each sphere represents the chemical atom.

There are, however, physical properties of gases which this theory fails to explain. The most important of these is the ratio of the specific heats at constant volume and constant temperature respectively. The specific heat of gas expanding while being heated under a constant pressure is greater than that of gas heated with a constant volume, as when it is contained in a rigid vessel, for the obvious physical reason that in the former case a portion of the heat is converted into mechanical work, namely, that performed by the expansion under the constant pressure. This ratio of the specific heat of gas under constant pressure to the specific heat with constant volume has been determined for many gases with great accuracy, chiefly from observations of the velocity of sound in such gases, in which velocity the value of this ratio bears a very important part.

Now, on the assumption of the gas being constituted of a number of elastic spheres in rapid but irregular motion among each other, and the physical property of temperature being represented or measured by the mean *vis viva* of each sphere, the ratio of these specific heats must be exactly 1½.

For, if v be the volume occupied by a unit of mass of this moving sphere medium, and τ the number of spheres to the unit mass, and if ρ be the density, it follows that

$$\tau m = \rho v = 1.$$

Also we know that p , the pressure referred to unit surface, is given by the equation

$$pv = \frac{2}{3} \tau \tau,$$

where τ is the mean *vis viva*. If now τ increase from τ to $\tau + \delta\tau$, while v remains constant, the increase of intrinsic energy must be, from definition, $\tau\delta\tau$. Also if there be a similar change in τ without the restriction of v being constant, but supposing p to be constant, there is external mechanical work performed equal to $p\delta v$, where δv is the increase of volume. Also

$$p\delta v = \frac{2}{3} \tau\delta\tau;$$

and therefore the whole energy required to be supplied from without must be in this case

$$\tau\delta\tau + \frac{2}{3} \tau\delta\tau$$

Or the ratio of the energies to be supplied from without, in order that the mean *vis viva* of the moving sphere medium should be increased by the same amount in the two cases respectively, becomes

$$\frac{\tau + \frac{2}{3} \tau}{\tau}, \text{ or } 1\frac{1}{3}.$$

If therefore the gaseous mass be adequately represented by the moving sphere medium, the ratio of the specific heats must be 1½.

Mercury vapour is the only gas for which the ratio has so large a value as this. Several of the more permanent gases have the ratio equal to 1.408, while in others it falls as low as 1.26. The value for mercury vapour, as determined by Kundt and Warburg

(*Poggendorff*, clvii. 353), is between 1.695 and 1.631, the mean of all the observations being somewhat under 1.6. If any value above 1.6 be insisted on it will be impossible to retain the theory as above enunciated. In point of fact we may say, in anticipation of what has yet to come, that there is no modification of the kinetic theory as hitherto treated which could give a higher value for the ratio in question than 1½.

It follows from what has been proved that either all known gases and vapours, except the vapour of mercury, and perhaps cadmium, must be polyatomic, or else that the attempts to explain the constitution of gases by the kinetic theory must be abandoned. We must therefore proceed further to investigate the physical properties of a medium consisting of compound atoms or molecules built up of atoms in any definite arrangement, such molecules being in a condition of irregular motion among themselves, such as we have supposed in the cases of the spherical atoms hitherto considered.

It will be observed, on reference to the cases of the spheres hitherto investigated, that, whether there be forces to fixed centres in action on the medium or not, the chance of any sphere having the coordinates of its centre and its component velocities between x and $x+dx$, y and $y+dy$, z and $z+dz$, u and $u+du$, v and $v+dv$, w and $w+dw$, is proportional to $e^{-hE} dx dy dz du dv dw$, where E is the total energy, kinetic and potential, of the sphere in the state of position and motion defined by x, y, z, u, v, w .

