

exerting an attractive force  $\frac{\mu}{r^2}$  and a repulsive force  $\frac{\mu'}{r^2}$ , we might define the molecule to be a sphere of radius  $a$ , such that  $\frac{\mu}{a^4} = \frac{\mu'}{a^4}$ . In like manner, regarding a molecule as a centre of force, repelling according to the law of the inverse fifth power of the distance, we might define the magnitude of a molecule as a sphere of radius equal to the least distance to which two molecules, whose relative velocity is equal to the mean velocity of the centres of force, approach each other in a direct encounter.

If on any hypothesis concerning the nature of a molecule, or the law of force which acts during encounters, we can calculate the coefficient of viscosity or diffusion analytically, a comparison of the analytical result with results obtained by experiment may afford the means of determining the absolute numerical value of the constants used in the analysis. For example, if we consider the molecules as elastic spheres, and if we consider for a moment Meyer's results as correct, or approximately correct, the coefficient of

viscosity for any single gas can be put in the form  $\frac{N m \bar{v}}{3 \pi \eta}$ , where  $N$  is the number of molecules in unit of volume,  $m$  the mass of a molecule. Now, for every value of  $\bar{v}$ , the mean free path of a molecule with that velocity is equal to  $\sqrt{\frac{2}{3}} \frac{1}{N \pi s^2}$ , where  $s$  is twice the radius of a molecule multiplied by a numerical factor which can be determined to any required degree of accuracy. Also at given temperature and pressure the numerical value of  $\sqrt{\frac{2}{3}}$  is known. It follows that we can calculate the numerical value of the coefficient of viscosity by analytical methods in terms of  $N \pi s^2$  to any required degree of accuracy. Let it be  $\frac{C}{N \pi s^2}$ . If by experiments on viscosity we can determine the numerical value of the same coefficient in the form  $C_1$ , when  $C_1$  is a mere numerical quantity, we have immediately the equation  $C_1 = \frac{C}{N \pi s^2}$ , or  $N \pi s^2 = \frac{C}{C_1}$ .

This gives in absolute numerical measure the value of  $N \pi s^2$ , or four times the sum of the great circle areas of all the molecules in unit of volume, supposing them to be spherical. If we attempt to use the coefficient of diffusion instead of viscosity in this method, we are met by the difficulty that the analytical result contains now two unknown quantities instead of one—namely, the radii of the respective molecules of the two gases in question. If this difficulty be got over by a comparison of results obtained in different experiments, the greater certainty attending the observations on diffusion might perhaps compensate for the additional mathematical difficulty, and render diffusion at least equally trustworthy with viscosity as a method for estimating molecular dimensions. Again, on the hypothesis of repulsion between molecules according to the law of the inverse fifth power of the distance, we can calculate analytically the rate of diffusion between two reservoirs connected by a tube as above described, the result containing only one unknown constant, viz.,  $\mu$ , the constant of absolute force. Comparing the analytical result with the results of experiments on diffusion through such a tube as above described, if we find them capable of being harmonized by attributing any numerical value to  $\mu$ , we should have good reason for concluding that the law of force assumed is to a certain extent at least the true law, and that the particular value of  $\mu$  is that which harmonizes the analytical with the experimental results. And the determination of  $\mu$ , the absolute force, corresponds to, or indeed is, the determination of the size of the molecule.

Until all the mathematical hypotheses have been fully developed, no very great reliance can be placed on the results of such comparisons, even assuming that the experimental results themselves are to be depended upon. However valuable the experiments may be for other purposes, they are not valuable for the purpose of determining molecular dimensions until our mathematical analysis is sufficiently advanced to enable us to interpret the experiment. At present it is perhaps impossible to deduce from the experiments any other result bearing on this question than that the coefficients of diffusion and viscosity increase with increasing temperature, and probably contain an important term proportional to the square root of the absolute temperature. If, indeed, it can be shown that that is the only term, and if it can be also shown that the density of one of two diffusing gases in a tube through which steady diffusion is going on tends to vary in geometrical progression, then the analysis will lead us to the conclusion that molecules of gases behave in their physical relations to each other as if they were elastic spheres.

