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E. P. Perman, W. Ramsay and J. Rose-Innes

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# VII. *An Attempt to Determine the Adiabatic Relations of Ethyl Oxide.*

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The object of the research described in this Memoir is the determination of the behaviour of ether, in the state of gas, approaching towards the state of liquid, when no heat is communicated to it, so that its condition is altered adiabatically. Some experiments have also been made on liquid ether, an account of which we append. After several proposals, depending for their success on the sudden expansion of the substance, so that it might cool without sensible entrance of heat, recourse was had to a modification of Kundt's process, whereby the velocity of sound in the liquid or gas is ascertained. The material for research, pure ether, was prepared and dried as already described in a paper by Dr. Young and one of the authors ('Phil. Trans.,' A, 1887, p. 57, *et seq.*). It had a constant boiling-point, identical with that already given.

The experiments were carried out by Edgar Perman and William Ramsay during the Session 1891–1892. Various attempts were made to deduce from the results, by a graphical method, the true position of the curves representing the adiabatic expansion of the gaseous ether, but with small success. At a later date, J. Rose-Innes examined the figures contained in the tables annexed, and making use of the fact that, without serious error, the isochoric lines, as in the case of isothermal expansion, may be regarded as straight, contributed the mathematical treatment given in Section 5.

For want of sufficient knowledge of the thermal data for liquid ether, a similar treatment has not been found possible; but it is the opinion of the authors that the experimental data should be published, inasmuch as they may be found in future to afford a means of determining the adiabatic relations of a liquid, of which the behaviour in the state of gas is now obvious.

## I. Apparatus Employed.

The pressure apparatus, A, was the same as that employed in the former research, but important modifications had to be made, so as to render it fit for its present purpose.

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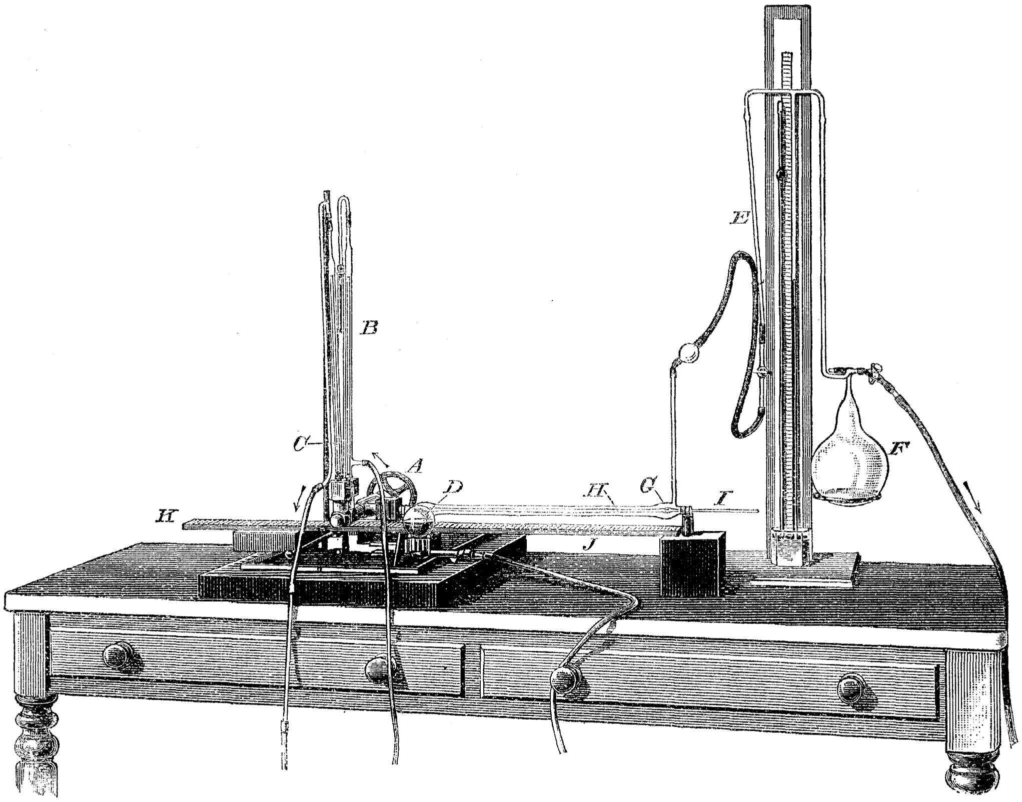
The tube containing the ether, DG, fig. 1, lay nearly horizontal, instead of, as before, standing vertical. The gauge-tubes B and C were, as before, one registering pressures from somewhat above that of the atmosphere to about 10 atmospheres; and a second, which began to show pressures of about 9 atmospheres, and continued to give reliable determinations up to 50 atmospheres, for its lower portion was expanded so as to form a reservoir. The gauges were jacketed by running water, the temperature of which was read from a small thermometer placed in a tube between the two gauges. The gauges were, as before, filled with dry air, and a correction was applied taken from the results of AMAGAT, on the coefficient of compressibility of air, by which the pressures were made to coincide with the readings of a theoretically perfect gas ('Compt. Rend.,' vol. 99, 1884, p. 1153). The low-pressure manometer was calibrated by comparison up to a pressure of 3 atmospheres with the readings of the height of mercury in a long open tube; and the high-pressure gauge was compared with the low-pressure one, and the pressures so controlled. Experiments made in this manner gave results not appreciably differing from those obtained by calculating pressure from the ratios of the volumes of air confined in the tubes to that present at the temperature and pressure of filling them. Both manometers were calibrated by weighing with mercury.

Fig. 1.



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The temperatures, as before, were obtained by jacketing with the vapours of various liquids, boiling under known pressures, and are those of an air-thermometer (see 'Trans. Chem. Soc.,' vol. 47, 1885, p. 640).

The "volume-tube" DGI (fig. 1) requires special description (see also fig. 2). It consisted of a piece of barometer-tubing, about 2·5 millims. in internal diameter, and 36 centims. long. To this was sealed a second piece, of 2 millims. diameter and 15 centims. in length. The end of the narrower tube was sealed, and blown into a small thick-walled bulb, G (B, fig. 2). A thin rod of glass, I (CD, fig. 2), 15 centims. long, was next sealed to the bulb so as to form a continuation of the bulb; and a piece of similar rod having been dropped into the barometer tube, was attached by sealing to the interior surface of the bulb. By careful fusion the internal and external rods were so manipulated as to be continuous with each other, the wall of the tube acting as a diaphragm. By rubbing the external rod longitudinally with a rag wet with alcohol, it gave a shrill note, and the vibrations were imparted to that portion in the barometer tube, and set in motion the gas contained in the tube.

It was found very difficult to construct such an apparatus which gave satisfactory vibrations. It appears necessary to have a fairly wide barometer tube, not too thick in the wall, else the vibrations produced are not those of the enclosed gas, but of the glass tube. After many attempts, a tube was at length found, in which no sign of "glass-vibrations" was noticeable; when lycopodium dust or powdered silica was introduced, and the rod was rubbed, the dust arranged itself in well-marked heaps, extending through the whole length of the tube. The difficulty was caused greatly by the necessity of having a tube sufficiently strong to withstand an internal pressure of 40 or 50 atmospheres, and yet capable of showing the wave-length of the contained gas.

This volume tube was graduated in millims., and calibrated by weighing with mercury. It served in all the experiments made.

