

3·17 feet less than the experimental value 1089·42 feet deduced by the same author from a large number of observations. For these reasons I consider the theoretical value of the velocity of sound to be

$$a\left(1 + \frac{4}{\pi^2}\right)^{\frac{1}{2}},$$

as deduced exclusively from hydrodynamical principles, such as I have defined them to be in the foregoing communication.

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IV. *On a Suggestion as to the Constitution of Chlorine, offered by the Dynamical Theory of Gases.* By A. W. RÜCKER, M.A., Professor of Physics in the Yorkshire College, Leeds\*.

IF a gas of density  $\delta$  consists of molecules each of which possesses  $m$  degrees of freedom, and if also the intermolecular forces are negligible, the specific heats at constant pressure ( $c_p$ ) and at constant volume ( $c_v$ ) are connected by the two well-known equations

$$(c_p - c_v)\delta = \cdot 0694, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{c_p}{c_v} = 1 + \frac{2}{m + e}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $e$  is a quantity which depends upon the potential energy of a molecule. Hence, if  $c_p$  is given by experiment,  $c_v$  can be calculated from the first of these equations; and then  $m + e$  is known from the second.

The accuracy of the value of  $m + e$  thus deduced will depend upon that of  $c_p$ , and on the legitimacy of the application of the two equations to the gas or vapour under consideration.

With respect to the first of these points, it may be remarked that E. Wiedemann has recently (*Pogg. Ann.* Bd. clvii. p. 1, 1876, and *Wied. Ann.* Bd. ii. p. 195, 1877) determined the specific heats at constant pressure of 14 out of the 35 gases and vapours studied by Regnault. The difference between the results of the two investigators amounts in two cases only (ethylene and ammonia) to 6 per cent.; in three cases it is about 5 per cent., and in all the others less. Thus even on the assumption that the later experiments are absolutely correct, it follows that Regnault's numbers may be trusted to 6 per cent. His results, however, can only be taken as true for the particular temperatures at which the experiments were made, as Wiedemann shows that in all but the most perfect

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gases the specific heat at constant pressure varies considerably with the temperature.

More recently still, Wüllner (*Wied. Ann.* Bd. iv. p. 321, 1878), using Kundt and Warburg's method, has determined the ratio of the specific heats of air, carbonic oxide, carbonic acid, nitrous acid, ethylene, and ammonia at  $0^\circ$  and  $100^\circ$  C. He finds that for gases which obey Boyle's law,  $c_p$  and  $c_v$  are constant, but that in the case of less perfectly gaseous bodies they increase with the temperature. The difference between them, however, is always very approximately constant and equal to the theoretical number—thus justifying the application of the first of the above equations to imperfect gases, and proving that the observed increase in the specific heats is due to work done within the molecules, and not against the intermolecular forces, which must therefore be negligible.

On the whole, then, the result of these researches is to show that  $m + e$  can be calculated very approximately from the above equations if  $c_p$  is given, and that Regnault's values of this quantity are probably trustworthy to 6 per cent.

One of the chief difficulties of the thermodynamic theory of gases has been to attribute to  $m$  and  $e$  values which would at once lead to the observed ratios of  $c_p$  to  $c_v$ , and satisfy any rational supposition as to the interior mechanism of a molecule. Kundt and Warburg proved that for mercury vapour  $\frac{c_p}{c_v} = 1.666$ , which is consistent only with the supposition that

the atoms of that substance are smooth rigid spheres. Boltzmann (*Pogg. Ann.* Bd. clx. p. 175, 1877) and Bosanquet (*Phil. Mag.* April 1877) have since drawn attention to the fact that, for a smooth rigid surface of revolution,  $m = 5$  and  $e = 0$ , which would make  $\frac{c_p}{c_v} = 1.4$ . The fact, therefore, that this number

agrees very closely with those given by experiment for a large number of gases (air, O, N, H, CO, and NO) would be accounted for by supposing their molecules to be surfaces of revolution. This condition would be fulfilled, as is pointed out by Mr. Bosanquet, by two spheres rigidly united, and would thus accord well with our conception of the atomic constitution of the above gases. It would perhaps be better to regard the spheres not as rigidly united, but as bound together by forces which prevent the separation of their surfaces, while leaving them otherwise free to move. The required five degrees of freedom would thus be obtained, and the hypothesis would better coincide with the supposition of the union of two *smooth* spheres to form the ultimate particles of the gases.

For a discussion of the difficulties offered to any such theory

by the spectroscope I must refer to the above papers; my present purpose is to point out an interesting fact connected with its application to chlorine and its compounds.

The maximum number of degrees of freedom which a molecule composed of  $n$  smooth rigid spheres could possess would be  $3n$ ; but the forces in play between the spheres might, as in the case of air and the other gases above referred to, reduce the number to much below this amount. Thus the value of  $m+e$  could not exceed, but might be less than  $3n+e$ . For gases in which the molecule consists of two atoms,  $e=0$ ; but in the cases of more complex combinations we can say only that, *ceteris paribus*, we should expect that its value would increase with the number of atoms in the molecule. Bearing these facts in mind, the following Tables lead to a curious result. In the first column of each are placed the symbols of the substances referred to. In the second columns are the ratios of the specific heats, deduced (except in the case of mercury) from Regnault's experiments by the use of equation (1). In the third are the values of  $m+e$  (omitting fractions) deduced by equation (2). In the fourth are the values of  $3n$ , where  $n$  is the number of atoms of which the molecule is composed.

TABLE I.