The following method has also been suggested for estimating the magnitude of molecules of mercury. Mercury is regarded by most chemists as monatomic. Let us assume that its molecules are conducting spheres; on that assumption we may calculate the specific inductive capacity of mercury vapour on Faraday's hypothesis to be  $\frac{1+2\lambda}{1-\lambda}$ , where  $\lambda$  is the ratio which the aggregate volume of all the

spherical molecules in unit volume bears to unit volume. If now  $K$ , the specific inductive capacity of mercury vapour, can be determined experimentally, the equation  $K = \frac{1+2\lambda}{1-\lambda}$  affords a ground for estimating the value of  $\lambda$ ,—that is, the aggregate volume of the molecules.

Another method, originally proposed by Van der Waals, is founded on the small deviations from Boyle's law observed in all gases. Suppose a vessel of volume  $V$  containing a number  $N_1$  of elastic spheres, each of mass  $m$ , moving with a certain average kinetic energy. Let  $p_1$  be the pressure. Let a second class of elastic spheres, in number  $N_2$ , each of the same mass  $m$  as the former class and having the same average kinetic energy, be introduced into the vessel. If the second class of spheres could freely penetrate the first, and *vice versa*, so that there should be no restrictions on a sphere of the first class and a sphere of the second being in the same place at the same time, then the pressure on the walls of the

vessel would be increased in the exact proportion  $\frac{N_1+N_2}{N_1}$ . Boyle's law would be exactly fulfilled. But if the spheres cannot penetrate each other, the volume occupied by the second class of spheres is not  $V$ , but  $V - \frac{4}{3} N_2 \pi r^2$ , if  $r$  be the radius of a sphere of the first class. Consequently, the pressure due to the second class of spheres is rather greater than it should be, and there is a small deviation from Boyle's law. Van der Waals treats the pressure as proportional to the number of encounters, and therefore inversely proportional to the mean free path, which is evidently diminished by any increase in the magnitude of the spheres, and diminished more than in proportion by any increase in the number.

(H. W. W.—S. H. B.)

#### CHEMICAL ASPECT.

The word *Molecule* is used by chemists to express the unit of a pure substance, that quantity of it which its formula ought to represent. What this quantity is, in any particular case, must be ascertained by studying the chemical actions by which the substance is produced and the chemical changes which it undergoes. We may give one or two illustrations to show how this can be done, as well as to indicate the limits within which these methods can be applied.

The formula usually assigned to acetic acid is  $C_2H_4O_2$ . This agrees with almost all the chemical actions in which it takes part. Thus, one quarter of the hydrogen is replaceable by other metals, as in  $C_2H_3KO_2$ , &c.; and one, two, or three quarters of the hydrogen can be replaced by chlorine. There must, therefore, be four (or a multiple of four) atoms of hydrogen in the molecule. Similarly, half of the oxygen can be replaced by sulphur, and one-half of the oxygen along with one-quarter of the hydrogen can be replaced by chlorine. There must, therefore, be two (or a multiple of two) atoms of oxygen in the molecule.

Again, the formation of marsh gas and carbonate of soda, when acetate of soda is heated with caustic soda, and the formation of aceto-nitrile from cyanide of potassium and iodide of methyl, show that the carbon in acetic acid is divisible by two, or that the molecule contains two (or a multiple of two) atoms of carbon.  $C_2H_4O_2$  is the simplest formula which fulfils these conditions, but the existence of an acid acetate of potash and an acid acetate of ammonia, the formulæ of which are usually written  $C_2H_3KO_2$ ,  $C_2H_4O_2$  and  $C_2H_5(NH_4)O_2$ ,  $C_2H_4O_2$ , as if these were compounds derived from two molecules of acetic acid, might lead us to  $C_4H_8O_4$ , as this shows that the hydrogen is divisible by eight. In the same way, we can easily satisfy ourselves that  $C_6H_{10}O_5$ , or some multiple of it, is the formula of starch; that  $C_8H_5NO$ , or some multiple of it, is the formula of indigo blue, and so on. But it is not easy to determine by purely chemical methods whether these formulæ themselves, or multiples of them, really represent the molecule. A simple formula may suffice for a great many of the reactions of a substance, and may enable us to represent a great many of its derivatives, and yet reactions and derivatives may be discovered which require a multiple of that simple formula. This has already been indicated in reference to acetic acid, and a very striking