To regulate the temperature, this experimental tube was surrounded by a jacket of glass, H (E, fig. 2), also lying horizontally; and at the end nearest the pressure apparatus a bulb, D, was sealed on, in which liquids could be boiled. It was necessary to ensure an air-tight junction between the external and internal tubes; hence it was necessary to employ indiarubber corks. But as most of the jacketing vapours used attack and dissolve indiarubber, the indiarubber cork was faced with ordinary cork, which protected it from the action of the vapour to a great extent. The other end of the jacket enclosed the small bulb at the end of the experimental tube, and was also provided with an indiarubber cork, faced with ordinary cork; through these the rod passed tightly, about 10 centims. of its length projecting outside (C, fig. 2). A small condenser sometimes surrounded the vertical tube at the further end of the jacket, which led to a manometer, E, and pump, so that the liquid in the bulb could be made to boil under any desired pressure, and therefore (within certain limits) at any required temperature. The liquids employed were chlorobenzene, giving a range of temperature

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between 100° and 130°; bromobenzene, giving a range of 130° to 150°; aniline, of 160° to 180°; and quinoline, of 180° to 200°. Observations were always made at even temperatures, the pressures being adjusted so as to cause the liquid to give off vapour of the temperature required—100°, 110°, 120°, &c., up to 200°.

The method of filling the tube also requires description. First, as regards the powder introduced to show the wave-lengths of the vibrating gas. In air and similar gases, lycopodium dust gives the most distinct figures; but it is a resinous substance, and hence it was not possible to place it in contact with ether. After many trials of magnesia, alumina, precipitated silica, &c., a quantity of somewhat impure silica was prepared, by fusing glass with carbonate of sodium and potassium, and treatment with hydrochloric acid; this gelatinous silica was not very well washed, but was dried in a somewhat impure state, containing a trace of common salt. It was ignited, and fritted together to rough lumps. These were powdered in an agate mortar, and sifted through gauze. The small fragments of microscopic size were approximately spherical, and flowed easily, not adhering to each other. Pure silica is too dusty; sand is too large-grained, or, if powdered, too angular; to obtain the best results the grains should be round and not too small.

A sufficient quantity of such sand was introduced into the experimental tube; its open end, A (fig. 3), was then sealed to a bulb, B, of the form shown in the woodcut; and the tube at the seal was drawn out into a wide capillary, C. Ether was placed in the bulb, and the open end, D, was then connected with a water-pump, and the bulb was exhausted. The ether began to boil and expelled air from the bulb. By admitting air, ether entered the experimental tube, A; and the bulb was again exhausted and then sealed at E. The amount of air was then reduced to that dissolved in the liquid ether. The experimental tube was next warmed, so as to boil the ether it contained; the vapour rushed up, driving pistons of liquid before it, and condensed in the bulb, which was artificially cooled. After about ten minutes, all possible air had been expelled from the tube into the bulb. On gently warming the bulb, B, and cooling the tube, A, liquid ether entered, and the absence of air was certain, inasmuch as the ether closed up rapidly and completely, no trace of a bubble being left in the tube. If even a small bubble were left, dissolving in the ether on its way up the sloping tube, the operation was repeated. The silica during this operation usually found its way into the bulb D (fig. 2) at the end of the experimental tube.

The tube was again warmed so as to expel ether. And here arose a difficulty. It was necessary to guess at the quantity of ether which was required. Usually, the experiments were adjusted to suit the particular quantity which accidentally remained. But with a little practice it was found possible to leave in the tube approximately the amount required. The capillary junction, C (fig. 3), between the experimental tube and the bulb was then sealed, leaving a thin tail of glass. The silica was then shaken out of the bulb of the experimental tube (see fig. 1, G, and fig. 2, B) into the tube itself, and distributed along its length as evenly as possible

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and the experimental tube was then screwed into the pressure apparatus by means of the iron cap for the purpose.

It was found that if mercury entered the space between the rod, D (fig. 2), and the internal wall of the experimental tube, A, it could not be removed by tapping, after the apparatus had been set up; and also that it interfered with the vibrations of the rod. Hence it was necessary to take precautions to prevent mercury entering the tube so far as to touch the end of the rod.

Fig. 2.

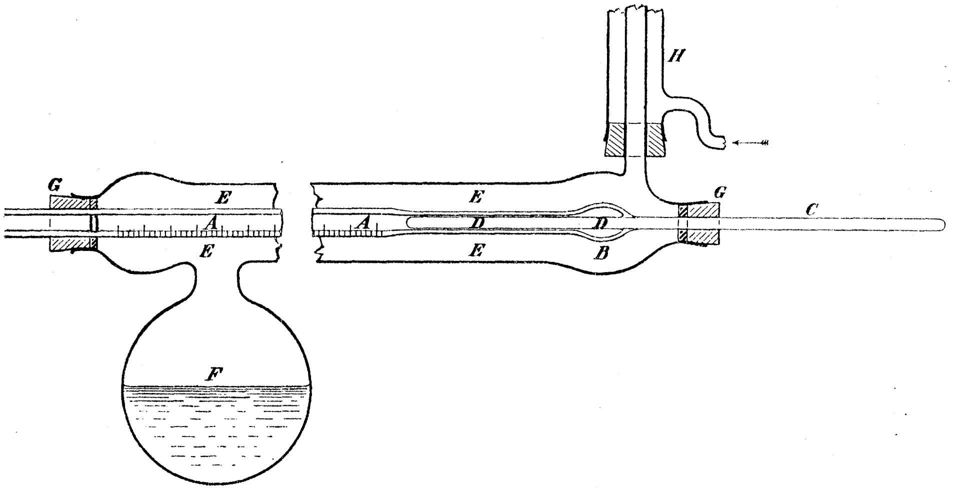
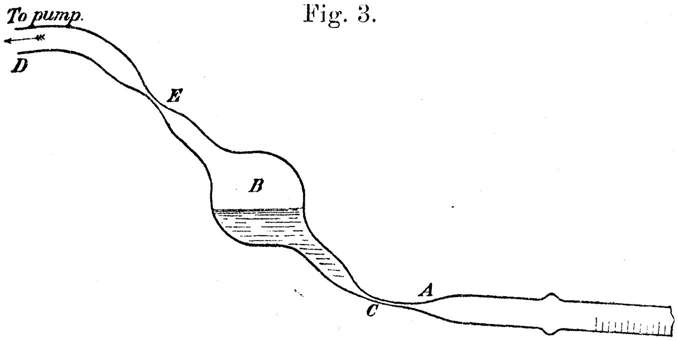


Fig. 3.



The experimental tube having been placed in position in the pressure apparatus, and the cap tightly screwed on, the temperature was raised to a given point, determined by the amount of ether left in the tube; the pressure was then raised by turning the screw of the pressure apparatus A (fig. 1), and when the end of the screw came in contact with the drawn-out capillary end of the experimental tube, C (fig. 3), which is there shown unsealed, it broke it. It was necessary so to regulate the temperature of the ether that only a little escaped when the capillary end was broken. If the pressure in the interior were too great, too much ether escaped; if too small, cold mercury entered, and came in contact with the internal rod. After some practice it was found possible to arrange the apparatus successfully nearly every

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time. During the breaking of the capillary point, the whole apparatus was tilted, so as to incline the experimental tube. The pressure was then raised so as to cause some mercury to enter the tube, which was then placed in a nearly horizontal position. By tapping, the silica was made to flow down, so as to form an evenly distributed layer in the experimental tube; the temperature was then finally adjusted, and after placing the mercury at a given mark on the tube, experiments were begun. At the temperature chosen the ether was wholly gaseous. On rubbing the projecting rod, the ether gas vibrated, and the silica arranged itself in heaps, which, when the ether gas was at its greatest volume, amounted to over thirty in number. They were, for the most part, regularly distributed. A millimetre scale etched on a slip of mirror, JK (fig. 1), was laid below the experimental tube, and the distance between the heaps was read. But instead of reading the actual position of all the heaps an average was taken in the following manner:—Suppose the total number of heaps to be 30; the 1st and 27th were read; the 2nd and 28th; the 3rd and 29th; and the 4th and 30th; and, dividing by the total number read, four averages were obtained. These usually agreed with each other to within 0·5 per cent.; the mean of all four was taken as the true wave-length.