We may generalize this proposition, and prove that when the sphere is replaced by a molecule of any shape and constitution, so as to be defined as to position and motion by r generalized coordinates q_1, \dots, q_r , with their corresponding momenta p_1, \dots, p_r , the chances of the molecule having its defining variables between the limits q_1 and q_1+dq_1, \dots, p_r and p_r+dp_r , or, what is the same thing, the number of such molecules at any time with variables thus limited, whether there be forces to fixed centres or not, and whether interatomic forces or intermolecular forces are or are not in action on the molecular aggregate, is proportional to

$$e^{-hE_r} dq_1 \dots dp_r,$$

where h is a constant, the same for all molecules, and E_r is the total energy, kinetic and potential, of the molecule in the free state as to position and motion, the potential energy being that of the fixed centre forces on the molecule, together with that of its interatomic forces, in the given position.

The problem before us may be stated thus:—

A number of similar molecules possessing in the whole n degrees of freedom, where n is very large, are in motion in a region of space bounded by a material envelope, under the action either of forces to fixed centres (called external forces) or of forces between different molecules and different parts of the same molecule, as well as by forces between the fixed boundary and the contained molecules, all of them conservative, so that the total energy, kinetic and potential, of the aggregate remains always the same; it is required to find the chance of a group of any one or more molecules possessing in the whole r degrees of freedom, defined by the coordinates q_1, \dots, q_r , and momenta p_1, \dots, p_r , where r is small compared with n , having its variables between the limits q_1 and q_1+dq_1, \dots, p_r and p_r+dp_r .

We might start with the assumption made above in the case of the spheres under central forces, that this chance must be of the form

$$\psi(\phi_1, \phi_2, \&c.) dq_1 \dots dp_r,$$

where $\phi_1 = \alpha_1, \phi_2 = \alpha_2, \&c.$, are obtained by the elimination of t between the equations of motion of the r group under the fixed centre and boundary forces and those between its component atoms, because there is nothing in the conception of a molecule beyond that of a system with a number of degrees of freedom, and under internal forces; and in this case, considering the generality of the assumption as to the external forces, it would be impossible to conceive the existence of any general equation, independent of the time, between the variables, except that of the conservation of energy, so that the chance in question becomes

$$\psi(E_r) dq_1 \dots dp_r,$$

where E_r is as above defined, and it remains to determine the form of ψ .

If we considered a second group of one or more molecules containing s degrees of freedom (where s may or may not be equal to r , but, like r , is much smaller than n), and defined by the coordinates and momenta $q_{r+1}, \dots, q_{r+s}, p_{r+1}, \dots, p_{r+s}$, then the two groups together contain $r+s$ degrees of freedom defined by the variables q_1, \dots, p_{r+s} and since $r+s$ is small compared with n , the chance of this group having its variables between q_1 and q_1+dq_1, \dots, p_{r+s} and $p_{r+s}+dp_{r+s}$ must be

$$\psi(E_{r+s}) dq_1 \dots dp_{r+s}$$

But this chance must be equal to the chance of the r group being fixed in the state $q_1, q_1+dq_1, \dots, p_r, p_r+dp_r$, multiplied by the chance of the remaining s group being in the state $q_{r+1}, q_{r+1}+dq_{r+1}, \dots, p_{r+s}, p_{r+s}+dp_{r+s}$ where the r group are so fixed.

Now to find this latter chance we observe that it is the chance of the s group being in their required limits of position and motion, when the internal forces between the r and s group become forces between the s group and fixed centres.

If the total kinetic energy of the r group in their given state be T_r , and that of the $r+s$ group be T_{r+s} , the total kinetic energy of the s group must be $T_{r+s} - T_r$.

Also if the total potential energy of the $r+s$ group under the influence of all forces be X_{r+s} , this is made up of—

- (1) X_r , the potential energy of the r group to fixed centres, and of its internal forces;
- (2) X_s , similarly taken for the s group; and
- (3) X_{rs} , the potential energy of the r and s group forces.

And when the r group is fixed the potential energy of the s group is reduced to (2) and (3), or is $X_{r+s} - X_r$.