illustration is supplied by mellitic acid. For a long time the formula  $C_6H_2O_4$  was used for this acid, and by means of it all the then known derivatives were represented. But later investigations by Baeyer proved that this formula must be multiplied by three, the new derivatives obtained by him not being capable of representation with any formula simpler than  $C_{12}H_6O_{12}$ . Very many examples of the same kind might be adduced, but those given may serve to show the nature of the difficulty of settling the formula and with it the molecular weight of a substance. It need scarcely be said that the multiple formula represents everything which the simple formula represents and something more, and that chemists as a rule take the simplest formula which will answer the purpose. These chemical methods of determining the formula and molecular weight apply equally to all pure substances, but they do not give us absolute values, only numbers to which the molecular weights are proportional. And for purely chemical purposes these are all that we require. Thus, when a chemist speaks of acting on a molecule of succinic acid with two molecules of pentachloride of phosphorus, he means that he mixes them in the proportion of 118 parts of the former to  $2 \times 177.5$  of the latter. For the sake of precision we sometimes speak of a molecule of water (or other substance) in grammes, or even of a *gramme-molecule*, a *grain-molecule*, &c. Thus, in the case just mentioned a *gramme-molecule* of succinic acid means 118 grammes of succinic acid, &c.

But, while for practical purposes these proportional numbers are quite sufficient, we cannot leave out of view their relation to the actual constitution of matter. There is good reason to believe that matter consists of discrete particles, and that every pure substance is made up of small portions of matter, all alike, so that one of them, if we could examine it, would give us a complete idea of the chemical composition, constitution, and character of the substance. These small portions, of which the smallest quantity of the substance which we can examine contains many millions, we may call *molecules*. From the character which we have supposed this molecule to possess—viz., that it fully represents all the chemical properties of the substance—it will be seen that these *real, ultimate* molecules must be proportional to the molecular weights ascertained by chemical means; so that, while for practical laboratory or manufacturing purposes we use the gramme, the pound, or the ton as our unit, and speak of 18 grammes, pounds, or tons, as the case may be, of water, as a molecule (or *gramme-molecule*, *ton-molecule*, &c.), in dealing with the actual constitution of matter we should use as our unit the mass of a single atom of hydrogen, and our *gramme-molecule* would then be a definite, very large, but not yet accurately ascertained, number of real molecules.

It has been already shown above that, on the kinetic theory of gas, a gas consists of a number of particles moving about in straight lines in all directions, and that in a homogeneous gas which follows Boyle's and Charles's laws these particles are all alike. The masses of the particles of different gases are therefore to one another in the same proportion as the densities of the gases, temperature and pressure being the same. Thus, in gases, the independently moving particles of the kinetic theory are the molecules of which the chemist is in search, and it becomes important that we should compare our chemically found molecular weights with the densities. Theoretically accurate results could be obtained only in the case of a perfect gas; but small deviations from Boyle's and Charles's laws do not interfere with the application of this method. Chemical methods, as we have already seen, lead us to a particular number, or a *multiple of it*, so that our choice is as a rule limited to two or three numbers widely differing

from one another. We find that if we do not exceed the limits of chemical stability a gas approaches the state of a perfect gas as the temperature increases, or as the pressure diminishes. Now if one of the numbers rendered probable by chemical evidence *nearly* coincides with that given by comparison of gas densities, under conditions where the substance sensibly deviates from Boyle's and Charles's laws, we find that by diminishing the pressure or increasing the temperature within the limits of chemical stability, and thus bringing the substance nearer the state of a perfect gas, the correspondence between these two numbers becomes closer. This has already been pointed out and illustrated in the article CHEMISTRY, vol. v. p. 469.