The middle of each heap of silica was taken as most easily read. The silica could hardly be said to form "heaps"; it distributed itself in streaks of varying length across the tube, each set of streaks forming an oval-shaped patch, of which the middle point could be estimated with fair accuracy.

The volume of the gas was then diminished, and another set of readings taken in a similar manner. The mercury entering the tube covered up a portion of the silica; but on again increasing volume it flowed away, leaving the silica as before. This, of course, made it difficult, if not impossible, to determine accurately the volume occupied by the ether gas; for the volume of the silica was an uncertain quantity. But the whole amount of silica was very small, certainly not amounting in volume to 0·5 per cent. of that of the ether. To compensate for this error, by one in the opposite direction, no correction was made for the increase in volume of the tube on rise of temperature. The error thus introduced is about the same order of magnitude and opposite in sign to that involved by neglecting the volume of the silica, and hence the two errors may be taken as compensating each other to some extent. Moreover, the volume of one gram of ether at definite temperatures and pressures had been determined by Dr. S. YOUNG and one of the authors; and it was necessary to know the actual volume merely for the purpose of deducing the weight.

The volume of the gas was successively decreased, and observations made similar to those described. The temperature having been raised by increasing the pressure on the boiling liquid, a fresh set of observations were made. It was necessary, however, whenever the jacketing vapour was changed, to refill the tube, because the contraction of the ether, owing to its condensation, brought the mercury into contact with the rod, and filled the space between it and the inner wall of the experimental

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tube. This, of necessity, made the experiments somewhat tedious and difficult; but we venture to think they are as accurate as the method allows.

## II. Method of Ascertaining the Weights of Ether Employed.

For each set of experiments with a single jacketing vapour, the tube had to be specially filled with ether. This involved a different weight of ether each time. It was necessary to know the weight, in order to calculate the volume occupied by 1 grm. of the vapour.

To ascertain the weight, the volume at any given pressure and temperature was ascertained from an isothermal diagram showing from previous experiments, by Ramsay and Young, the relations between volume, temperature, and pressure. From this the weight was calculated at each different volume. All the results thus obtained were averaged, and the mean results accepted as the weight.

To take an instance:—At the temperature 140° C., the actual observed volumes and pressure were found as in the first two columns. The volume of 1 grm., corresponding to the pressure in each case, is given in the third column, and is taken from the Memoir referred to; and the weight, calculated from the volume of 1 grm., is to be found in the fourth column. The mean result of all these determinations was taken as the true weight. The volumes of 1 grm. were then calculated by dividing each observed volume by the mean weight. The details of one set of observations are given in the following table:—

| Temperature 140° C. | | | | |
|---|---|---|---|---|
| Pressure. | Actual volume. | Volume of 1 grm. (from diagram). | Weight. | Corrected volumes. |
| Millims. | | | | |
| 4586 | 2·279 | 67·60 | ·03371 | 67·29 |
| 5070 | 1·973 | 60·25 | ·03275 | 58·26 |
| 5649 | 1·791 | 53·00 | ·03379 | 52·88 |
| 6394 | 1·552 | 45·80 | ·03388 | 45·82 |
| 6798 | 1·433 | 42·60 | ·03364 | 42·31 |
| 7290 | 1·315 | 39·00 | ·03371 | 38·81 |
| 7830 | 1·197 | 35·75 | ·03348 | 35·34 |
| 8725 | 1·079 | 31·10 | ·03470 | 31·86 |
| 9487 | 0·9615 | 27·80 | ·03459 | 28·39 |
| 9912 | 0·9027 | 26·20 | ·03445 | 26·95 |

Similar sets of observations at other temperatures with the same ether were taken, and from them the mean weight was ascertained. But it frequently happened that the results at one temperature did not coincide with those at another. It must be remembered that the tube lay horizontally, and that on tilting it, after a set of observations had been made, more ether would escape up the tube. For the hot mercury in passing down gasified ether remaining in that portion of

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the experimental tube which was inside the pressure apparatus, and the result was that the ether was almost invariably increased somewhat in amount at the higher temperature. Thus, in the above case, calculation of weight at 130° C., 140° C., and 150° C., gave the following numbers as means :—0·03246, 0·03387, 0·03474, the individual results agreeing as closely as those in the preceding table. Each temperature was therefore treated on its merits, and unless no alteration in weight had been proved to occur on changing temperature, the calculations were made on the basis of measurements at different volumes and pressures at the same temperature.

## III. DETERMINATION OF THE FREQUENCY OF THE VIBRATING ROD.

Ten sets of experiments were made in order to ascertain accurately the wave-length in air of the note given by the glass rod. The mean result of each is here given ; the temperature was 15·5° C.

| I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | X. |
|---|---|---|---|---|---|---|---|---|---|
| 19·4 | 19·5 | 19·2 | 19·2 | 19·3 | 19·44 | 19·22 | 19·71 | 20·05 | 19·33 |

Mean 19·46 millims.

From these results the number of vibrations per second of the rod may be calculated by the formula

$$n = V/\lambda.$$

The velocity of sound in air was taken as 33253 centims. per second at 0° C. (‘Encyc. Brit.,’ Article *Sound*). The wave-length at 0° is 18·93 millims. Hence $n$ = 17,566 per second. The note was a shrill squeak.

The close agreement of the values for the wave-length quoted above seems to show that the accidental sources of error are here only trifling ; and they may be considered as practically eliminated from the final mean value. But it is still possible that there may be some constant source of error affecting all the experiments equally ; thus it is well known that the wave-length in gases is affected by the diameter of the tube, and this effect may become quite noticeable if the tube is narrow. It is not likely that such an effect really existed in the above experiments, for though the tube was rather narrow, the pitch of the note was exceedingly high. But it was thought as well to make quite certain, and a set of experiments was carried out to test the accuracy of the value of $n$ obtained.

### (1.) *Confirmatory Experiments with Hydrogen.*

The velocity of sound in hydrogen has been made the subject of investigation by a large number of experimenters, some of whom used tubes sufficiently wide to obviate

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all possibility of any marked friction effects occurring. The final result of such experiments is that the velocity of sound in hydrogen is to the velocity in air at the same temperature as the square roots of the specific volumes. Now the mean of nine readings with hydrogen, at 17·5° C., gave 7·36 centims. as the wave-length for the note of the vibrator. Taking the density of air as compared with hydrogen to be 14·47, this gives $n = 17{,}526$ per second as the frequency of the vibrator.

