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On the Ratio of the Specific Heats of the Paraffins, and their Monohalogen Derivatives

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PHILOSOPHICAL TRANSACTIONS.

I. *On the Ratio of the Specific Heats of the Paraffins, and their Monohalogen Derivatives.*

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§ 1. *Introduction.*

The experiments to be described in the present paper were undertaken in the hope of obtaining data which would throw light on one of the most obscure points of the kinetic theory of gases, namely, the distribution of energy in the molecule.

The properties of gases on which the kinetic theory gained its reputation were the constancy of the product of pressure and volume, and the uniformity of the coefficient of expansion. For the explanation of these in the case of the hypothetical perfect gas, no knowledge of the special constitution of the molecule is required, but for most other properties, and especially thermal properties, the kinetic theory fails to explain the facts from want of information concerning the dynamical peculiarities of the molecules of different gases.

From the ratio of the two specific heats of a gas we can calculate the relative rates of increase per degree rise of temperature of the energy of translation of the molecule as a whole, and the energy due to the motion of the atoms relatively to the centre of gravity of the molecule.

If β is the ratio of the rate of increase of the internal energy to that of the translational energy, we have the well-known equation—

$$\beta + 1 = 2/\{3(\gamma - 1)\},$$

where γ is the ratio of the specific heats of the gas.

Thus the constant γ has a high theoretical value as leading directly to a fundamental dynamical property of the molecule, and a knowledge of its value for a large number of gases suitably chosen would not improbably afford material on which to base a theory of the configuration and motions of the atoms in a molecule, or would at least give valuable data by which to test theories based on other considerations.

Stated briefly the following is the present state of our experimental knowledge of the ratio of the specific heats.

Almost all the older work was rendered valueless by RÖNTGEN'S showing (POGGENDORFF'S 'Annalen,' vol. 141, p. 552 and vol. 148, p. 580) how great an effect the size of the apparatus has on the results. His own values for air and carbonic acid are probably near the truth, but the difficulty he experienced in finding a suitable pressure gauge, and the large size of the apparatus, have caused his method to be put out of the field by KUNDT'S Dust Figure method (POGG. 'Ann.,' vol. 127, p. 497, and vol. 135, pp. 337 and 527).

The earliest experiments by this latter method are those of KUNDT and WARBURG (POGG. 'Ann.,' vol. 157, p. 353) on Mercury Vapour, by which it was shown that β is zero for the mercury molecule, and hence the molecule has no power of absorbing internal energy, thus confirming the chemical view that the molecule is monatomic.

Next we have the work on Carbon Monoxide, Carbon Dioxide, Nitrous Oxide, Ethylene, and Ammonia, by WÜLLNER (WIED. 'Ann.,' vol. 4, p. 321), who, using KUNDT'S earliest single-ended form of apparatus, found that with the exception of air these gases all have ratios of the specific heats that fall considerably with rise of temperature.

Up to this time it was thought that all diatomic gases have γ equal to 1·4. To test the point further STRECKER (WIED. 'Ann.,' vol. 13, p. 20, and vol. 17, p. 85) investigated the halogens and their hydracids. He found that hydrochloric, hydrobromic, and hydriodic acids have the value 1·4, but that the simple halogens and iodine chloride have values near 1·3. The ratios of the specific heats of all seven gases were found to be unaffected by change of temperature over a wide range.

Beyme ('Beiblätter,' vol. 9, p. 503) made some experiments on the saturated vapours of ether, carbon bisulphide, chloroform, benzene, and water, by a modification of Kundt's method, but as he made no attempt to determine the densities of the vapours, his work does little more than show that sound is conducted freely through saturated vapours.

P. A. Müller (Wied. 'Ann.,' vol. 18, p. 94) investigated the ratios of the specific heats of a large number of gases by a method devised by Assmann (Pogg. 'Ann.,' vol. 85, p. 1). Müller assumes that alternate compressions and rarefactions, with a period of half-a-second in a globe holding about a litre of gas, are adiabatic. In the light of the work of Röntgen and Kundt on the effect of the size of the apparatus, it is evident that this cannot be the case, and we might expect Müller's results to be too low. In almost every case where comparison is possible his result is lower than that obtained by methods recognized as trustworthy.

The experiments of Jäger (Wied. 'Ann.,' vol. 36, p. 165) were intended to test the question whether γ depends on the degree of saturation of the gas or not. He concludes that for the vapours of ether, alcohol, and water the degree of saturation has no effect on γ, but the experiments are hardly accurate enough to be conclusive.

Other papers on single gases are those of Kayser (Wied. 'Ann.,' vol. 2, p. 218), on Air, of Martini ('Revist. Scient. Ind.,' vol. 13, p. 146), on Chlorine, and of E. and L. Natanson, on Nitrogen Peroxide.

It appears that the gases hitherto investigated have not been chosen with a view to elucidating the constitution of the molecule, and are not suitable for this purpose. Almost all are inorganic gases which, it is true, are easily prepared fairly pure, but are too irregular in their properties to lead to much of theoretical value. Each gas has peculiarities of its own which are not shared with others, and we have nothing corresponding to the homologous series of organic chemistry. It can hardly be doubted that the success of physico-chemical methods of late years would have been much less striking if inorganic bodies only had been available.

Amongst the carbon compounds we have many series of gases or volatile liquids proceeding by regular increments of CH_2 to the molecule, the members of any one series showing such striking similarities in their properties as to point to similarity of constitution of the molecule. We have, too, the advantage of accurately determined graphic formulæ, and though we are not justified in regarding these as concrete representations of the molecule, yet the consistency with which the system of notation has been applied to thousands of compounds shows that it has its basis in some physical fact, and makes it well suited to serve as the "independent variable" in expressing other properties as functions of the complexity of the molecule.

For these reasons I have chosen the paraffins and their monohalogen derivatives as being simply related to each other, easily volatile, and stable.

The method adopted for the determination of the ratio of the specific heats was KUNDT's velocity of sound method. It has the disadvantage of requiring the density of the gas to be known, and hence being very sensitive to impurities; but this is probably counterbalanced by our knowing from KUNDT's investigations all the conditions on which accuracy depends.

Most of the gases used diverge considerably from agreement with BOYLE's law, and have not had their vapour densities determined except by the rough methods used in fixing molecular formulæ; and even if they had, it would be unsafe to trust the results, for the usual test of the purity of organic liquids, constancy of boiling point, may easily lead to erroneous conclusions, as will be seen by the work on ethyl bromide described below. To avoid error from this source a direct experimental determination has been made on the compounds as they were used in the velocity of sound experiment.

The formula that has been used by most investigators for calculating the ratio of the specific heats from the velocity of sound is

$$\gamma = \gamma' \rho \, (l/l')^2$$

where

$\gamma' =$ the ratio of the specific heats of air,
$\rho =$ the specific gravity of the gas referred to air at the same temperature and pressure,
$l =$ the wave-length in the gas,
$l' =$ the wave-length in air.

This formula is only true for a perfect gas, for the square of the velocity of sound is γpv only if pv is a constant at any one temperature.

In the present work I have used a formula obtained as follows:—

The equation $u^2 = (dp/d\rho)_\phi$, where the symbols have their usual meanings, is true for any homogeneous substance. (RAYLEIGH's Sound, § 244.)

From this we have

$$u^2 = - \gamma v^2 (dp/dv)_t.$$

But

$$dpv/dv = p + v dp/dv,$$

the differentiation being at constant temperature.

Hence

$$\left(\frac{dp}{dv}\right)_t = \frac{1}{v}\left(\frac{d}{dv}[pv]\right)_t - \frac{p}{v},$$

and

$$\begin{aligned} u^2 &= \gamma v \, (p - dpv/dv) \\ &= \gamma pv \, (1 - 1/p \, . \, dpv/dv) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1). \end{aligned}$$

Hence, neglecting the square of $1/p \,.\, dpv/dv$, we have

$$\gamma = \gamma' \rho \left(\frac{l}{l'}\right)^2 (1 + 1/p \, dpv/dv) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Equation (1) is quite general, but the assumption that $1/p \,.\, dpv/dv$ is small, limits (2) to gases.

To find the value of the last factor, I have determined experimentally the vapour densities of the gases at various pressures, and plotted a curve connecting pv and v, the slope of which, at any point, gives the value of dpv/dv at that point.

It is, of course, of no consequence what units are used, as the dimensions of $1/p \,.\, dpv/dv$ are those of a number.

The formula can be put in various forms, but that given above seems to lead most directly to the required result. It is not, however, easy to determine the correction very accurately, for the variation of pv is not rapid, and a small error in the density observations, or in the drawing of the curve, may make a considerable change in the slope of the curve. For most of the gases that I have used, the correction is from one to two per cent. of the whole value of γ.

WÜLLNER, STRECKER, and others used the uncorrected formula, and, though they worked on gases with low boiling points, their results would be quite appreciably raised by the correction.