We can now compare the results, in the case of gases, of the chemical and of the physical determination of molecular weight, by giving some examples, placing side by side the formula and molecular weight adopted by chemists, and the mass, in grammes, of the gas occupying the volume of  $22.33 \times 760/p \times (273+t)/273$  litres. This volume is that which one gramme of an ideal gas having the molecular weight 1, and perfectly following Boyle's and Charles's laws, would occupy at pressure  $p$  millimetres of mercury and temperature  $t^\circ$  C. If, then,  $w$  be the molecular weight of any gas,  $w$  grammes of it should occupy this volume, and slight deviation from this would indicate slight deviation from Boyle's and Charles's laws. In the annexed table  $w$  is the molecular weight and  $m$  the mass contained in  $22.33 \times 760/p \times (273+t)/273$  litres. Where the temperature is not specially stated, the determinations were made under the usual atmospheric conditions.

| Name.                       | Formula.                          | $w$ . | $m$ . |            |
|-----------------------------|-----------------------------------|-------|-------|------------|
| Sulphuretted hydrogen       | H <sub>2</sub> S                  | 34    | 34.04 |            |
| Nitrous oxide               | N <sub>2</sub> O                  | 44    | 44.08 |            |
| Ammonia                     | NH <sub>3</sub>                   | 17    | 17.12 |            |
| Carbonic acid               | CO <sub>2</sub>                   | 44    | 44.14 |            |
| Marsh gas                   | CH <sub>4</sub>                   | 16    | 16.13 |            |
| Olefiant gas                | C <sub>2</sub> H <sub>4</sub>     | 28    | 28.44 |            |
| Hydrogen                    | H <sub>2</sub>                    | 2     | 2     |            |
| Oxygen                      | O <sub>2</sub>                    | 32    | 32    |            |
| Chlorine                    | Cl <sub>2</sub>                   | 71    | 71.27 | at 100° C. |
| Phosphorus                  | P <sub>4</sub>                    | 124   | 125.9 | " 500° C.  |
| Arsenic                     | As <sub>4</sub>                   | 300   | 294.5 | " 860° C.  |
| Sulphur                     | S <sub>8</sub>                    | 192   | 194   | " 500° C.  |
|                             | S <sub>2</sub>                    | 64    | 63.5  | " 1000° C. |
| Bromide of aluminium        | Al <sub>2</sub> Br <sub>6</sub>   | 534   | 537.5 | " 440° C.  |
| Ferric chloride             | Fe <sub>2</sub> Cl <sub>6</sub>   | 325   | 328.8 | " 440° C.  |
| Sal-ammoniac                | NH <sub>4</sub> Cl                | 53.5  | 29.6  | at 350° C. |
| Oil of vitriol              | H <sub>2</sub> SO <sub>4</sub>    | 98    | 50.24 | " 440° C.  |
| Pentachloride of phosphorus | PCl <sub>5</sub>                  | 208.5 | 140   | " 200° C.  |
|                             |                                   |       | 105.4 | " 300° C.  |
| Sulphide of ammonium        | (NH <sub>4</sub> ) <sub>2</sub> S | 68    | 22.76 | " 80° C.   |

A comparison of the values of  $w$  and  $m$  leads to the following conclusions:—