## (2.) *Confirmatory Experiments with Argon.*

Experiments were made by one of the authors on the velocity of sound in argon; these experiments were originally undertaken to determine the value of the ratio of the specific heats for argon, but as some observations were carried out with the actual tube described above, they can be used for our present purpose. The following are the measurements observed :—

| | |
|---|---|
| Mean of 40 readings in original tube with argon at 17·5° C. . . . . . . | 1·808 centims. |
| „ „ „ 0° . . . . . | 1·753 „ |
| Mean of 6 readings in wider tube with argon at 6·5° C. . . . . . . . | 3·1 centims. |
| „ „ „ 0° . . . . . . . | 3·064 „ |
| Mean of 5 readings in wider tube with argon at 8·64° C. . . . . . . . | 3·131 centims. |
| „ „ „ 0° . . . . . . . | 3·083 „ |
| Mean of 11 readings in wider tube with argon at 11·49° C. . . . . . . | 3·168 centims. |
| „ „ „ 0° . . . . . . . | 3·103 „ |
| Mean of 5 readings in wider tube with air at 6·7° C. . . . . . . . | 3·373 centims. |
| „ „ „ 0° . . . . . . . . | 3·332 „ |
| Mean of 5 readings in wider tube with air at 7·22° C. . . . . . . . . | 3·41 centims. |
| „ „ „ 0° . . . . . . . . | 3·366 „ |
| Mean of 11 readings in wider tube with air at 11·2° C. . . . . . . . | 3·423 centims. |
| „ „ „ 0° . . . . . . . | 3·355 „ |

From these numbers we easily find that the mean wave-length at 0° in the wider tube is for argon 3·083 centims., and for air 3·351; this gives us $n = 17{,}452$ in the original tube.

## (3.) *Confirmatory Experiments with the Phonograph.*

An attempt was made to discover the number of vibrations emitted per second by the rod with the aid of a phonograph. Such an experiment, if it could have been carried out, would have been extremely valuable as affording a direct determination of the frequency required. Unfortunately, the sound produced by the vibrator was too feeble to make a distinct impression upon the wax cylinder. A long tube of the same kind of glass was, therefore, taken, and this produced a much graver and

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stronger note, capable of leaving a distinct trace upon the wax; the experiment was also repeated with a shorter tube. The following results were obtained :—

| | Length. | No. of points in one revolution. |
|---|---|---|
| | millims. | |
| Tube No. 1 . . . | 155·59 | 766 |
| " 2 . . . | 100·02 | 1190 |

A tuning-fork, of frequency 1024, was found to leave 232 impressions in one revolution. This gives as the velocity of sound in this particular kind of glass 263,000 and 262,700 centims. per second for the two tubes respectively.

We may take the mean, 262,850 centims. per second, as the velocity of sound in the glass rod, and this assumption, though we have no guarantee of its exact truth, is unlikely to introduce any serious error. We then find that a rod 28·3 centims. long will emit 18,578 vibrations per second, and this number may be accepted as giving roughly the frequency of the glass rod when performing free vibrations. In the actual apparatus used, the rod was sealed on to a glass tube, near its middle, and this may well have had the effect upon it of a rider on a tuning-fork, and lowered the tone. The test in the present case is, therefore, only a rough one, but it has some value all the same, as it shows that the dust-heaps observed in all these experiments were really due to the vibrations of the fundamental note in air, and not to the higher harmonics in the glass.

It was decided upon the whole to adopt the value of $n$, derived from the experiments with air, as there is less manipulation required in this case, and, therefore, less liability to experimental error. By comparing the experiments with air, hydrogen, and argon, it will be seen that the value of the frequency is uncertain, to an extent of about $\frac{1}{2}$ per cent.; but it will be shown later on that the particular manner in which this constant enters into the equations renders the uncertainty of far less importance than might at first appear.

## IV. Calculations of the Adiabatic Elasticity.

Having ascertained the volume of 1 grm. corresponding to each pressure and temperature observed, and having also found the corresponding mean wave-lengths, the velocity of sound in the ether-gas was calculated by the formula—

$$V = n\lambda,$$

where V is velocity, $n$ the number of vibrations per second, 17,566, and $\lambda$ the wave-length. The following results were obtained :—

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| Pressure. | Volume of 1 grm. | Wave-length in millims. | (Velocity in centims. per second)$^2$. |
|---|---|---|---|
| Temperature 100° C. | | | |
| 3,932 | 71·22 | 11·41 | 4·0174 $\times 10^8$ |
| 4,761 | 55·97 | 11·08 | 3·7884 |
| 4,422 | 61·67 | 11·00 | 3·7338 |
| 4,843 | 52·20 | 10·94 | 3·6933 |
| 4,876 | 50·35 | 10·88 | 3·6528 |
| 4,921 | Condensed. | | |
| Temperature 110° C. | | | |
| 4,089 | 69·49 | 11·54 | 4·1190 $\times 10^8$ |
| 4,629 | 60·17 | 11·41 | 4·0175 |
| 5,016 | 54·66 | 11·36 | 3·9823 |
| 5,289 | 50·93 | 11·14 | 3·8296 |
| 5,609 | 47·32 | 11·04 | 3·7611 |
| 5,905 | 43·70 | 11·04 | 3·7611 |
| 6,080 | 40·08 | 10·67 | 3·5131 |
| 6,100 | Condensed. | | |
| Temperature 120° C. | | | |
| 4,232 | 69·50 | 11·87 | 4·3478 $\times 10^8$ |
| 4,803 | 60·26 | 11·65 | 4·1882 |
| 5,218 | 54·62 | 11·47 | 4·0597 |
| 5,833 | 47·32 | 11·25 | 3·9054 |
| 6,196 | 43·71 | 11·37 | 3·9892 |
| 6,623 | 40·09 | 10·97 | 3·7136 |
| 7,073 | 36·50 | 10·71 | 3·5396 |
| 7,301 | 34·70 | 10·60 | 3·4673 |
| 7,452 | 32·91 | 10·75 | 3·5661 |
| 7,579 | Condensed. | | |
| Temperature 130° C. | | | |
| 4,378 | 70·51 | 12·08 | 4·5031 $\times 10^8$ |
| 4,965 | 61·06 | 11·98 | 4·4288 |
| 5,389 | 55·42 | 11·49 | 4·0739 |
| 6,073 | 48·01 | 11·85 | 4·3332 |
| 6,447 | 44·34 | 11·25 | 3·9054 |
| 6,900 | 40·67 | 11·25 | 3·9054 |
| 7,424 | 37·03 | 11·34 | 3·9682 |
| 8,001 | 33·39 | 10·85 | 3·6327 |
| 8,299 | 31·57 | 10·44 | 3·3633 |
| 8,683 | 29·75 | 10·22 | 3·2231 |
| 9,331 | Condensed. | | |
| Second filling. Bromobenzene jacket. Temperature 130° C. | | | |
| 4,317 | 70·22 | 12·06 | 4·4882 $\times 10^8$ |
| 4,940 | 60·80 | 11·88 | 4·3552 |
| 5,366 | 55·26 | 11·71 | 4·2314 |
| 6,061 | 47·81 | 11·43 | 4·0315 |
| 6,432 | 44·16 | 11·26 | 3·9124 |
| 6,883 | 40·50 | 11·29 | 3·9332 |
| 7,419 | 36·88 | 10·86 | 3·6394 |
| 7,971 | 33·26 | 10·58 | 3·4542 |
| 9,073 | 29·62 | 10·37 | 3·3184 |
| 9,272 | 27·81 | 10·30 | 3·2738 |
| 9,445 | Condensed. | | |