If there is any impurity present in the gas, ρ will be the specific gravity of the mixture. In the case of Marsh Gas and Ethane, this was got by calculation from the analysis of the gas, and in the case of the rest of the compounds by direct experiment.

The result is the ratio of the specific heats of the mixture, and requires a further correction if the γ of the impurity is not the same as that of the gas under investigation.

A formula for effecting this may be obtained in the following way, the gas being assumed perfect as the correction is small :—

Let

T = the total kinetic energy of translation of all the molecules in unit mass of the gas.

T_1, T_2, &c., the same for each of the components.

P, the pressure of the mixture.

p_1, p_2, &c., the partial pressures of the components.

δT, the increment of T ; for a rise of temperature, $\delta\theta$.

$\beta\delta T$, the increment of the internal energy of the molecules ; for a rise of temperature, $\delta\theta$.

C_p, the specific heat of the mixture at constant pressure.

C_v, „ „ „ „ „ volume.

Then

$$\begin{aligned} C_p\,\delta\theta &= \delta T + \beta\,\delta T + p\,dv, \\ &= \Sigma\,(\delta T_1 + \beta_1 \delta T_1 + p_1\,dv), \end{aligned}$$

dv being the same for each component.

But

$$p_1 v = \tfrac{2}{3} T_1,$$

for unit mass of a gas.

Therefore

$$p_1 \delta v = \tfrac{2}{3}\,\delta T_1.$$

Therefore

$$C_p\,\delta\theta = \Sigma\,(\overline{1 + \beta_1} + \tfrac{2}{3})\,\delta T_1.$$

But, since the average kinetic energy of a molecule is the same for each of the constituents, and the pressure is proportional to the number of molecules,

$$T_1/p_1 = T_2/p_2 = \ldots = T/P,$$

or,

$$\delta T_1 = (p_1\,\delta T)/P, \qquad \delta T_2 = (p_2\,\delta T)/P, \text{ \&c.}$$

Therefore

$$C_p\,\delta\theta = \Sigma\,(\overline{1 + \beta_1}\,p_1/P + \tfrac{2}{3})\,\delta T.$$

Similarly

$$C_v\,\delta\theta = \Sigma\,(\overline{1 + \beta_1}\,p_1/P)\,\delta T.$$

Therefore

$$C_p/C_v = \Gamma = 1 + \tfrac{2}{3}/\Sigma\,(\overline{1 + \beta_1}\,.\,p_1/P),$$

and since, for a single gas,

$$1 + \beta = 2/\{3\,(\gamma - 1)\},$$

the above reduces to

$$P/(\Gamma - 1) = \Sigma\,p_1/(\gamma_1 - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

This equation is equivalent to

$$P\,(1 + \beta) = \Sigma p_1\,(1 + \beta_1),$$

and merely expresses the fact that the total increment of energy per degree rise of temperature is equal to the sum of the increments for each of the components.

Analyses of the marsh gas and ethane used showed that there was always a little air present. The correction for this, calculated from (3) was only one or two parts in a thousand, which is within the errors of observation, so that for the other gases, where nothing was known as to the nature or amount of the possible impurities, no appreciable error is likely to have resulted from omitting it.

A point requiring some consideration was the question at what temperature the experiments should be made. According to WÜLLNER carbonic acid, carbon monoxide, nitrous oxide, and ammonia have values of the ratio of the specific heats which change in some cases by as much as 4 per cent. between 0° and 100°, and if this were so in all cases, it might well be asked at what temperature the results would be comparable. There are many gases, however, for which γ is constant; oxygen and nitrogen are such, and STRECKER showed that over a long range of temperature the change, if it existed at all, was very small for the halogens and halogen acids. MÜLLER, too, found no indications of change in the gases investigated by him. His assumption that the compressions and rarefactions in his apparatus are adiabatic is so improbable that we are bound to suppose his results are too low, but the method should be capable of showing relative changes.

In fact, no observer but WÜLLNER has ever found any appreciable change of γ with the temperature, and it is possible that the arrangement of his apparatus at least exaggerated the change he found.

Hence, so far as previous observations go, there is a presumption in favour of the constancy of γ.

Independently of this, there is something to be said in favour of choosing some constant temperature, for as the chief interest of γ arises from its relation to the internal energy, it seems desirable to secure that either the internal, the translational, or the total energy should be constant, and we can make the translational energy constant by working at a constant temperature. Consequently it was decided to work at the temperature of the room.

§ 2. *The Kundt Apparatus.*

The apparatus used for the determination of the velocity of sound in the gases was in all essential features the same as that described by KUNDT in 'POGGENDORFF'S Annalen,' vol. 135. The double apparatus was used, as it makes accurate temperature observations unnecessary, the tubes containing air and the gas under investigation lying side by side. It also ensures the figures in air and in the other gas corresponding to exactly the same note, so that change of pitch in the vibrating tube from change of temperature or any other cause has no effect.

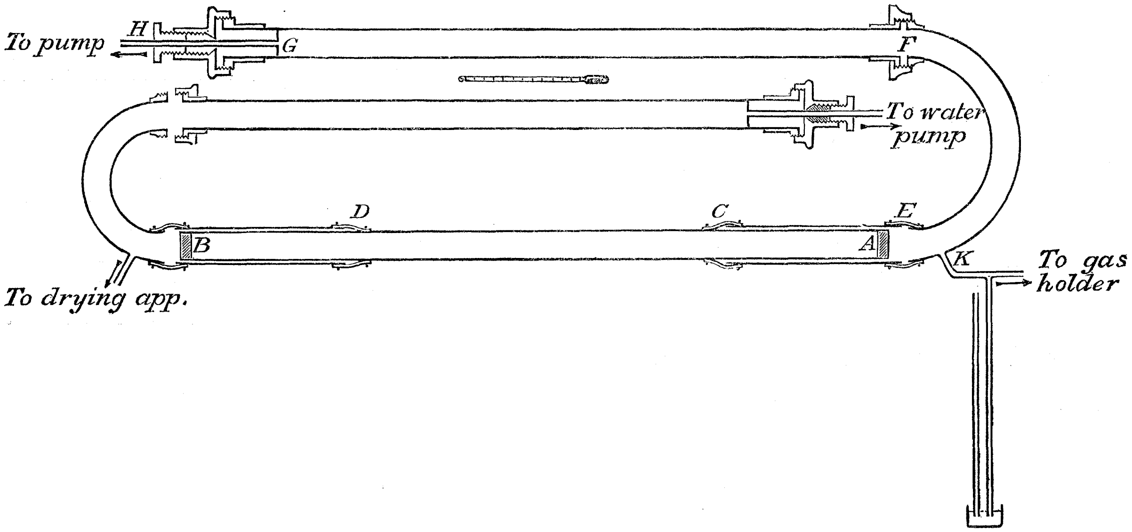
It will be sufficient to describe one end, as the two are almost identical in arrangement.

The vibrator, AB (see fig. 1), is a closed glass tube 150 centims. long and 35 millims. in diameter, and was chosen from a considerable number tried as giving the best figures. It is not desirable that it should give a very loud tone, for this scatters the dust too much, but it should speak readily, so that the intensity can be adjusted. An important point is to choose one that gives a note as free from overtones as possible, for these injure the sharpness of the figures very much, and make them difficult to measure.

Covering one quarter the length of this tube is a slightly wider one, EC. The joint at C was first made according to KUNDT's directions, by wrapping a strip of thin india-rubber many times round, and wiring it down, but this proved very unreliable. It requires a great deal of care to make such a joint even approximately tight, and it is continually getting leaky and requiring to be patched up with india-rubber solution, so, finally, I had made a wide tube with thick walls of the best soft rubber, and on slipping this on and wiring it down a perfectly tight joint was made.

The same rubber tube was used for connecting CE with the semi-circular copper tube EF, thus making a flexible joint and preventing the conduction of the sound through the walls of the tube

Fig. 1.



The tube FG, in which the dust figures are made, is 125 centims. long, and 26 millims. in internal diameter. At the end, F, a brass union is fixed on with sealing-wax, and by screwing up tightly the two brass faces with a lead washer between, a joint is made that is air-tight, but can easily be taken apart to measure the figures and put in fresh dust. At the other end, G, is a similarly detachable cap bearing a stuffing box. Through this passes a narrow brass tube with a disc on the end, G, by means of which the vibrating length of the column of air can be varied, so as to give the best figures.

For apparatus such as this, lead glass seems to be much better than soft German. It is impossible to put on the caps without some strain, and with the German glass much trouble was caused by the tubes breaking at awkward times and wasting precious gas. Since lead glass has been put in, there have been no breakages.

Through the tube H connection can be made with either a Töpler mercury pump for exhausting the apparatus, a Sprengel for extracting a sample of the gas for analysis, or a water pump for regulating the pressure of the contents.