(1) In the case of a very great number of substances, of which only a few specimens are given in the table, the two determinations agree, the slight differences often observed being evidently due to deviation of the substance from the state of a perfect gas. (2) In a considerable number of substances, physical evidence leads to a multiple of the simplest number satisfying the chemical conditions. This cannot be looked upon as a disagreement between the methods, because, if a particular formula satisfies the chemical conditions, any multiple of it will necessarily do so; and indeed, in many of the cases we are now considering, it is possible from chemical considerations to justify the higher molecular weight after it has been suggested, although such chemical considerations might not in all cases have warranted its adoption without external support. Thus, we are not without chemical evidence in

favour of the formulæ  $H_2, Cl_2, O_2$ , or even  $Al_2Br_6$  and  $Fe_2Cl_6$ , although chemists would probably have contented themselves with  $H, Cl, O, AlBr_3$ , and  $FeCl_3$ , had it not been for the evidence of gas and vapour density, and certainly without the latter no one would have thought of  $P_4, As_4$ , or  $S_8$ .<sup>1</sup> (3) There are a number of substances in the case of which there is an apparent disagreement between the results of the two ways of determining molecular weight. Such substances are said to have an anomalous gas or vapour density. The expression anomalous vapour density is sometimes applied to the case of such substances as phosphorus and arsenic, but not very accurately. It would be better to say that these substances have an unexpected vapour density, because their complex molecular formulæ, while not clearly indicated by their chemical character, are not at variance with any established law.

We shall therefore reserve the term "anomalous vapour density" for those substances the molecular weight of which as given by their vapour density is not reconcilable with any formula which is chemically admissible. In the case of some substances, such as the oxides of chlorine, it has been shown that the discrepancy was due to errors of observation, impure specimens having been used in the experiments; but there still remain many substances having, in the sense above indicated, an anomalous vapour density. These substances have therefore been examined with special care, with the result of completely vindicating the kinetic theory, and of disclosing a very interesting and theoretically important kind of chemical change. We shall take, as instances of such anomalous vapour densities, the substances in the last division of the table, and show how the anomaly has in these cases been explained.

Sal-ammoniac has the composition represented by the formula  $NH_4Cl$ . This formula agrees with all the chemical actions of the substance and of all the substances in any way related to it, but it does not agree with the results of vapour density determinations. When sal-ammoniac is heated it is converted into vapour or gas, and this vapour or gas is reconverted into solid sal-ammoniac when it is cooled. This looks exactly like the process of sublimation, and it was universally supposed that the vapour given off when sal-ammoniac is heated was really sal-ammoniac vapour. But its vapour density corresponds, not to the formula  $NH_4Cl$  and the molecular weight 53.5, but to the half of this. Now this formula does not admit of division, and the explanation at once suggests itself, that the vapour examined was not really the vapour of sal-ammoniac, but of hydrochloric acid and ammonia gases, the products of the decomposition of sal-ammoniac.

This would of course completely explain the apparent anomaly; each molecule  $NH_4Cl$  dividing into two molecules  $NH_3$  and  $HCl$ , the gas from a given weight of sal-ammoniac would of course contain twice as many molecules and occupy twice the space which it would do if no such decomposition had occurred. On this supposition the mixed gases would remain uncombined as long as the temperature was above the decomposing point of sal-ammoniac; if the temperature fell below this point they

<sup>1</sup> It is important as a matter of scientific history to note that this agreement of gas density and chemical molecular weight was first indicated by Gay-Lussac, who showed that the ratio of the densities of two gases stood in a very simple arithmetical relation to the ratio of their chemical equivalents. Avogadro in 1811 brought forward his famous hypothesis, that the number of molecules in a given volume of gas is independent of the nature of the gas, or that the densities of gases (temperature and pressure being the same) are to one another as the masses of their molecules. This hypothesis is now shown to be in accordance with the kinetic theory of gas, and is known as "Avogadro's law." See ATOM, vol. iii, p. 40, where a slight confusion has been caused by using the word "equivalent" instead of "molecule," and by not sufficiently distinguishing between the discovery of Gay-Lussac and the hypothesis of Avogadro.

would unite and reproduce sal-ammoniac. It was necessary, however, to prove that this decomposition occurs.