| Pressure. | Volume of 1 grm. | Wave-length in millims. | (Velocity in centims. per second)$^2$. |
|---|---|---|---|
| Temperature 140° C. | | | |
| 4,586 | 67·29 | 12·28 | 4·6534 $\times 10^8$ |
| 5,070 | 58·26 | 12·14 | 4·5479 |
| 5,649 | 52·88 | 11·90 | 4·3699 |
| 6,394 | 45·82 | 11·73 | 4·2459 |
| 6,798 | 42·31 | 11·67 | 4·2025 |
| 7,290 | 38·81 | 11·53 | 4·1023 |
| 7,830 | 35·34 | 11·48 | 4·0668 |
| 8,725 | 31·81 | 11·00 | 3·7338 |
| 9,487 | 28·39 | 10·62 | 3·4883 |
| 9,912 | 26·65 | 10·56 | 3·4410 |
| 10,373 | 24·92 | 10·44 | 3·3633 |
| Temperature 150° C. | | | |
| 4,830 | 65·61 | 12·37 | 4·7218 $\times 10^8$ |
| 5,451 | 56·81 | 12·23 | 4·6156 |
| 5,930 | 51·56 | 12·14 | 4·5479 |
| 6,685 | 44·67 | 11·94 | 4·3992 |
| 7,147 | 41·26 | 11·92 | 4·3846 |
| 7,632 | 37·84 | 11·57 | 4·1308 |
| 8,422 | 34·46 | 11·44 | 4·0386 |
| 9,281 | 31·07 | 11·21 | 3·8778 |
| 10,098 | 27·68 | 10·83 | 3·6193 |
| 11,074 | 24·29 | 10·75 | 3·5661 |
| Third filling. Bromobenzene jacket. Temperature 140° C. | | | |
| 10,898 | 23·00 | 10·06 | 3·1230 $\times 10^8$ |
| 11,550 | 21·20 | 9·87 | 3·0061 |
| 11,618 | 20·90 | 9·59 | 2·8439 |
| 11,675 | 20·75 | 9·70 | 2·9034 |
| Temperature 150° C. | | | |
| 11,401 | 22·80 | 10·55 | 3·4346 $\times 10^8$ |
| 12,469 | 19·80 | 10·14 | 3·1729 |
| Fourth filling. Fresh ether. Aniline jacket. Temperature 150° C. | | | |
| 5,483 | 57·10 | 12·28 | 4·6534 $\times 10^8$ |
| 6,733 | 44·88 | 12·00 | 4·4436 |
| 7,627 | 38·88 | 11·67 | 4·2025 |
| 8,657 | 32·94 | 11·43 | 4·0315 |
| 10,081 | 27·04 | 11·06 | 3·7746 |
| Temperature 160° C. | | | |
| 5,719 | 56·39 | 12·43 | 4·7677 $\times 10^8$ |
| 7,051 | 44·32 | 12·03 | 4·4659 |
| 7,973 | 38·40 | 11·89 | 4·3624 |
| 9,048 | 32·53 | 11·78 | 4·2822 |
| 9,413 | 26·70 | 11·33 | 3·9612 |

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| Pressure. | Volume of 1 grm. | Wave-length in millims. | (Velocity in centims. per second)$^2$. |
|---|---|---|---|
| Fifth filling. Aniline jacket. Temperature 170° C. | | | |
| 18,195 | 12·13 | 9·14 | $2·5779 \times 10^8$ |
| 18,649 | 11·48 | 8·56 | 2·2611 |
| 19,112 | 10·83 | 8·08 | 2·3249 |
| 19,191 | 10·05 | 7·97 | 1·9602 |
| Temperature 180° C. | | | |
| 19,339 | 12·04 | 9·30 | $2·6689 \times 10^8$ |
| 20,596 | 10·42 | 8·59 | 2·2769 |
| 21,471 | 9·46 | 8·26 | 2·1054 |
| 22,481 | 8·20 | 7·42 | 1·6990 |
| 22,533 | 7·57 | 7·55 | 1·7590 |
| Temperature 185° C. | | | |
| 19,756 | 12·06 | 9·52 | $2·7903 \times 10^8$ |
| 21,177 | 10·44 | 8·80 | 2·3896 |
| 22,135 | 9·48 | 8·30 | 2·1258 |
| 23,267 | 8·21 | 7·74 | 1·8486 |
| 23,847 | 7·58 | 7·37 | 1·6380 |
| 24,305 | 6·96 | 6·90 | 1·4692 |
| 24,368 | 6·33 | 6·65 | 1·3646 |
| Sixth filling. Aniline jacket. Temperature 150° C. | | | |
| 7,845 | 37·07 | 12·23 | $4·6156 \times 10^8$ |
| 8,893 | 32·10 | 11·27 | 3·9193 |
| 9,578 | 29·13 | 11·00 | 3·7338 |
| 10,626 | 25·24 | 10·64 | 3·4934 |
| 11,232 | 23·31 | 10·37 | 3·3184 |
| 11,884 | 21·38 | 10·28 | 3·2610 |
| 12,025 | 19·47 | 10·25 | 3·2420 |
| 13,371 | 17·55 | 9·67 | 2·8856 |
| 13,687 | 16·60 | 9·58 | 2·8321 |
| Temperature 170° C. | | | |
| 8,509 | 36·95 | 11·94 | $4·3992 \times 10^8$ |
| 9,526 | 31·99 | 11·83 | 4·3185 |
| 10,276 | 29·04 | 11·55 | 4·1165 |
| 11,477 | 25·16 | 11·15 | 3·8363 |
| 12,890 | 21·31 | 10·90 | 3·6663 |
| 14,656 | 17·50 | 10·39 | 3·3313 |
| 19,246 | Condensed. | | |
| Temperature 180° C. | | | |
| 8,755 | 37·35 | 12·27 | $4·6467 \times 10^8$ |
| 9,854 | 32·35 | 12·12 | 4·5328 |
| 10,644 | 30·04 | 11·78 | 4·2822 |
| 11,893 | 25·44 | 11·44 | 4·0386 |
| 13,398 | 21·55 | 11·25 | 3·9054 |
| 14,268 | 19·62 | 11·12 | 3·8157 |
| 15,294 | 17·69 | 10·71 | 3·5396 |

| Pressure. | Volume of 1 grm. | Wave-length in millims. | (Velocity in centims. per second)$^2$. |
|---|---|---|---|
| Seventh filling. Quinoline jacket. Temperature 185° C. | | | |
| 19,650 | 12·27 | 9·26 | $2·6460 \times 10^8$ |
| 21,056 | 10·63 | 8·75 | 2·3626 |
| 21,914 | 9·65 | 8·32 | 2·1360 |
| 22,488 | 9·00 | 7·91 | 1·9308 |
| 22,671 | 8·36 | 8·92 | 1·9848 |
| 23,281 | 7·72 | 7·63 | 1·7964 |
| Temperature 190° C. | | | |
| 20,119 | 12·44 | 9·51 | $2·7908 \times 10^8$ |
| 21,583 | 10·77 | 9·06 | 2·5330 |
| 22,613 | 9·77 | 8·52 | 2·2400 |
| 23,904 | 8·47 | 7·96 | 1·9552 |
| 24,530 | 7·82 | 7·64 | 1·8012 |
| 25,028 | 7·17 | 7·35 | 1·6671 |
| 25,478 | 6·53 | 7·00 | 1·5121 |
| 26,372 | 5·89 | 6·76 | 1·4102 |
| Temperature 193·8° C. | | | |
| 20,495 | 12·42 | 9·65 | $2·8736 \times 10^8$ |
| 22,085 | 10·75 | 9·17 | 2·5948 |
| 23,107 | 9·76 | 8·90 | 2·4443 |
| 24,466 | 8·45 | 8·21 | 2·0799 |
| 25,205 | 7·81 | 7·86 | 1·9064 |
| 25,904 | 7·16 | 7·50 | 1·7358 |
| 26,235 | 6·52 | 7·17 | 1·5864 |
| 26,860 | 5·88 | 6·92 | 1·4777 |
| 27,302 | 4·92 | 6·14 | 1·1633 |
| 27,357 | 4·60 | 6·31 | 1·2286 |
| Temperature 195° C. | | | |
| 20,613 | 12·42 | 9·75 | $2·9334 \times 10^8$ |
| 22,188 | 10·88 | 9·24 | 2·6346 |
| 23,260 | 9·76 | 8·90 | 2·4443 |
| 24,679 | 8·45 | 8·83 | 2·0952 |
| 25,315 | 7·81 | 7·91 | 1·9308 |
| 26,583 | 6·52 | 7·22 | 1·6086 |
| 27,144 | 5·88 | 7·04 | 1·5294 |
| 27,518 | 5·24 | 6·74 | 1·4018 |
| Temperature 200° C. | | | |
| 21,056 | 12·81 | 9·98 | $3·0735 \times 10^8$ |
| 22,739 | 11·09 | 9·47 | 2·7674 |
| 23,806 | 10·06 | 9·12 | 2·5666 |
| 25,252 | 8·72 | 8·39 | 2·4498 |
| 26,024 | 8·05 | 8·62 | 2·2929 |
| 26,707 | 7·39 | 7·99 | 1·9700 |
| 27,438 | 6·73 | 7·69 | 1·8249 |
| 28,082 | 6·06 | 7·50 | 1·7358 |