At K is a side tube connected through a pressure gauge with the gas holder and drying apparatus.

With the connections made as thus described, there was found to be very little leakage in the apparatus. When it was exhausted as completely as possible the rise of pressure was only a very small fraction of a millimetre per hour.

Different methods of filling were adopted according to the material used. In the earlier experiments a water pump only was used. By means of this, the apparatus was exhausted to from 15 to 20 millims., and the gas admitted slowly through the purifying train, the process being repeated several times; but the method was too extravagant for the more costly materials, and took too much time, so, in the later experiments, a Töpler pump was used. This has a large reservoir, and with an hour's pumping the pressure was reduced so low that it was often difficult to see whether the gauge or the barometer by the side of it stood the higher.

When the gas was admitted through purifying and drying apparatus, this apparatus was usually exhausted with the rest, but as in most cases Geissler bulbs were used, the vacuum got gradually worse in the successive bulbs from the pressure of the contained liquid, so they were first filled with the gas by exhausting them two or three times and allowing it to stream in.

When a volatile liquid was used, it was contained in a small bottle with a tight cork, through which passed a glass tube, and wired on the end of this was a piece of thick-walled india-rubber tube. Before attaching it to the Kundt apparatus, the liquid was made to volatilize freely by warming it, or by connecting the bottle to a water pump, and when the air was driven out the india-rubber tube was closed with a clamp, and joined to the dust tube, so that when the exhaustion had been completed, by opening the clamp, the vapour could be admitted free from air.

For the hydrocarbons and methyl and ethyl chlorides, lycopodium powder was used in the dust tube, as it gave decidedly better figures than silica, but with the dense gases it was found to become sticky, so that it could not be made to move, and for these silica was used.

A preliminary experiment was always needed to fix the position of the piston, for though with the denser gases figures of some sort could be got with it in any position, yet they were generally unsymmetrical unless it was carefully placed. The position which gave the strongest agitation gave the most symmetrical figures, but they were seldom perfect in this respect, and for this reason the proper distribution of the dust in the tube is a matter of importance. There is usually a tendency for the powder to encroach on the node from one side more than from the other, and this is more marked the greater the quantity of dust used, so that if the quantity per centimetre varies from end to end of the tube, the result is an apparent shifting of the nodes to an extent that is not the same at different points.

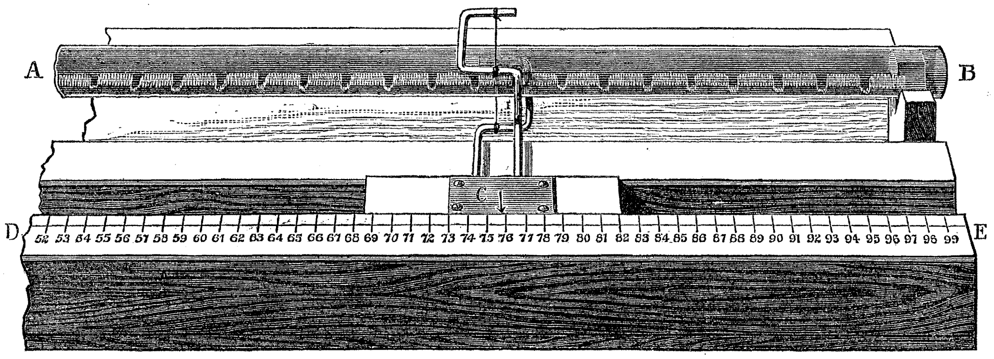
If the dust is uniformly spread, this want of symmetry has no influence on the measurements.

The method I employed for putting in the dust was to draw through the tube a dry cloth which cleaned out what was left from the previous experiment and slightly electrified the glass. The tube was then placed in a sloping position, and the powder poured in at the end through a small funnel, and allowed to run through gently in a narrow stream. It was then turned end for end, and the dust poured through in the opposite direction, the result of which was that the small electrification caused as much to adhere to the glass in a narrow uniform strip as served for the purpose of the experiment.

When it was placed in position and the figures were to be made the tube was turned round, so that the dust did not lie along the bottom but was a little way up the side; then, on rubbing the vibrator with a piece of wet flannel, the powder ran down to the lowest point everywhere but at the nodes, which were left as clear spaces, narrow and sharply bounded, separating rectangular patches of dust of great regularity.

Fig. 2 shows part of a set of figures obtained with isopropyl bromide.

Fig. 2.



For the measurement of the figures two parallel platinum wires were carried on a framework sliding along a steel scale divided to millimetres (fig. 2). These wires were placed so that the tube lay between them, and their plane passed through the centre of the clear space at the node, and the position of the framework was read on the scale, tenths of a millimetre being estimated with the help of a lens. When the figures were of average quality the setting could be repeated so that the positions did not vary by more than two or three tenths of a millimetre.

Table I. gives a typical set of measurements. They were made in one of the methyl bromide experiments, and are chosen as being neither the best nor the worst of the sets, but a fair average.

The first column gives the scale-readings, and the second column the half-wave-lengths got by subtracting the consecutive readings from each other. The first halfdozen figures next the vibrating tube are omitted. This was generally done, as they were almost always found to be irregular and less distinct than the rest.

TABLE I.

Scale reading.	Half wave-length.	Scale reading.	Half wave-length.	Scale reading.	Half wave-length.
155·5	..	486·0	25·1	815·9	25·1
180·6	25·1	511·2	25·2	841·3	25·4
205·6	25·0	536·9	25·7	866·6	25·3
231·4	25·8	562·2	25·3	892·2	25·6
257·0	25·6	587·3	25·1	917·6	25·4
282·4	25·4	612·8	25·5	943·0	25·4
308·3	25·9	638·2	25·4	968·3	25·3
333·4	25·1	663·6	25·4	993·4	25·1
358·7	25·3	688·8	25·2	1019·0	25·6
384·2	25·5	714·0	25·2	1044·6	25·6
409·8	25·6	739·7	25·7	1070·2	25·6
434·9	25·1	765·5	25·8	1095·4	25·2
460·9	26·0	790·8	25·3		

The mean value for the half wave-length is 25·399, and it will be seen that no single measurement differs from this by more than six-tenths of a millimetre. In two or three sets where the figures were poor the divergence from the mean reached as much as a millimetre, but was never greater. In some of the propyl chloride experiments it was not more than a quarter of a millimetre.

The method of calculation of the mean was to divide the readings of the nodes into two equal sections, subtract each reading in the first section from the corresponding one in the second, take the mean of these differences and divide by the number of half wave-lengths between the first readings of the two sections.

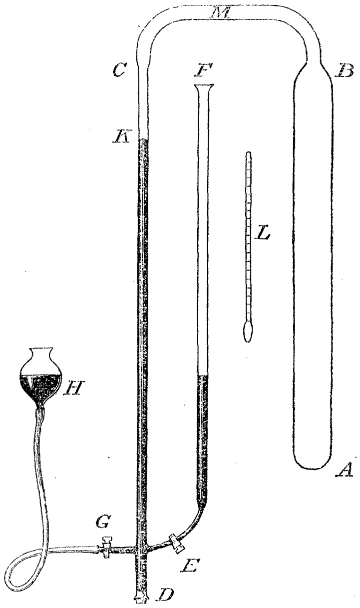
§ 3. *The Vapour Density Apparatus.*

The ordinary methods for determining vapour densities are not very suitable for an investigation such as this. HOFMANN'S, VICTOR MEYER'S and DUMAS' are scarcely accurate enough, and the two latter are not applicable without modification to pressures other than that of the atmosphere. REGNAULT'S, though very accurate, would take too much time when so many determinations have to be made.

As the vapour densities are only required at the temperature of the room, the conditions are much simplified, and I have devised a form of apparatus, using HOFMANN'S principle, which gives results concordant to $\frac{1}{10}$ per cent. without any great expenditure of time. Doubtless with greater precautions for securing uniformity of temperature higher accuracy might be obtained, but an error of one part in a thousand is well within the experimental errors of the rest of the work.

AB is a glass tube 60 centims. long and 35 millims. in diameter (see fig. 3), closed at A and sealed at B to the curved tube CB, the middle part of which is straight and horizontal. Before sealing this to the tube CD, the latter is calibrated, and the volume determined between the end D and a file mark at K, near the upper end. CD is then attached to AC, and the volume of the whole determined by filling with water and weighing. Subtracting from this the volume of DK we get the volume of AK, and as the tube CD has been already calibrated the volume to any other point is known if required

Fig. 3.



Next the side tube, EF, of the same bore as CD, is sealed on, and the three-way tap, G, making connection with an air pump or with the mercury reservoir, H.

L is a thermometer graduated to fifths of a degree.

A small quantity of the liquid whose vapour density is required is sealed up in a small tube with capillary ends and weighed. This is introduced at D, and made to rest at M, by inverting the apparatus for a moment.