As has been shown above (p. 618), the rate of diffusion of a gas depends upon its density. In this case the two gases into which the substance may be supposed to break up at the moment of volatilization differ considerably in density; we ought, therefore, to be able to effect partial separation by means of diffusion, and it has been shown that such partial separation actually does occur. Thus, if we have hydrogen gas on one side of a porous diaphragm and volatilized sal-ammoniac on the other side, we find after a time that, mixed with the hydrogen on the one side, we have what we may for shortness call sal-ammoniac vapour—that is, a vapour which when cooled forms solid sal-ammoniac—with an excess of ammonia, which, being less dense than hydrochloric acid gas, has diffused faster; while on the other side, also mixed with hydrogen which has diffused through the diaphragm, we have sal-ammoniac vapour with excess of hydrochloric acid, the denser and more slowly diffusing gas. This of course proves that the decomposition has occurred, but it does not prove that the vapour of sal-ammoniac consists entirely of hydrochloric acid and ammonia mixed with one another. That this in fact is not the case has been shown by an ingenious experiment. The two gases were separately raised to a temperature higher than that at which sal-ammoniac volatilizes, and were then allowed to mix in a vessel kept at the same temperature as the two gases. In this vessel a delicate thermometer was placed, and it was found that the mixing of the two gases was accompanied by a small but very decided evolution of heat. This proves that some chemical combination takes place, and that the mixed gases must contain some vapour of  $NH_4Cl$ . Moreover, careful determinations of the vapour density of sal-ammoniac prove that it is a little more than the mean of the densities of ammonia and hydrochloric acid (as compared with air at the same temperature and pressure, 1.01 instead of 0.9255 at 350°C.); and this increase of density on mixing the hot gases is easily explained by supposing that a small proportion is in the condition of  $NH_4Cl$ , while the most of the gas consists of separate  $NH_3$  and  $HCl$  molecules.

In a similar way it has been shown that the vapour of oil of vitriol is a mixture of two vapours,—that of water,  $H_2O$ , and that of sulphuric anhydride,  $SO_3$ ; and that sulphide of ammonium when volatilized breaks up into two volumes of ammonia and one of sulphuretted hydrogen,  $(NH_4)_2S = 2NH_3 + H_2S$ . We find, therefore, that in the former case, as in that of sal-ammoniac,  $w = 2m$ , and in the latter,  $w = 3m$ .

This peculiar kind of decomposition is now known by the name "dissociation." (See vol. v, pp. 475, 476.) In the cases we have mentioned the substances undergo nearly complete dissociation at the temperature at which they volatilize, and recombination takes place when they are cooled and again assume the solid, or, as in the case of oil of vitriol, the liquid state. These substances are therefore not suited for the illustration of the whole course of dissociation. This has been carefully studied in the case of some compounds, in which the dissociation is far from complete, at the boiling point of the substance, with the result that, if  $AB$  be the compound dissociating into the separate molecules  $A$  and  $B$ , we may represent the amount of dissociation as the ratio of the number of pairs of separate  $A$  and  $B$  molecules to the total number of pairs of  $A$  and  $B$ , both separate and combined. This ratio we may call  $R$ , so that when dissociation is complete  $R = 1$ .

(1)  $R$  increases as the temperature rises. (2)  $dR/dt$  (where  $t$  is temperature) is a maximum when  $R = \frac{1}{2}$ . (3) The presence of excess of either  $A$  or  $B$  diminishes the value of  $R$ . For instance,  $PCl_5$  is nearly completely dissociated into  $PCl_3$  and  $Cl_2$  at 300°C.; but if a large excess of  $PCl_3$  is mixed with the vapour it is found to contain scarcely any  $Cl_2$ , so that dissociation is greatly diminished by the presence of excess of  $PCl_3$ . These experimental results are capable of explanation on the kinetic theory of gas, if we adopt Pfaunder's hypothesis. This is, that for each case of dissociation there is a