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| Pressure. | Volume of 1 grm. | Wave-length in millims. | (Velocity in centims. per second)$^2$. |
|---|---|---|---|
| Eighth filling. Saturated vapour. Temperature 190° C. | | | |
| 26,030 | 5·577 | 6·79 | 1·4227 × $10^8$ |
| 26,026 | 4·830 | 6·75 | 1·4060 |
| Temperature 193·8° C. | | | |
| 27,538 | 5·577 | 6·35 | 1·2433 × $10^8$ |
| 27,595 | 4·830 | 6·26 | 1·2092 |
| 27,595 | 4·383 | 6·09 | 1·1445 |
| 27,595 | 4·088 | 6·23 | 1·1977 |
| 27,646 | 3·798 | 6·22 | 1·1938 |
| 27,584 | 3·508 | 6·36 | 1·2482 |
| 27,584 | 3·217 | 6·55 | 1·2938 |
| 27,674 | 2·929 | 6·63 | 1·3564 |
| 27,758 | 2·929 | 7·07 | 1·5424 |
| 28,291 | 2·785 | 8·50 | 2·2295 |
| 29,722 | 2·641 | 10·45 | 3·3699 |
| Temperature 195·15° C. | | | |
| 27,949 | 5·577 | 6·48 | 1·2957 × $10^8$ |
| 28,147 | 4·830 | 6·13 | 1·1452 |
| 28,233 | 4·383 | 5·95 | 1·0925 |
| 28,258 | 4·088 | 5·85 | 1·0561 |
| 28,288 | 3·798 | 5·60 | 0·9677 |
| 28,389 | 3·508 | 5·47 | 0·9233 |
| Temperature 193·8° C. | | | |
| 27,441 | 5·577 | 6·35 | 1·2443 × $10^8$ |
| 27,605 | 4·830 | 6·37 | 1·2521 |
| 27,553 | 4·383 | 6·27 | 1·2131 |
| 27,553 | 4·088 | 6·21 | 1·1900 |
| 27,553 | 3·798 | 6·41 | 1·2679 |
| Liquid. | | | |
| 27,553 | 3·798 | 6·08 | 1·1407 × $10^8$ |
| 27,553 | 3·508 | 6·25 | 1·2054 |
| 27,553 | 3·217 | 6·31 | 1·2287 |
| 27,580 | 2·929 | 6·65 | 1·3646 |
| 27,627 | 2·856 | 6·75 | 1·4060 |
| 27,958 | 2·785 | 7·93 | 1·9405 |
| 28,415 | 2·713 | 8·22 | 2·0850 |
| 28,817 | 2·641 | 9·15 | 2·5835 |
| 29,702 | 2·584 | 10·06 | 3·1230 |
| Temperature 195·15° C. | | | |
| 27,888 | 5·577 | 6·49 | 1·2997 × $10^8$ |
| 28,140 | 4·830 | 6·38 | 1·2561 |
| 28,166 | 4·383 | 6·19 | 1·1824 |
| 28,195 | 4·088 | 6·02 | 1·1183 |
| 28,206 | 3·798 | 5·44 | 0·9132 |
| 28,222 | 3·508 | 5·26 | 0·8538 |
| 28,275 | 3·362 | | |
| 28,337 | 3·217 | | |
| 28,598 | 3·073 | | |
| 28,857 | 2·929 | | |
| 29,253 | 2·856 | | |
| 29,679 | 2·785 | | |
| 30,358 | 2·713 | | |
| Temperature 195·15° C. | | | |
| 28,235 | 3·362 | 5·24 | 0·8473 × $10^8$ |
| 28,278 | 3·217 | 5·57 | 0·9574 |
| 28,337 | 3·073 | 5·80 | 1·0381 |
| 28,598 | 2·929 | 6·99 | 1·5078 |
| 28,857 | 2·856 | 7·62 | 1·7918 |
| 29,253 | 2·785 | 8·54 | 2·2506 |
| 29,679 | 2·713 | 8·70 | 2·3357 |
| 30,358 | 2·641 | 9·72 | 2·9155 |
| Temperature 195·15° C. | | | |
| 27,968 | 5·577 | 6·45 | 1·2838 × $10^8$ |
| 28,137 | 4·830 | 6·07 | 1·1370 |
| 28,165 | 4·383 | 5·92 | 1·0815 |
| 28,207 | 4·088 | 5·72 | 1·0096 |
| 28,223 | 3·798 | 5·49 | 0·9301 |
| 28,223 | 3·508 | 5·18 | 0·8280 |
| 28,311 | 3·217 | 5·42 | 0·9065 |
| 28,625 | 2·929 | 7·06 | 1·5380 |
| 28,892 | 2·856 | 7·51 | 1·7404 |
| 29,158 | 2·785 | 8·50 | 2·2295 |
| 29,649 | 2·713 | 8·97 | 2·4829 |
| 30,225 | 2,641 | 9·91 | 3·0305 |
| Temperature 200° C. | | | |
| 29,432 | 5·577 | 6·82 | 1·4353 × $10^8$ |
| 29,870 | 4·830 | 6·39 | 1·2600 |
| 29,964 | 4·383 | 6·26 | 1·2092 |
| 30,258 | 4·088 | 6·16 | 1·1709 |
| 30,355 | 3·798 | 6·13 | 1·1596 |
| 30,457 | 3·508 | 6·39 | 1·2600 |
| 30,823 | 3·217 | 7·00 | 1·5121 |

From these observations a set of isothermal curves was constructed, where $V^2$ was plotted against volume (see fig. 4). The results are not very concordant; some