Next, D is closed with an india-rubber stopper, E being also closed, whilst the apparatus is exhausted through the three-way tap, G, after which operation G is turned so as to allow the mercury to flow in from the reservoir, and E is opened.

The difference of the levels of the mercury in the two tubes is read by means of a cathetometer, and this difference subtracted from the height of the barometer gives the pressure of any air left in the apparatus.

The small tube is then broken, by tilting the apparatus a little and allowing it to slide over into AB, where the capillary end breaks off and allows the liquid to evaporate.

By reading the levels a second time we get the pressure of the vapour, and knowing its weight, volume, and temperature, we have all the materials required for calculating its specific gravity.

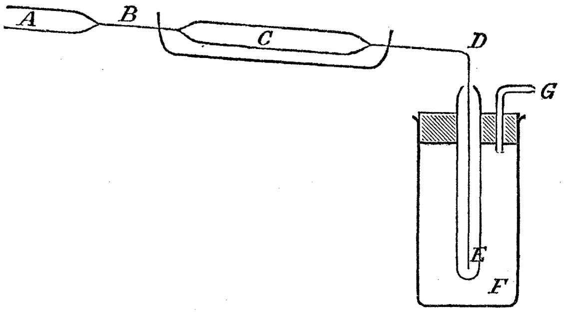
It is not advisable to exhaust the apparatus very completely in the first instance, for then the evaporation of the liquid is so violent that fragments of glass, and sometimes even the whole tube, get blown over the bend at the top on to the surface of the mercury, making it difficult to read the position of the surface. If 15 or 20 millims. of air is left in this seldom happens, but time must of course be given to allow the gases to diffuse into each other.

To avoid draughts and inequalities of temperature, the whole apparatus, with the exception of the reservoir, H, is enclosed in a box, with vertical openings at the front and back, through which the levels can be read with the cathetometer.

The calculations are simplified if the reservoir is always adjusted so that the level of the mercury in CD stands at the same point. This makes the pressure of the residual air the same in the two measurements, provided the temperature is constant. In my experiments I always brought the level to the file mark, K.

To empty the apparatus the reservoir is lowered till the mercury in CD sinks to the level of G—E being of course closed—and air is allowed to enter through the three-way tap.

Fig. 4.



The vapour densities were generally required in the neighbourhood of certain determinate pressures. To secure this the liquid was always sealed in a tube of the same diameter, and a preliminary filling and weighing being made with water, a simple calculation gave the length required in any case. It was then easy to draw off a piece of such a length as would hold within 5 or 10 per cent. of the required amount.

When the liquid has a very low boiling point special arrangements are needed for filling and sealing the tubes. The following method has been found to be quite satisfactory, but requires careful manipulation to avoid breaking the capillaries.

A piece of glass tube is drawn out into the form ABCDE (fig. 4), with a capillary part at B, and a capillary end, DE, and weighed.

The end, A, is then connected with a water pump, by means of a piece of india-rubber tube closed with a spring clamp. The part C, which is that which is to be filled, rests in a lead tray, slightly inclined, and filled with a suitable freezing mixture, and the capillary end, DE, dips below the level of the liquefied gas, which is contained in a tube surrounded by a freezing mixture. By opening the clamp for a moment the liquid is drawn into C, and the capillaries sealed off by a small blow-pipe, at B and D. On weighing C with the parts drawn off we get the amount of liquid enclosed.

Methyl chloride requires a temperature below − 20° to liquefy it, and, for this, ether and solid carbonic acid is most convenient, but has the disadvantage of giving off an inflammable vapour, which might take fire from the blow-pipe flame. Hence the tube C was packed round with solid carbonic acid, moistened with chloroform, which forms quite as effective a freezing mixture and does not readily take fire. The condenser, F, was closed with a stopper, through which passed a tube to carry the ether vapour beyond the reach of danger.

§ 4. *Marsh Gas.*

As was to be expected this gas gave much more trouble than any of the others. It cannot be freed from air by liquefaction, as was done with most of the others, and as the density of the gas is a factor in calculating the ratio of the specific heats, it was necessary to make a set of analyses after each experiment to determine the percentage of air. The correction for this is by no means inappreciable, on account of the low density of methane; roughly speaking, one per cent. of air makes an alteration of one per cent. in the result.

In the case of such gases as the paraffins, the quantity which can be taken for analysis is so small that any error in its measurement from want of accuracy in the calibration of the measuring tube, or other causes, has a large effect on the calculation of the percentage of air. Adding to this all the other sources of error incidental to gas analysis, such as incomplete combustion, oxidation of the nitrogen present, temperature errors, &c., the result is that the accuracy is less than that attainable in the velocity of sound determination.

It is unfortunate too that this additional source of error should enter most prominently in the case of methane, which is notably a most difficult gas to prepare pure. The consequence is that the range of values found for the ratio of the specific heats is greater than for any other gas, and the most that can be said is that the mean is probably within one or two per cent. of the truth.

For the preparation of marsh gas two methods were used, FRANKLAND's method by the action of zinc methyl on water, and GLADSTONE and TRIBE's by the action of the copper-zinc couple on methyl iodide and alcohol.

The latter method appears simple when the original memoir describing it is read, but in practice it requires considerable care. It would be tedious to recount the discouraging series of failures before gas was obtained sufficiently pure for the experiments, so the conditions on which success was found to depend will be stated simply.

There must be no water left in the apparatus, or in spite of chemical equations some free hydrogen will be given off. The couple was several times washed with alcohol, which had been scrupulously dried with lime and anhydrous copper sulphate. The copper-zinc couple itself seemed to be the best drying agent for removing the last traces of water, for the apparatus gave purer methane the second or third time of using than it did the first time; hence, after setting it up it is advisable to put in a little methyl iodide, and allow it to stand for a day or two with a Bunsen valve or some such arrangement attached.

The gas that comes over first is purest, so that no attempt should be made to secure a theoretical yield.

A considerable quantity of methyl iodide escapes the scrubber, and must be removed in some way. A set of Geissler bulbs filled with fuming sulphuric acid was used in this and similar cases and proved quite effective. The first bulb blackened and deposited iodine long before the second was coloured, and many litres of gas could be passed through before the colour reached the third bulb. This introduced sulphur dioxide into the gas, to remove which it was collected in a gas-holder over soda solution and shaken with it.

It was admitted into the Kundt apparatus through three U-tubes, the first containing solid potash, to remove any sulphur dioxide still remaining, the second containing nine grams of palladium black as a precaution to retain any free hydrogen, and the third containing pumice soaked in sulphuric acid to dry the gas.

Palladium is not altogether satisfactory for the removal of hydrogen; it is very fickle in its action, sometimes for no obvious reason refusing to absorb it. In the preliminary experiments and in the preparation of propane, to be described later, 30 grams of thin foil, superficially oxidized by ignition in air, was used, but this, though quite effective in removing the greater part of the hydrogen, which was all that was wanted in the case of propane, failed to take out the last traces; so 9 grams of the foil was converted into "black," ignited in air, and placed in a U-tube kept in boiling water, according to HEMPEL'S directions in the methane experiments.

To remove the air from the Gladstone and Tribe apparatus, a little dry alcohol was put in, and it was then connected with a water pump and warmed till nearly all the alcohol had boiled away, but the large volume of the apparatus, the great absorbing power of alcohol for air and other gases, and the long train of purifying apparatus required, must be taken as the excuse for the large percentage of air present.

Two analyses and the calculation of the result are given in full for the first experiment.

	I.	II.
Gas taken	100·61	98·85
After adding oxygen	369·43	461·83
After explosion	171·49	268·23
After absorption of the CO_2 with potash	72·06	171·80

The first gives as half the contraction 98·97, and the CO_2 formed 99·43, their ratio being ·9954.

The second gives 96·80 for the half-contraction, and 96·43 for the CO_2, their ratio being 1·003.

These ratios should be unity for pure methane.

The difference between half the contraction and the volume of gas taken, and between the CO_2 formed and the original gas, gives two estimates of the air from each analysis. These are 1·64 and 1·18 from the first, and 2·05 and 2·42 from the second. The discordance of these is wider than was usually obtained. An error of $\frac{3}{10}$ millims. in reading the level of the mercury when measuring the volume of the gas taken would account for the difference. The measuring tube of the Dittmar gas analysis apparatus was rather too narrow, as the shape of the meniscus varied with the state of the surface of the mercury.

The mean of the four gives 1·88 per cent. for the air.

The S.G. of the gas is got from the equation

$$100\rho = 1{\cdot}88 + 98{\cdot}12 \times {\cdot}5528,$$

which gives

$$\rho = {\cdot}5612.$$

Two sets of measurements of the methane figures gave as the half wave-lengths 63·126 millims. and 63·130 millims., and the length of the air figures was 48·880 millims., the temperature being 19·2°.