Therefore the chance of the s group having its variables within the required limits when the r group is fixed must be

$$\psi(E_{r+s} - E_r) dq_{r+1} \dots dp_{r+s}$$

Therefore $\psi(E_r) \psi(E_{r+s} - E_r) dq_1 \dots dp_{r+s} = \psi(E_{r+s}) dq_1 \dots dp_{r+s}$

or $\psi(E_r) \psi(E_{r+s} - E_r) = \psi(E_{r+s})$.

Therefore $\psi(x) = e^{Cx} = e^{-hX}$ suppose.

And the chances of the r group having its variables between the limits q_1 and q_1+dq_1, \dots, p_r and p_r+dp_r , must, in the state of permanent or stable motion, be proportional to

$$e^{-hE_r} dq_1 \dots dp_r,$$

which was to be proved.

Supposing now that the aggregate of molecules under consideration consists of a number of sets of similar molecules, the number of molecules in one of these sets being N , where N is very large, and suppose that each of these N molecules possesses σ degrees of freedom defined by the coordinates q_1, \dots, q_σ with the momenta p_1, \dots, p_σ , and that its mass is m . Three of these coordinates may be taken as the rectangular coordinates of its centre of mass, in which case the corresponding momenta will be mu, mv, mw , where u, v, w are the component velocities of translation of that centre of mass. Then in this case, if $q_4, \dots, q_\sigma, p_4, \dots, p_\sigma$ be the remaining coordinates and momenta of the molecule, the chance of the molecule's variables being within the limits x and $x+dx, \dots, p_\sigma$ and $p_\sigma+dp_\sigma$ will be proportional to

$$e^{-h(\chi + T)} dx dy dz dq_4 \dots dp_4 e^{-\frac{h}{2} m(u^2 + v^2 + w^2)} du dv dw \dots (I),$$

where T , the kinetic energy of the molecule, is equal to
$$\frac{m}{2}(u^2 + v^2 + w^2) + f,$$

where f is a quadratic function of the p 's, having as coefficients known functions of the q 's.

If we integrate the expression (I) for all possible values of $x, y, z, q_4, \dots, q_\sigma, p_4, \dots, p_\sigma$, we obtain an expression of the form

$$Be^{-\frac{h}{2} m(u^2 + v^2 + w^2)} du dv dw \dots (II),$$

where B is independent of u, v, w , and $c^2 = u^2 + v^2 + w^2$. From the form of (II) it follows, exactly as in the cases of the elastic spheres, that the chances of all directions of the velocity of translation of a molecule are equal, that the mean velocity and mean square velocity of translation of each molecule are

$$\frac{2^{\frac{3}{2}} \sqrt{\pi}}{\sqrt{m h}} \text{ and } \frac{3}{m h}$$

respectively, and that the mean kinetic energy of translation is $\frac{3}{2h}$,

and the same for a molecule of any set.

Again, if \bar{T} be the mean total kinetic energy of the molecule, then

$$\bar{T} = \frac{\int \dots \int T e^{-h(\chi + T)} dx \dots dp_\sigma}{\int \dots \int e^{-h(\chi + T)} dx \dots dp_\sigma} \dots (III);$$

and if we evaluate this expression, paying attention to the form of T as a quadratic function of the p 's mentioned above, we shall find for (II) the expression $\frac{\sigma}{2h}$.

It follows from this result that each additional degree of freedom of the molecule increases the mean total kinetic energy of the molecule by the quantity $\frac{1}{2h}$, which is the mean kinetic energy of translation parallel to any one of the axes, and that the total kinetic energy is proportional to the number of such degrees of freedom.

If, again, we integrate the expression (I) for all values of the momenta, we obtain an expression of the form

$$Ce^{-hX} dx dy dz dq_4 \dots dq_\sigma \dots (IV),$$

where χ is the potential energy of the molecule due to fixed centre

and to interatomic forces in the position defined by $x, y, z, q_4, \dots, q_\sigma$. The dimensions of the molecule are so small that we may regard forces from each fixed centre on different parts of the molecule as parallel and equal and functions of the distance of the centre of mass from that fixed centre, so that, if the part of χ arising from these fixed centre forces be called χ_1, χ_2 , will be a function of x, y, z , and of these variables only, the remaining part of χ (arising from interatomic forces), which may be called χ_3 , will be a function of the $\sigma - 3$ variables q_4, \dots, q_σ .