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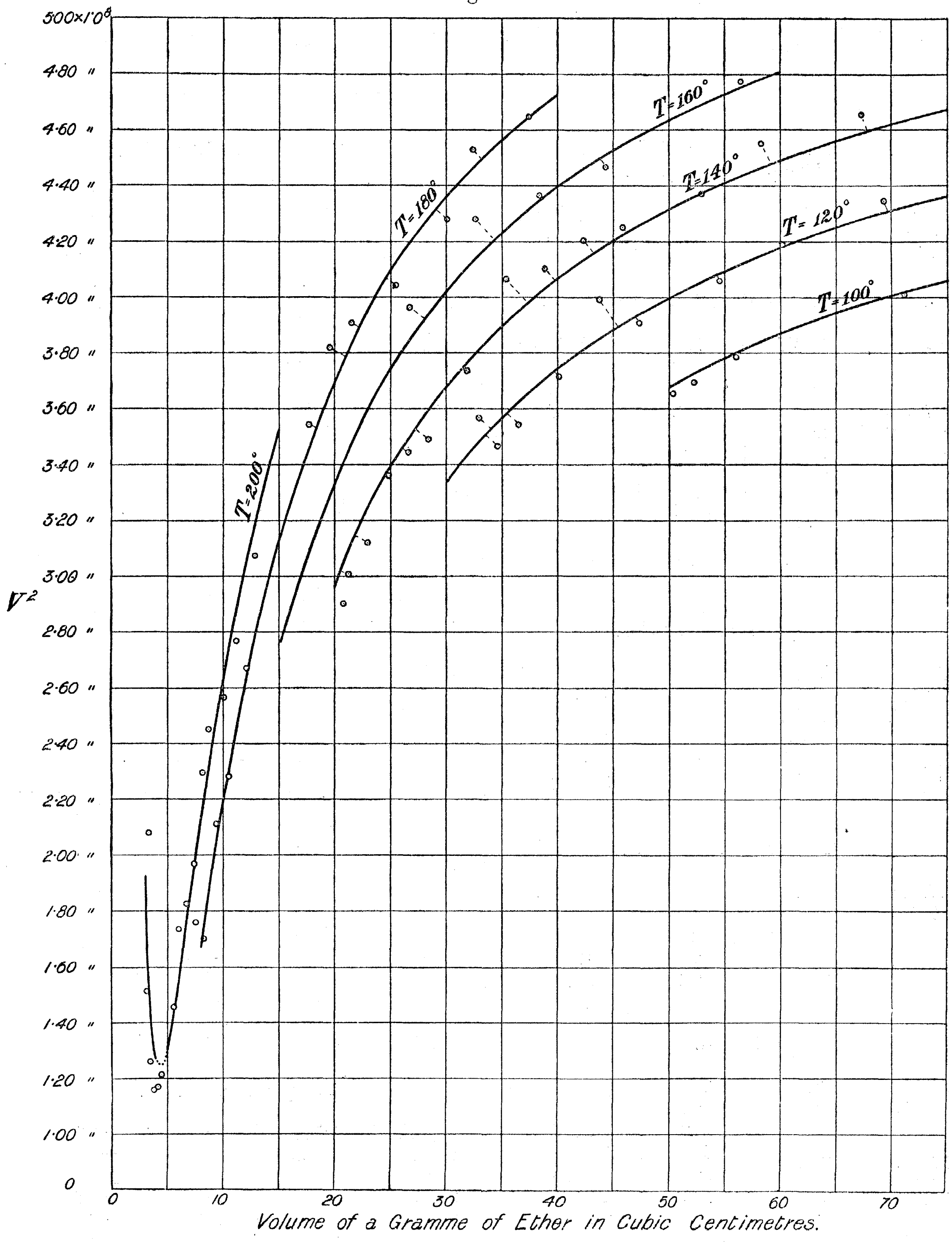
Fig. 4.



are altogether erratic, and this is to be expected, for it was not always possible so to rub the rod as to produce the required tone. A rod so placed is capable of many kinds of vibrations, and the particular rate of vibration, though the one most usually produced, may, by some difference in the method of rubbing, be replaced by another.

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But, on the whole, the resulting curves show good concordance. Where a number of curves such as these, differing from each other by regular intervals, is drawn, the position of each of them lends control to that of its neighbour, and a close approximation to accuracy may be deduced from very unpromising material.*

These curves were then further utilized by reading off the values of $V^2$ for equal volumes, 70, 65, 60, and so on, at intervals of 5 down to volume 20 cub. centims. per grm., and at smaller intervals, viz., 17·5, 15, 14, 13 cub. centims. per grm., and so on, down to 4 cub. centims. per grm. at smaller volumes.

From these numbers a second diagram was constructed, representing the values of $V^2/v$ plotted against temperature, the lines being isochoric. These curves were observed not greatly to deviate from straight lines—they intersected at small volumes. They would probably also intersect at larger volumes if produced. It has not been thought necessary to reproduce this figure as it is virtually contained in fig. 4.

The value of $V^2/v$ is, of course, the same as the adiabatic elasticity, and, like the isothermal elasticity, it has the dimensions of a pressure. It will be remembered that V was measured in centimetres per second, and $v$ in cub. centims. per grm. Consequently, the elasticity, as calculated above, must be given in absolute units, or dynes per sq. centim. It was found more convenient to change to pressures measured in millimetres of mercury, and this can be readily done by dividing all the former numbers by 1334·2.

## V. Mathematical Discussion of Preceding Results.

We noticed above that for equal volumes the adiabatic elasticity is roughly a linear function of the temperature, and this fact seems to hold out some hope of bringing all the experimental results obtained under the power of analysis. An inspection of the diagram shows that the difference between the isochorals actually drawn and straight lines is no greater than the uncertainty due to experimental errors, so that as far as the direct evidence goes it is possible that the isochorals are really straight. Even if it should turn out on subsequent investigation that the isochorals are slightly curved, the treating them as straight lines may be considered as a first approximation to the truth, and as a justifiable simplification of a very complex problem.

Let us call the adiabatic elasticity measured in millimetres of mercury E, then we may put

$$E = gT - h,$$

where $g$ and $h$ are functions of the volume only. Now, it was shown by one of the authors, in conjunction with Dr. Sydney Young, that for constant volumes there is a

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* The curves actually given in fig. 4 have been calculated by means of the formula on p. 183; they are the smoothed version of a set of similar curves drawn to represent the actual observations. They agree with the observations better than the original free-hand curves.

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linear relation between the temperature and pressure, so that we may put

$$p = b\mathrm{T} - a,$$

where $b$ and $a$ are functions of the volume only ('Phil. Mag.,' vol. 23, p. 436). From these two equations it is possible to eliminate the temperature, and we obtain

$$\mathrm{E} = \frac{g(p+a)}{b} - h,$$

$$= \frac{g}{b}p - h + \frac{ga}{b}.$$

Thus we see that for constant volumes E may be expressed as a linear function of $p$; the next step is evidently to find the value of $g/b$. For this purpose the isochoral diagram was employed; a straight edge was laid so as to pass as near as might be to the drawn points, and the slope of this edge was then determined; this slope gave the value of $g$. To obtain $b$ nothing more was needed than to use the values given in RAMSAY and YOUNG'S paper (*loc. cit.*, p. 441). On calculating the value of $g/b$ for various volumes, it was found to be nearly constant; such deviations as existed were not arranged in any orderly manner, but occurred sometimes to one side and sometimes to another, as if fluctuating about a mean value. It appeared as if $g/b = 11/9$ might be taken as a fair mean between all the values obtained. We may therefore put

$$\mathrm{E} = \frac{11}{9}p - h + \frac{11}{9}a,$$

and this leads to the equation

$$\mathrm{V}^2 = 1631\,pv - f(v),$$

where $f(v)$ is a function of $v$ only. In order to determine the value of $f(v)$, the above was written

$$f(v) = 1631\,pv - \mathrm{V}^2.$$

Keeping the volume constant, and changing the temperature, this equation gives values of $f(v)$ differing slightly from one another; the arithmetical mean was chosen as giving the value of $f(v)$ for that particular volume. In this way $f(v)$ was determined for a large number of volumes, and it was found that its values could be approximately represented by means of the empirical formula

$$f(v) = \frac{785{,}300{,}000}{v^{2/3}} - \frac{317{,}700{,}000}{v^{4/3}} - \frac{3{,}114{,}000{,}000}{v^2}$$

The above formula was selected from a large number that were tried, and it reproduced the found values of $f(v)$ fairly well, but it is not suggested as being anything more than an empirical formula. Unfortunately the Kinetic Theory of Gases is not sufficiently advanced to enable us to form any *à priori* notion as to

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what form the function $f(v)$ might be expected to have, so that we are perforce driven to employ an empirical formula. With a large amount of time and labour it might be possible to find a formula for $f(v)$ simpler in character, and more exact in its results, but it did not seem worth while to undertake the amount of trouble involved in such a search. The formula can be successfully used for the purposes of interpolation within the field of observation, but any use of it for extrapolation would be hazardous.