limiting value for the internal kinetic energy<sup>1</sup> of a molecule of  $AB$ . If a molecule of  $AB$ , by encounters with other molecules or with the wall of the vessel containing the gas, acquires a greater amount of internal kinetic energy than this limit, it at once breaks up into  $A$  and  $B$ , so that in the gaseous mixture there are no molecules of  $AB$  having more internal kinetic energy than the limit. Further, if two molecules, one of  $A$  and one of  $B$ , meet one another with such a velocity and with such an amount of internal kinetic energy that together the internal kinetic energy is less than the limit, they will unite to form a molecule of  $AB$ . Thus the molecules with great internal kinetic energy will separate molecules of  $A$  and  $B$ ; those with small internal kinetic energy will mostly be united as  $AB$ . This hypothesis has been to a considerable extent worked out and applied by Pfaunder and by Naumann, and the deductions from it agree fairly well with the results of experiment; but in some points the theory has not been fully developed, and in some it does not seem altogether to accord with observed facts. Some of these difficulties have been mentioned above. We know enough of the nature of dissociation to see that it belongs to the class of balanced chemical actions, in which a chemical change is reversible, and equilibrium is kept up, with constant external conditions, by the two opposite chemical changes taking place to an equal extent in a given time. We can see that all such cases are explicable by the statistical method, but we cannot apply this method mathematically until we know more of the intimate nature of the molecules and of the way in which they act upon one another. In this discussion of dissociation we have looked specially at the cases in which  $A, B$ , and  $AB$  are all gaseous, because it was the question of anomalous vapour densities which led us to treat of the subject. Dissociation also occurs where one or two of the substances are solid or liquid.

We now see with what restrictions the method of vapour density is applicable to the determination of molecular weight, and we can understand more fully the example given in the article CHEMISTRY, vol. v, p. 469. It is there shown that acetic acid vapour does not conform to the laws of Boyle and Charles until the temperature is raised to about 250°, at the ordinary barometric pressure. At and above that temperature the vapour density corresponds to the formula  $C_2H_4O_2$ . At lower temperatures the density corresponds to a higher molecular weight. Now Playfair and Wanklyn determined the vapour density at much lower temperatures than the ordinary boiling point of acetic acid, by greatly diminishing the pressure of the

acetic acid vapour. This they accomplished by mixing it with a large quantity of hydrogen, so that the pressure due to acetic acid vapour formed only a small fraction of the total pressure. The vapour density of acetic acid at the low temperatures at which they worked was found to correspond very nearly with the formula  $C_2H_4O_2$ , and, by comparing this result with what has been said (p. 620) of the chemical evidence as to the molecular weight of acetic acid, we may reasonably conclude that the molecule of acetic acid at low temperatures is  $C_2H_4O_2$ , and that as the temperature is raised it undergoes dissociation, each molecule dividing into two of  $C_2H_2O_2$ . This is then a case where  $A$  and  $B$  are equal, and  $AA$  divides into  $A + A$ . Another instance of the same kind is probably to be found in peroxide of nitrogen (CHEMISTRY, p. 513), where  $N_2O_4$  divides into  $NO_2 + NO_2$ . Similarly, sulphur vapour has, at temperatures below 500°C., a density corresponding to the formula  $S_8$ . This dissociates as the temperature rises until, about 1000°C., the density corresponds to the formula  $S_2$  (CHEMISTRY, p. 498).

We have now seen that chemistry receives great assistance in the determination of molecular weight from physics, but this assistance is almost entirely confined to the case of gases, or of substances which can be volatilized. The phenomena of the diffusion of liquids show us that there also there are independently moving particles; but the laws of liquid-diffusion have not been sufficiently generalized to give us much help in the determination of the relative masses of these particles. In liquids it is probable that the particles are very near each other, and that their shape and their mutual action, as well as their mass and the temperature, determine their rate of motion.