Hence, the ratio of the specific heats of the mixed gases is

$$1{\cdot}408 \times {\cdot}5612 \times \left(\frac{63{\cdot}128}{48{\cdot}880}\right)^2 = 1{\cdot}316.$$

Finally, from the equation

$$P/(\Gamma - 1) = p_1/(\gamma_1 - 1) + p_2/(\gamma_2 - 1),$$

we have

$$100/{\cdot}316 = 1{\cdot}88/{\cdot}408 + 98{\cdot}12/(\gamma - 1),$$

which gives

$$\gamma = 1{\cdot}314.$$

The results of the remaining two experiments made on methane prepared by GLADSTONE and TRIBE's method are given in the second and third line of Table II., with the temperature, the ratio of semi-contraction to CO_2, and the percentage of air.

The next three experiments were made on marsh gas got by the action of zinc methyl on water.

This method is not attractive from the offensive nature of the zinc compound and the violence of its reaction with water, but it gives a pure product.

The zinc-methyl was made by digesting methyl iodide with a copper-zinc couple on the water bath, and distilling off the product on an oil bath.

The reaction was very complete, the contents of the flask after the first operation being quite dry on cooling, but to ensure the removal of any unaltered methyl iodide a stream of carbonic acid was passed through the flask for some time whilst it was kept at 100°.

In the final distillation the end of the condenser dipped below the surface of dry ether cooled in ice, by means of which loss was prevented and an almost theoretical yield obtained.

The principal reason for mixing the zinc-methyl with ether will be detailed at length in the description of the preparation of ethane, which was the first gas investigated. What is said there will in all probability apply with even greater force here, where the compound is more easily dissociated, and the reaction more violent. The addition of ether adds very much to the comfort of the experiment, for the mixture can be poured from one vessel to another without any greater inconvenience than strong fuming.

To prepare the methane the mixture of ether and zinc-methyl was dropped slowly into a flask containing distilled water and the gas evolved collected without purification over boiled water, with which it was shaken to remove as much ether as possible.

It was passed into the Kundt apparatus through two sets of Geissler bulbs of strong sulphuric acid to remove the ether and traces of methyl iodide, one of potash to absorb any sulphur dioxide formed in the first two, and another of sulphuric acid to dry it. After this treatment it issued without smell.

In experiment IV. the potash was by mistake omitted, and the consequence was that the gas was found to contain ·5 per cent. of sulphur dioxide.

The results of the three experiments are shown in lines III., IV., and V., of Table II.

TABLE II.

	t.	$\frac{1}{2}\ \frac{\text{Contr}^{\text{n}}}{CO_2}$.	Air, &c.	γ.	Method of preparation.
			Per cent.		
I.	19·2	·9954 1·003	Air 1·88	1·314	GLADSTONE and TRIBE
II.	20	1·009	„ 1·15	1·314	
III.	16·6	1·002	„ 1·71	1·313	
IV.	19·1	1·012	SO_2 ·5 Air 2·6	1·332	FRANKLAND
V.	18·3	·999	„ ·8	1·300	
VI.	17·4	1·002	„ 1·4	1·305	
			Mean . .	**1·313**	

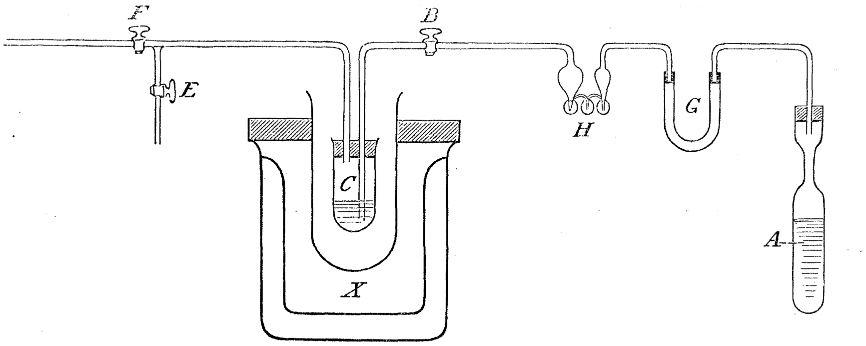
I have no data from which to calculate the correction factor $1 - 1/p \, . \, dpv/dv$. From the fact that the gas is at ordinary temperatures far above its boiling point, $d \, pv/dv$ is probably small and has been neglected.

§ 5. *Methyl Chloride.*

The material was made by passing a stream of hydrochloric acid gas into a boiling solution of zinc chloride in methyl alcohol, contained in a flask with a reversed condenser.

In the first two experiments recorded below the issuing gas was passed through potash solution, and collected in a gas-holder over strong brine, as it is too soluble in water.

Fig. 5.



It was admitted into the Kundt apparatus through one set of Geissler bulbs containing potash, and one containing sulphuric acid.

As the gas liquefies at — 17° it seemed desirable in order to have greater certainty of the absence of air to use the liquefied gas. This was done in the remaining experiments.

The gas on issuing from the apparatus in which it was prepared, was passed through potash solution and sulphuric acid, and was then condensed in a glass tube standing in a freezing mixture of ether and solid carbonic acid. Part was then redistilled into the apparatus shown in fig. 5, which was also used in a similar manner in the propane experiments.

A is the tube in which the methyl chloride was collected on its evolution from the apparatus in which it was prepared.

The condenser X consisted of two beakers, one inside the other, with a large boiling tube suspended in the inner one by the wooden cover. This tube contained the freezing mixture, and in it was the small test-tube C, closed air-tight by a stopper through which passed two glass tubes, one of them reaching to the bottom.

F being closed and B and E open, the liquid in A evaporated off quite slowly in consequence of the cooling produced by this operation, and passing through G, which contained soda-lime, and H, which contained sulphuric acid, was condensed in C, anything remaining uncondensed passing into the air at E. When the tube C was almost full B was closed, and the tube of methyl chloride taken out of the freezing mixture, which caused it to evaporate and drive out the air from above it. When this evaporation had gone on for a short time, E was closed and F opened, admitting the vapour into the Kundt apparatus.

Four determinations of the vapour density gave the following results, the pressure and temperature being recorded in each case.

TABLE III.

p.	t.	ρ.
382	14·6	1·754
602	12·6	1·762
533	13·9	1·759
660	13·5	1·765

In the experiments the pressures were read to ·05 millim. In this and all the following tables I have given them to the nearest millimetre.

The numbers in the third column are the specific gravities of the gas referred to air at the same temperature and pressure.

These values are plotted in fig. 6, and from the curve the values of the density are taken for the pressures at which the velocity of sound experiments were made.

To find the correction factor $1/p \, . \, d(pv)/dv$, the following method was adopted:—Taking the reciprocals of the densities given in Table III., we get values of pv in arbitrary units. Dividing these by the pressures, the corresponding volumes are obtained. These are given in Table IV., and in fig. 7 they are plotted on a curve, taking pv as ordinate and v as abscissa. The inclination of this curve to the horizontal axis at any point gives the value of $d(pv)/dv$ at that point. To get the v corresponding to the pressures used in the velocity of sound experiments, it is sufficient to take an approximate value of pv and divide by the pressure. The volumes so obtained are given in the second column of Table V., and, dividing the rate of change of pv at these points by the pressures, we get the numbers shown in the third column.

Fig. 6.

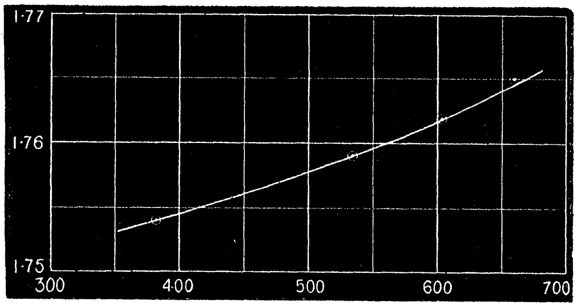


Fig. 7.

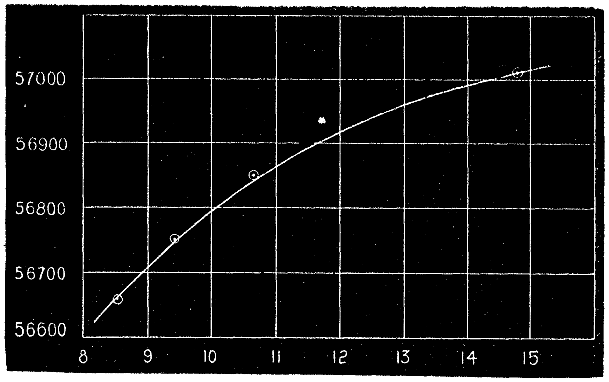


TABLE IV.

p.	pv.	v.
382	57012	14·93
602	56752	9·43
533	56850	10·65
660	56657	8·58

TABLE V.

p.	v.	$\frac{1}{p}\frac{d(pv)}{dv}$
380	14·9	·007
580	9·8	·014
600	9·5	·014
680	8·3	·015

We have then, finally, the following table for the ratio of the specific heats, where—

p = the pressure of the gas in the Kundt tube.
t = the temperature of the gas in the Kundt tube.
l = the half wave-length in methyl chloride.
l' = the half wave-length in air.
ρ = the S.G. of the methyl chloride at the pressure given in the first column.