If in (IV) we write $\chi_1 + \chi_2$ for χ , and then integrate for all values of q_4, \dots, q_σ , we obtain an expression of the form

$$D e^{-hX_1} dx dy dz \dots (V),$$

where D is independent of x, y, z , and therefore ρ the density of the N molecule matter in the neighbourhood of the point x, y, z , is
$$m D e^{-hX_1}.$$

From these results all the propositions proved above with reference to the aggregate of elastic spheres or monatomic molecules, as to the correspondence of the physical properties of such an aggregate with those of gases as indicated by the gaseous laws, may be deduced also for this aggregate of polyatomic molecules. So that if \bar{T} be equal to $\frac{3}{2h}$, or the mean kinetic energy of agitation of any one of the aggregate of moving molecules, if v be the volume occupied by unit of mass, τ the number of molecules in unit of volume, and m the mass of each molecule, we have, exactly as in the case referred to,

$$m\tau = 1, \rho v = 1, \text{ and } pv = \frac{2}{3} \tau \bar{T}.$$

We also get the ordinary hydrostatical equations

$$\frac{dp}{dx} = \rho X, \frac{dp}{dy} = \rho Y, \frac{dp}{dz} = \rho Z$$

from this expression for p combined with the equation

$$\rho = m D e^{-hX_1},$$

remembering that

$$\frac{dX_1}{dx} = -mX, \frac{dX_1}{dy} = -mY, \frac{dX_1}{dz} = -mZ,$$

whence the coincidence of the physical properties of this aggregate of polyatomic moving molecules with those of a gas, on the assumption that the temperature represents the mean kinetic energy of agitation, is at once apparent.

It can be shown also that the aggregate of moving molecules, such as we conceive a gas to be, possesses another very important physical property which, by its analogy to the second law of thermodynamics, affords additional evidence of the relation between the phenomena of heat and those of aggregates in some kind of motion,—the property in question being that, if in any aggregate of moving molecules the mean kinetic energy of any one of them be called τ , and if δQ be an increment of energy imparted to the aggregate from without, then $\frac{\delta Q}{\tau}$ is a perfect differential.

If to this aggregate we apply a certain small quantity δQ of heat or energy from without, and if $\delta \tau$ be the increase of the mean kinetic energy of agitation when the volume is unaltered, then this constancy of volume prevents any of the energy δQ from being absorbed in doing external work; but it is conceivable that the increase of τ may cause such a change in the average state of the molecule as to produce a variation $\delta \chi$ in the mean potential energy of the molecule, $\delta \chi$ being proportional to $\delta \tau$.

Therefore
$$\delta Q = r \left\{ \frac{d\bar{T}}{d\tau} + \frac{d\chi}{d\tau} \right\} \delta \tau.$$

But
$$\bar{T} = \frac{\sigma}{2h} = \frac{\sigma}{3} \cdot \frac{3}{2h} = \frac{\sigma}{3} \tau;$$

therefore
$$\delta Q = r \left\{ \frac{\sigma}{3} + \frac{d\chi}{d\tau} \right\} \delta \tau.$$

If the volume vary by δv , the pressure being constant, then we must add external work, or $p\delta v$, to the energy absorbed, so that if the whole external energy now applied be δQ , and the increase of temperature $\delta \tau$ be the same in both cases, we have

$$\frac{\delta Q}{\delta \tau} = \frac{r \left(\frac{\sigma}{3} + \frac{d\chi}{d\tau} \right) \delta \tau + p\delta v}{r \left(\frac{\sigma}{3} + \frac{d\chi}{d\tau} \right) \delta \tau}$$

But if p be constant, then as before

$$p\delta v = 2 \frac{r}{3} \delta \tau,$$