In solids we have no independently travelling particles, and it is perhaps scarcely correct to speak of a molecular structure of solids at all. Solids are no doubt composed of atoms, and these atoms are evidently arranged in what may be called a tactical order. When the solid is fused or dissolved or volatilized, it breaks into molecules, each repetition of the pattern, if we may use the expression, being ready to become an independent thing under favourable circumstances. But, while these potential molecules of solids cannot perhaps be properly called molecules in a physical sense,<sup>2</sup> for chemical purposes we may call them so, for they are the smallest portions of the substance which fully represent it chemically, and, as we have seen, this is the chemical molecule, the quantity which should be represented by the formula. (A. C. B.)

MOLESKIN is a stout heavy cotton fabric of leathery consistence woven as a satin twill on a strong warp. It is finished generally either as a bleached white or as a slaty drab colour, but occasionally it is printed in imitation of tweed patterns. Being an exceedingly durable and economical texture, it was formerly much more worn by workmen, especially outdoor labourers, than is now the case. It is also used for gun-cases, carriage-covers, and several purposes in which a fabric capable of resisting rough usage is desirable.

MOLESWORTH, SIR WILLIAM (1810-1855), the eighth baronet, was born in London, 23d May 1810, and succeeded to the extensive family estates in Devon and Cornwall in 1823. On the passing of the Reform Act of 1832 he was returned to parliament, though only twenty-two years old, for the eastern division of the county of Cornwall, to support the ministry of Lord Grey. For some time he took little part in the debates of the House of Commons; but in April 1835 he founded, in conjunction with Mr. Roebuck, the *London Review*, as an organ of the politicians known to the world as "Philosophic Radicals." After the publication of two volumes he purchased the *Westminster Review*, and for some time the united magazines were edited by him and J. S. Mill. From 1837 to 1841 Sir William Molesworth sat for the borough of Leeds, and during those years acquired considerable influence in the House of Commons by his speeches and by his tact in presiding over the select committee on Transportation. From 1841 to 1845 he remained in private life, occupying his leisure time in editing the works in Latin and English of Thomas Hobbes of Malmesbury, a recreation which cost him no less than £6000. In the latter year he

was returned for the borough of Southwark, and retained that seat until his death. On his return to parliament he devoted special attention to the condition of the colonies, and delivered many speeches in favour of a reduction in colonial expenditure and on their better administration. His arguments on these questions changed the opinions of the members of the House of Commons; and the criticisms of the daily press, aided by the printing of his speeches, led to the gradual acceptance of his views by the electors at large. It was not, however, until many years afterwards that he was allowed full opportunity for working out the difficult problems connected with the government of Great Britain. Office was conferred upon him in December 1852 by Lord Aberdeen, but it was the minor post of directing the public improvements and crown lands of his own country, and the chief work by which his name was brought into prominence at this time was the construction of the new Westminster Bridge. At last, in July 1855, he was called to preside over the Colonial Office, but unfortunately its duties were no sooner entrusted to his care than he was cut off by death (22d October 1855), to the universal regret of his countrymen, for he had lived down the animosities of his youth, and had attracted to himself the sympathies of all thoughtful men. The influence which his views had acquired, and still retain, may be judged from the fact that in 1878 the delegates of the Transvaal Government put forward, as the chief argument for the withdrawal of the English from the Transvaal, the substance of his speech on the abandonment of the Orange River Territory in 1854.

A full pedigree of the Molesworth family is printed in Sir John Maclean's *Trigg Minor*, vol. i.; the titles of his speeches and works

<sup>1</sup> By internal kinetic energy is meant the kinetic energy of motion of the parts of the molecule relatively to one another, in contradistinction to the kinetic energy of motion of the molecule as a whole.

<sup>2</sup> It may be urged that the cleavage of crystals indicates that they possess a molecular structure, but a tactical or pattern-like arrangement of atoms may easily be supposed to present planes of easier separation, without the assumption of really independent molecules.