TABLE VI.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d\,pv}{dv}$.	γ.
380	16	34·94	48·89	1·754	1·007	1·271
580	15·2	34·65	48·55	1·761	1·014	1·280
600	16	34·73	48·68	1·762	1·014	1·280
680	16·3	34·72	48·63	1·766	1·015	1·286
					Mean . .	1·279

In the last experiment there was 1·05 per cent. of air in the gas; the result is corrected for this.

§ 6. *Methyl Bromide.*

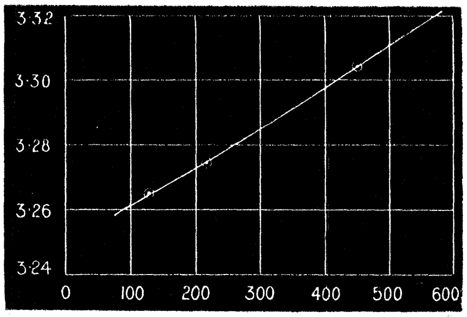
The material was obtained from KAHLBAUM, and was dried with calcium chloride and redistilled.

The results of the vapour density determinations are shown in Table VII. and fig. 8.

TABLE VII.

p.	t.	ρ.
131	15·8	3·265
221	15·6	3·275
451	15·9	3·305

Fig. 8.



The densities used in the calculation of the ratio of the specific heats are taken from this curve.

The correction factors are determined in exactly the same way as was explained under methyl chloride.

It is needless to give the intermediate tables and curves in every case, so, for the remaining gases, I shall content myself with giving the experimental data from which the correction was calculated, and its value.

The following table gives the final results for methyl bromide :—

TABLE VIII.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
255	19·4	25·58	48·96	3·278	1·013	1·277
312	15·9	25·34	48·62	3·286	1·014	1·274
440	20	25·40	48·96	3·302	1·015	1·270
530	15·8	25·20	48·61	3·314	1·016	1·274
					Mean . .	**1·274**

§ 7. *Methyl Iodide.*

The material was purchased from KAHLBAUM, and was dried with calcium chloride and fractionated.

Table IX. and fig. 9 show the results of three vapour density determinations. Table X. gives the final results, the columns having the same meanings, and being obtained in the same way as before.

TABLE IX.

p.	t.	ρ.
179	15·6	4·914
217	16·4	4·939
255	16·1	4·969

Fig. 9.

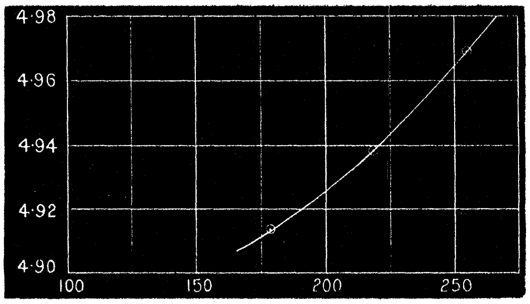


TABLE X.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
190	18·4	20·70	48·82	4·920	1·023	1·274
210	20	20·81	48·99	4·934	1·029	1·285
220	18·7	20·78	48·89	4·940	1·030	1·294
220	20·2	20·78	48·97	4·940	1·030	1·290
225	19·5	20·72	48·93	4·942	1·032	1·287
					Mean . .	**1·286**

§ 8. *Ethane.*

The first attempts to prepare ethane were by the electrolysis of a saturated solution of potassium acetate. Since these were made, Dr. T. S. MURRAY has published an account* of an extensive investigation of the method, so that it is needless to give any detailed account of my failure. The sample first analyzed was made by using a strong current for a short time, and proved to be almost pure ethane, but as the apparatus soon began to get hot, a much smaller current was used when preparing a large quantity for a velocity of sound determination, and the result was that the gas was not good enough for use. This agrees with MURRAY'S conclusion that high current density and low temperature are necessary, and shows that the method is not suitable for making a large supply, as a strong current and low temperature are not easily secured together.

This method having failed, it was decided to use the reaction between zinc-ethyl and water.

The zinc-ethyl was prepared in the same way as the zinc-methyl previously described.

For the preparation of ethane, the zinc-ethyl was mixed with twice its weight of

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* 'Chem. Soc. Journ.,' January, 1892.

dry ether and dropped into distilled water. The gas came off without undue violence, and the deposit of zinc oxide left in the flask was pure white.

The gas was collected over a large quantity of boiled water, and shaken with it to remove as much of the ether as possible, and in the first two experiments it was passed slowly into the Kundt apparatus through two sets of Geissler bulbs containing sulphuric acid.

On opening the apparatus the ethane was found to be without smell, but to ensure the removal of ethyl iodide which, from its high density, would have a very prejudicial effect, in the other experiments, the gas was passed through one set of bulbs of Nordhausen acid, two of potash, and two of strong sulphuric acid.

As it seemed undesirable, however, to introduce ether vapour, an attempt was made to prepare the ethane by dropping the zinc-ethyl itself on ice without diluting with ether.

The result showed that the ether was necessary, for after repeated attempts, the residue left in the flask instead of being white, was always dark grey, and effervesced slightly with acid, showing the presence of metallic zinc.

Moreover, analysis showed that there were heavy hydrocarbons present, for 100 volumes of the gas gave, on explosion with oxygen, 227 volumes of carbon dioxide. After passing the ethane slowly through Nordhausen acid, 100 volumes gave 207 volumes of CO_2, so that the impurities are mainly unsaturated hydrocarbons, but probably there is some butane present.

The cause of the impurity of the gas appears to be the violence of the reaction. The zinc-ethyl never got clear of the dropping tube, but was immediately acted on by the water vapour, and formed a great spongy clot round the end. This absorbed more zinc-ethyl, which was decomposed in its pores, and so the temperature rapidly rose high enough to bring about dissociation. It is known that at a moderately high temperature zinc-methyl decomposes into zinc and hydrocarbons, and probably a similar thing happened here.

Table II. shows the results of the experiments, taking for the specific gravity of the gas the theoretical density, 1·0367. In all the experiments the pressure was that of the air.

TABLE XI.

t.	l.	l'.	Percentage of air.	γ.
9·8	43·40	48·10	1·8	1·185
12	43·48	48·29	0	1·183
14·4	43·61	48·52	not determined	1·180
16·6	43·82	48·66	not determined	1·184
16·1	43·80	48·65	2·9	1·179
			Mean . . .	**1·182**

From the approximate equality of the densities of ethane and air the presence of 1 per cent. of the latter makes a change of less than $\frac{1}{10}$ per cent. in the value of γ, so that even if there were as much as 5 per cent. of air in experiments III. and IV., the result would be hardly affected.

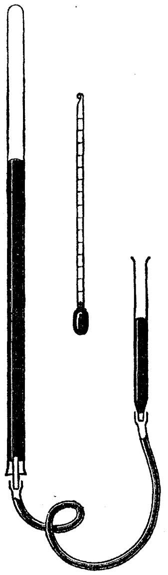
From want of experimental data I have omitted the factor $1 + 1/p \,.\, d\,(pv)/dv$, but, as in the case of methane, it probably does not differ much from unity.

§ 9. *Ethyl Chloride.*

The material was prepared by passing hydrochloric acid into a boiling solution of zinc chloride in ethyl alcohol, the resulting gas being passed through water and sulphuric acid, and condensed in a freezing mixture. It was then redistilled, shaken with lime to remove hydrochloric acid which was still present, allowed to stand two days over calcium chloride, and again distilled through a tube of lime.

With the vapour density apparatus that I was using at the time, tubes containing enough ethyl chloride to give pressures above 450 millims. would not go round the bend at the top. Six determinations were made at pressures ranging from 100 millims. to 453 millims., and the rest of the curve got from the relative densities as given by a direct observation of the values of the product pv for a constant mass of the gas in the usual way.

Fig. 10.



A glass tube one metre long, closed at one end and graduated approximately in cubic centims., was carefully calibrated.

After being filled with mercury, a little ethyl chloride was allowed to bubble up into it, and it was then connected at the lower end by an india-rubber tube with another glass tube of the same bore, and open to the air.

By altering the position of this second tube the pressure on the gas could be varied, and readings taken by means of a cathetometer of a series of pairs of corresponding values of p and v.

As a test of the accuracy of the calibration and the various temperature corrections, several preliminary experiments were made on air, which made the product pv appear to increase at low pressures by as much as 1 per cent.