I.	II.	III.	IV.
	$\frac{c_p}{c_v}$	$m+e$	$3n$
Hg .....	1.666	3	3
Air .....	1.413	5	6
O <sub>2</sub> .....	1.403	5	6
N <sub>2</sub> .....	1.409	5	6
H <sub>2</sub> .....	1.417	5	6
NO .....	1.403	5	6
CO .....	1.416	5	6
N <sub>2</sub> O .....	1.243	8	9
H <sub>2</sub> O .....	1.302	7	9
H <sub>2</sub> S .....	1.335	6	9
CO <sub>2</sub> .....	1.265	8	9
SO <sub>2</sub> .....	1.276	7	9
CS <sub>2</sub> .....	1.198	10	9
NH <sub>3</sub> .....	1.300	7	12
CH <sub>4</sub> .....	1.290	7	15
C <sub>2</sub> H <sub>4</sub> .....	1.144	14	18
C <sub>2</sub> H <sub>6</sub> O .....	1.110	18	27
C <sub>4</sub> H <sub>10</sub> O .....	1.059	34	45
C <sub>4</sub> H <sub>10</sub> S .....	1.059	34	45
C <sub>2</sub> H <sub>5</sub> N .....	1.283	7	27
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> .....	1.060	33	42
C <sub>2</sub> H <sub>6</sub> O .....	1.091	22	30
C <sub>6</sub> H <sub>6</sub> .....	1.072	28	36
C <sub>10</sub> H <sub>16</sub> .....	1.031	64	78

TABLE II.

I.	II.	III.	IV.	V.
	$\frac{cp}{cv}$	$m+e$	$3n$	
Cl <sub>2</sub> .....	1·286	7	6	18
HCl .....	1·408	5	6	12
C <sub>2</sub> H <sub>5</sub> Cl .....	1·131	15	24	30
CHCl <sub>3</sub> .....	1·118	17	15	33
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> .....	1·097	21	24	36
PCl <sub>3</sub> .....	1·122	16	12	30
AsCl <sub>3</sub> .....	1·111	18	12	30
SiCl <sub>4</sub> .....	1·098	20	15	39
SnCl <sub>4</sub> .....	1·092	22	15	39
TiCl <sub>4</sub> .....	1·089	22	15	39

The first Table contains a number of simple and more or less complex compound gases and vapours; the second is confined to chlorine and its compounds alone. The difference between the two is most marked. In the first the value of  $m+e$  is for every substance (with one exception) less than  $3n$ , or than the maximum possible value of  $m$ . In the second the reverse statement holds good in more than two thirds of the whole number of cases.

This difference can hardly be accidental; nor can it be explained by an error of 6 per cent. in Regnault's experiments. It might be accounted for by supposing that in the case of chlorine  $e$  is abnormally large—and that this gas differs from others in which the molecule is built up of two spheres, in that the spheres are not necessarily in contact, and are probably therefore less firmly united.

Another supposition, however, would meet the case equally well, viz. that  $n$  has been taken too small, that the symbol Cl<sub>2</sub> is incorrect, and that the atoms of chlorine, and therefore the molecules of its compounds, contain a larger number of sub-atoms or atoms than has been supposed. It need hardly be added that this supposition fits in most satisfactorily with the results of the recent researches of Prof. Victor Meyer on the vapour-density of chlorine; and in the fifth column of Table II. are given the values of  $3n$  calculated on the assumption that throughout the first column we ought to write Cl<sub>3</sub> for Cl. Hydrochloric acid now offers a difficulty, as a body composed of four spheres could only possess so small a number of degrees of freedom as five if the spheres were rigidly connected with their centres in one straight line. With this exception, however, columns III. and V. of Table II. now present differences of the same sign and order as those in the corresponding columns in Table I.

The number of degrees of freedom attributed to each sub-

stance may perhaps be wrong by one in some of the simpler bodies, and by rather larger numbers in some of the more complex; but the general character of the Tables is probably beyond the reach of any such changes. An error *e. g.* of 6 per cent. in the specific heat at constant pressure of the tetrachlorides would only reduce the number of their degrees of freedom by one. Much greater alterations would be introduced by taking the specific heats at other temperatures than those at which they were determined by Regnault. Chloroform is the only compound of chlorine of which the law of the variation of the specific heat with the temperature was studied by Wiedemann; and using his results, I find that at 0° C. the number of degrees of freedom of this substance would be one less instead of two greater than 15.

In spite, however, of the uncertainty thus introduced, the comparison of the two Tables is sufficiently suggestive to induce me to lay them before the Physical Society. The fact that the application of the theory of gases to the specific heats of a large number of substances, determined as far as might be under similar circumstances, leads to the alternatives that the atoms of which a molecule of free chlorine is composed are either less strongly united or are more numerous than in the case of other elements, is not unimportant.

It remains to add that the ratios of the specific heats of bromine and of the only one of its compounds which has been studied agree with those of chlorine and the corresponding chlorine compound.

TABLE III.

I.	II.	III.	IV.	V.
	$\frac{c_p}{c_v}$	$m + e$	$3n$	
Br <sub>2</sub> .. . . . . .	1·302	7	6	18
C <sub>2</sub> H <sub>5</sub> Br ...	1·114	18	24	30

*Note.*—Since the above was written, the conclusions at first drawn from Prof. V. Meyer's research have been questioned (*Chem. News*, Nov. 21, 1879, p. 244) on the ground that experiments made by Seelheim, of Utrecht, indicate the possibility of the formation of a volatile chloride of platinum at high temperatures. However this may be, the cause of the anomalous specific heats of chlorine and its compounds remains to be explained; and the above statement of the alternative suppositions to which the theory discussed leads may not be uninteresting, even if it should be proved that one of them lacks the support which, at the time of writing, Prof. V. Meyer's research was supposed to afford it.