After re-calibrating the tube and hunting in every direction for the cause of this, it was at last found to be due to an error in the scale of the barometer that was being used. Making a correction for this, the pv of air came out quite constant, and hence it was concluded that the calibration of the tube and the temperature corrections were right.

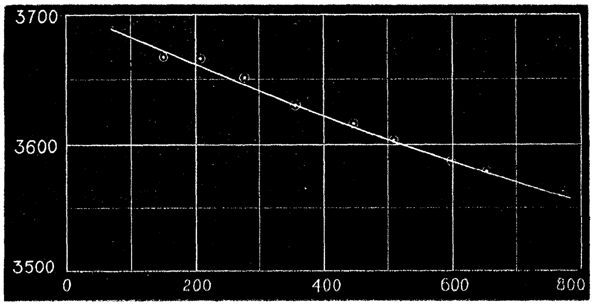
The following table gives the details of the experiment made on ethyl chloride. The first three columns give the corresponding values of pressure, volume, and temperature, and the last gives the quantity pv/t, which is inversely proportional to the specific gravity, referred to a perfect gas at the same temperature and pressure.

TABLE XII.

p.	v.	t.	$\frac{pv}{t + 273}$
149·85	70·2	13·5	3670
205·26	51·2	13·6	3667
273·96	38·2	13·65	3651
356·64	29·2	13·7	3632
446·96	23·2	13·7	3617
511·34	20·2	13·7	3603
597·85	17·2	13·65	3587
674·97	15·2	13·7	3578
773·54	13·2	13·75	3561

These values of pv/t are plotted on the curve in fig. 11.

Fig. 11.



Next six determinations of the S.G. of the vapour were made with the apparatus previously described. These had a range of pressures from 179 millims. to 453 millims., and the results are given in the first three columns of Table XIII.

To extend the values to the higher pressures the following method was adopted. From the curve in fig. 11 the values of pv/t were taken for the pressures at which the absolute determinations were made. These are given in the fourth column of the table, and should give a constant if multiplied by the numbers in the third column. The fifth column gives these products. The extreme variation is one part in a thousand, and the numbers do not increase progressively in either direction, which shows the consistency of the two series, and is a test of the degree of accuracy reached in the vapour density determinations.

TABLE XIII.

p.	t.	ρ.	$\frac{pv}{t + 273}$.	$\frac{pv\rho}{t + 273}$.
179	13·6	2·244	3667	8229
242	10·2	2·251	3655	8227
301	13	2·256	3644	8221
329	13·5	2·262	3637	8227
357	15	2·265	3631	8224
453	12·8	2·276	3615	8228
			Mean . .	**8226**

To find the best value of the constant of the pv curve, the mean of the six values of $pv\rho/t$ was taken, and this mean divided by the ordinate of the curve of fig. 11 for any pressure gives the S.G. of the vapour at that pressure.

Using the values so obtained, the following table gives the final results for the ratio of the specific heats, the columns having the same meanings as in the case of the previous gases.

TABLE XIV.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{(dv)}$.	γ.
200	12·8	29·34	48·32	2·245	1.012	1·180
205	15·4	29·48	48·54	2·245	1·012	1·180
285	14·2	29·41	48·45	2·255	1·016	1·189
295	15	29·31	48·49	2·257	1·016	1·180
400	16·4	29·49	48·75	2·270	1·019	1·191
400	17·8	29·49	48·81	2·270	1·019	1·188
410	15·5	29·31	48·61	2·271	1·019	1·184
560	16·5	29·21	48·61	2·290	1·025	1·193
610	17·1	29·22	48·72	2·294	1·025	1·190
630	16·4	29·15	48·61	2·297	1·025	1·192
					Mean . .	**1·187**

Two other experiments were made at pressures below 100 millims., which gave results about 2 per cent. below these, but the dust figures obtained were poor, and the density and correction factor had to be obtained by extrapolation. As the *pv* curve is getting a little irregular, so as to make the correction term uncertain, even at the lowest pressures actually observed, it is unsafe to go beyond the limits of direct experiment, hence they have been omitted.

§ 10. *Ethyl Bromide.*

In the case of this compound the experiments were conducted in a slightly different way from those already described. A vapour density determination was made in the usual way with a particular sample of the liquid, and when the pressure had been measured, the Kundt apparatus was filled to the same pressure with the vapour of an exactly similar specimen. Thus each line in the table below gives the result of a pair of parallel experiments, the vapour density determinations not being comparable with each other, as they were made on samples of liquid which had received different treatment.

Ethyl bromide seems to be more subject to impurity than any of the other substances. The first sample used was given to me by a friend, but its vapour density was so abnormally low that I discarded it without attempt at purification, and procured a supply from KAHLBAUM. This had a fairly steady boiling point, almost all coming over between 38° and 39°, and was used after a simple fractionation in the first experiment.

The vapour density determination gave a result ·3 per cent. below the theoretical value. As the boiling point was constant and at the right temperature, this raised a suspicion that there was some impurity present which had nearly the same boiling point as ethyl bromide, but a lower vapour density. If, as is not unlikely, the substance had been prepared from potassium bromide, alcohol, and sulphuric acid, the impurity might be ether, so the remainder was shaken with strong sulphuric acid and redistilled, which raised the density by nearly 1 per cent. This shows the insufficiency of the boiling point alone as a test of the purity of a liquid, and the value of a vapour density determination as a confirmatory test.

The second and third experiments were made on the liquid after this treatment, and the fourth, after a repetition of the process.

The densities obtained in this way are insufficient to give the correction factor, so a BOYLE'S Law experiment was made in addition, with the following results, all at a temperature of 19°:—

TABLE XV.

p.	v.	pv.	
117·5	64·8	7613	
171·9	44·2	7597	
236·1	32·	7555	
370·5	20·2	7484	Nearly saturated
379·5	19·6	7438	Part liquefied

From these the correction factors were determined, the final results being shown in Table XVI.

TABLE XVI.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d\,(pv)}{dv}$.	γ.
200	12·4	22·67	48·30	3·755	1·017	1·184
205	14·6	22·70	48·50	3·787	1·017	1·188
232	15	22·71	48·56	3·796	1·020	1·192
225	14·4	22·60	48·52	3·809	1·020	1·187
					Mean . . .	**1·188**

It is assumed, in making these calculations, that small changes in the state of purity of the liquid do not appreciably alter the relative vapour densities, for one curve is used to give the correction term for all.

§ 11. *Propane.*

This gas was prepared by SCHORLEMMER'S method of reducing isopropyl iodide with zinc and hydrochloric acid. The presence of free hydrogen in the gas is of no consequence, as it is removed by the liquefaction.

The isopropyl iodide was made from glycerine, phosphorus, iodine, and water, using the proportions given by BEILSTEIN. It boiled very constantly at 89°, showing that no considerable quantity of allyl iodide was present—any small quantity of this, however, would not interfere, for the propylene produced by its reduction would be removed by Nordhausen acid.

To prepare propane from the isopropyl iodide, it was placed in a flask with granulated zinc and dilute hydrochloric acid. The issuing gas was first washed with water, and then passed through fuming sulphuric acid to remove the isopropyl iodide. Next it was passed through potash solution, and over 30 grams of palladium foil, to remove the hydrogen. This is, of course, not essential, but prevents waste of propane in the liquefaction.

Finally it was collected in a gas-holder, over caustic soda solution, to remove any sulphur dioxide still present.

The liquefaction of the gas was carried out in the apparatus described under methyl chloride and by the same method, the soda-lime tube being omitted.

In consequence of an accident only a single determination of the absolute density of the gas was made, according to which the specific gravity is 1·511 at 20°·2 and under a pressure of 260 millims.

To extend the result to the higher pressures a determination of the relative densities was made in the same way as for ethyl chloride.

Table XVII. and fig. 12 show the results:

TABLE XVII.

p.	v.	t.	$\frac{t+273}{pv}$
209·24	53·6	19·4	2607
249·24	45·0	19·45	2607
293·30	38·2	19·5	2610
377·94	29·6	19·5	2615
574·10	19·4	19·5	2626
694·54	16·0	19·5	2632

Fig. 12.

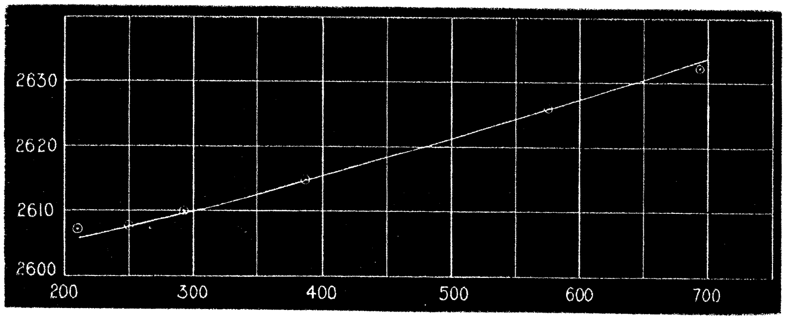


Table XVIII. gives the results for the ratio of the specific heats. The values of the specific gravity are taken from the curve above, an ordinate 2608 being taken to correspond to a specific gravity 1·511.

Table XVIII.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\cdot\frac{d\,(pv)}{dv}$.	γ.
450	17·45	35·31	48·79	1·517	1·010	1·130
650	16·6	35·06	48·74	1·524	1·016	1·128
650	15·9	35·02	48·62	1·524	1·016	1·131
					Mean . .	**1·130**

§ 12. *Normal Propyl Chloride.*

The material was obtained from Kahlbaum, and was dried and re-distilled. Almost all came over between 46° and 47°, the small residue being rejected.

The results of the experiments are shown in the tables and curve below.

Table XIX.

p.	t.	ρ.
135	13	2·747
183	19	2·751
248	22	2·759

Fig. 13.

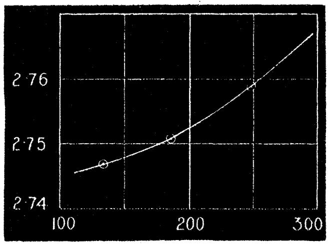


Table XX.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\cdot\frac{d\,(pv)}{dv}$.	γ.
270	22·6	26·38	49·18	2·762	1·011	1·132
240	25·5	26·52	49·43	2·758	1·010	1·129
250	25·	26·38	49·35	2·759	1·010	1·121
200	21·2	26·31	49·10	2·762	1·009	1·123
					Mean . .	**1·126**

§ 13. *Isopropyl Chloride.*

The material used was obtained from KAHLBAUM. On fractionating nothing came over below 35°·5, and almost all before the temperature reached 36°. The small residue was neglected.

Table XXI. and fig. 14 give the results of the vapour density experiments, and Table XXII. gives the final values for the ratio of the specific heats.

TABLE XXI.

p.	t.	ρ.
193	22	2·738
274	18·2	2·744
300	23	2·746
367	24·6	2·755

Fig. 14.

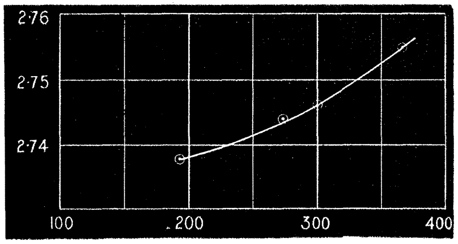


TABLE XXII.

p.	t.	l.	l'.	ρ.	$1+\frac{1}{p}\frac{d(pv)}{dv}$.	γ.
224	18·9	26·35	48·94	2·739	1·007	1·126
290	21	26·34	49·08	2·745	1·010	1·125
300	22·2	26·48	49·16	2·746	1·011	1·134
325	21	26·24	49·05	2·749	1·013	1·122
360	19·8	26·20	48·92	2·754	1·014	1·128
					Mean . .	**1·127**

§ 14. *Isopropyl Bromide.*

The material was obtained from KAHLBAUM, and boiled very constantly at 60°.

As the maximum vapour pressure at the atmospheric temperature is low, only a small range of pressures was available. Hence all the experiments were made at pressures near 90 millims., and instead of plotting a curve from the vapour density determinations, the mean of the three was taken and used in the calculation of γ.

The values are shown in Table XXIII.

TABLE XXIII.

p.	t.	ρ.
96	12·9	4·288
90	13·2	4·279
94	15·1	4·281
	Mean . .	**4·283**

These will not give the correction factor, hence a determination of the relative densities was made with the following result :—

TABLE XXIV.

v.	p.	t.	pv.	
68·4	79·35	15	5428	
55·6	97·40	..	5414	
45·2	120·0	..	5388	
35·8	144·5	..	5153	Nearly saturated

The curve plotted from these gave ·017 for $1/p \,.\, d(pv)/dv$, and using this value, Table XXV. gives the values obtained for γ.

TABLE XXV.

p.	t.	l.	l'.	ρ.	$1 + \frac{1}{p}\frac{d(pv)}{dv}$.	γ.
99	12·7	20·77	48·37	4·283	1·017	1·131
90	11·6	20·74	48·27			1·132
90	12·6	20·80	48·43			1·131
					Mean . .	**1·131**

§ 15. *Discussion of the Results.*

Gathering the results together, we have the following table :—

TABLE XXVI.

Name.	Formula.	γ.
Methane	CH_4	1·313
Methyl chloride	CH_3Cl	1·279
Methyl bromide	CH_3Br	1·274
Methyl iodide	CH_3I	1·286
Ethane	C_2H_6	1·182
Ethyl chloride	C_2H_5Cl	1·187
Ethyl bromide	C_2H_5Br	1·188
Propane	C_3H_8	1·130
Normal propyl chloride	C_3H_7Cl	1·126
Isopropyl chloride	C_3H_7Cl	1·127
Isopropyl bromide	C_3H_7Br	1·131

It will be seen on referring back to the separate results for methyl and ethyl chlorides and a few others of the gases that the values of γ are slightly higher at the higher pressures. This circumstance suggests a doubt as to the lawfulness of taking the mean, for if the change were at all considerable, the right thing to do would be to extend the range of the observations till a constant value was reached, and use this value for comparison. The change observed can hardly be said to be beyond the range of experimental error in any case, and is perhaps only accidental.

The only experiments I am acquainted with that have been made to test the question whether γ varies with the pressure or not are those of JÄGER ('WIED.,' vol. 36, p. 165), who concluded that it does not. His results for ether vapour show close concordance at saturation and half saturation, but the discordance of the results for alcohol and water lessens the value of those for ether.

The specific heat at constant pressure includes the change of potential energy due to separation of the molecules, and hence γ will probably not be quite independent of the pressure, if the gas does not obey BOYLE'S Law,* but if the change in γ is due only to this, it is not likely to be great.

The question has arisen quite incidentally in my work, for I was not looking for any such effect, and did not plan the experiments so as to make it perceptible. I have in no case used a very long range of pressures, and have always avoided going near saturation, where the effect might be expected to be most noticeable.

The point is one that ought to be settled. Meanwhile, the obvious law to which

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* See Professer FITZGERALD, 'Roy. Soc. Proc.,' vol. 42, p. 50.

the mean results conform, affords some justification for regarding the value of γ as approximately independent of the pressure.

It is plain that the gases fall into four groups, the members of any one group having within the limits of experimental error the same ratio of the specific heats. These groups are

1. Methane.
2. Methyl chloride, bromide, and iodide.
3. Ethane and its derivatives.
4. Propane and its derivatives.

So that with the single exception of methane, compounds with similar graphic formulæ have the same γ.

Methane was almost the last gas that I investigated, and it was in consequence of its appearing to fall away from the law, that exceptional trouble was taken to secure that it should be pure. All who have worked with this gas know how difficult it is to prepare it free from hydrogen, and the presence of hydrogen would raise the value of γ; but the precaution taken of passing the gas over palladium, the concordance of the results for methane prepared by the two different methods, and the evidence of the analysis show that there could not be anything approaching enough hydrogen present to account for the difference. Nor can we account for the difference by supposing the results for the three methyl compounds to be too low, for, apart from the fact that there *are* three of them, and that their values for γ agree fairly well with each other, the most likely error in their case is that due to the presence of air and moisture, which would make the results too high. Hence we must conclude that methane has not the same γ as its three substitution products.

It is strange that it should break through a law that appears to hold for all the other gases, but the circumstance is not without parallel. MENSCHUTKIN'S etherification values for the fatty acids, for instance, show a similar feature, as do PERKIN'S molecular rotation constants, and the viscosity coefficients of the same series of acids. In each of these cases a law is found to hold for all the members of the series except the first one or two.

It appears, then, that as a law to which marsh gas is an exception, one hydrogen atom of a paraffin can be replaced by a halogen atom, without affecting the γ of the gas, and consequently without altering the internal energy of the molecule. This result is similar to that which STRECKER obtained for the hydracids of the halogens, for he showed that hydrochloric, hydrobromic, and hydriodic acids have all approximately the same γ as hydrogen. It should however be noticed that he found the introduction of a second halogen atom caused a large fall in γ, the elementary gases, chlorine, bromine, and iodine, having ratios nearly equal, but much lower than those of the acids, from which fact we may anticipate a similar feature in the case of the paraffins.

I am at present working on the substitution products that have more than one halogen atom in the molecule, and intend also to determine whether other chemically similar atoms, such as oxygen and sulphur, or carbon and silicon can be interchanged without altering the value of γ. Until these experiments are finished, it would be premature to enter into a discussion of the theoretical bearing of the results.