We may now write the equation for $V^2$ as

$$V^2 = 1631\,pv - \frac{785{,}300{,}000}{v^{2/3}} + \frac{317{,}700{,}000}{v^{4/3}} + \frac{3{,}114{,}000{,}000}{v^2}.$$

This formula has been obtained as the result of four consecutive approximations, and it is possible that each succeeding approximation has led us further from the facts. On the other hand, it is conceivable that the errors of the various approximations have to a large extent neutralised one another. It was thought advisable therefore to test the above formula by calculating out the isothermals, and comparing them with the observed measurements. The result is shown in fig. 4; and it is easily seen that the calculated isothermals may be fairly taken as a system of smooth lines passing through the observed points.

From the equation to $V^2$ we obtain

$$E = \frac{11}{9}p - \frac{785{,}300{,}000}{1334{\cdot}2}v^{-5/3} + \frac{317{,}700{,}000}{1334{\cdot}2}v^{-7/3} + \frac{3{,}114{,}000{,}000}{1334{\cdot}2}v^{-3},$$

or,

$$-v\frac{dp}{dv} = \frac{11}{9}p - \frac{588{,}600}{v^{5/3}} + \frac{238{,}100}{v^{7/3}} + \frac{2{,}334{,}000}{v^3}.$$

Multiply by $-v^{2/9}$ and we get

$$v^{11/9}\frac{dp}{dv} + \frac{11}{9}pv^{2/9} = \frac{588{,}600}{v^{13/9}} - \frac{238{,}100}{v^{19/9}} - \frac{2{,}334{,}000}{v^{25/9}}$$

Integrating

$$pv^{11/9} = k - \frac{9}{4} \times \frac{588{,}600}{v^{4/9}} + \frac{9}{10} \times \frac{238{,}100}{v^{10/9}} + \frac{9}{16} \times \frac{2{,}334{,}000}{v^{16/9}}.$$

Hence,

$$p = \frac{k}{v^{11/9}} - \frac{1{,}324{,}000}{v^{5/3}} + \frac{214{,}300}{v^{7/3}} + \frac{1{,}313{,}000}{v^3}.$$

The constant $k$ is at our disposal, and we may choose it so that the adiabatic shall pass through any assigned point. By giving a series of different values to $k$ we obtain a system of adiabatic lines. We may get a convenient system by giving to $k$ succes-

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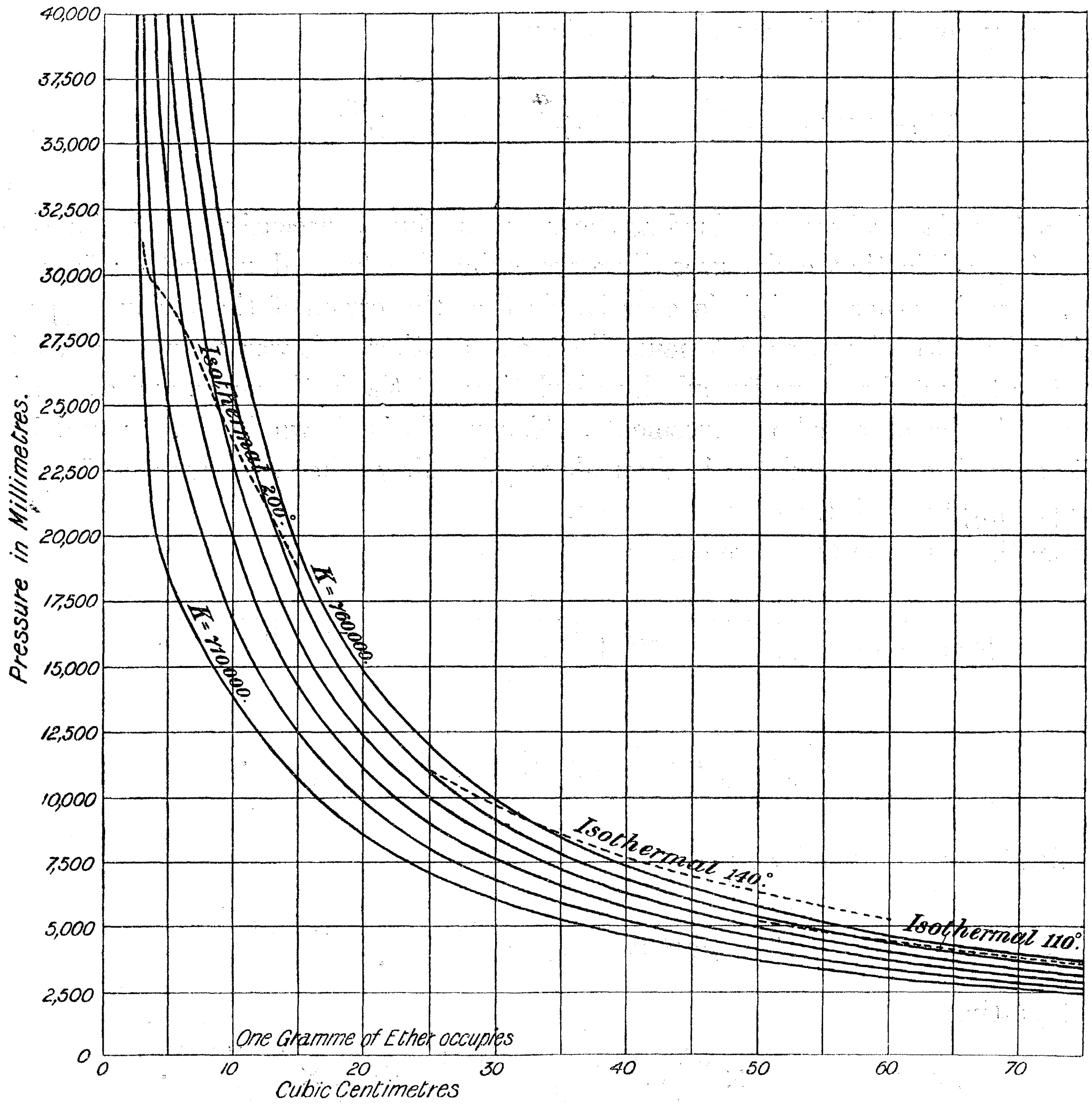
sively the values 710,000, 720,000, 730,000, 740,000, 750,000, 760,000 ; such a system is shown in fig. 5 ; the curves have been drawn for a great part of their length so as to exhibit to the eye their general shape, but only that portion of the system which is intersected by the drawn isothermals has been really investigated experimentally, and can, therefore, be safely trusted. The adiabatic for $k = 720,000$ passes close to the critical point.

Fig. 5.



The system of isothermals and adiabatics intersecting one another divides the plane of $pv$ into a set of curvilinear parallelograms, such as that suggested in MAXWELL's 'Theory of Heat' (p. 156) ; and, if our interpretation of the experimental results is correct, it ought to be possible so to select the system of adiabatics that the areas of all the parallelograms are equal. The following thermo-dynamic investigation will show to what extent this can be done.

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Let us assume that the equation to the isothermals of a gas can be written in the form

$$p = b\mathrm{T} - a,$$

where $b$ and $a$ are functions of the volume only. Let us also assume that the equation for the adiabatic elasticity E can be put in the form

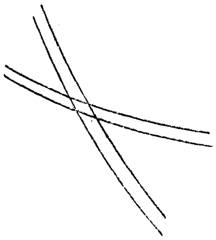
$$\mathrm{E} = g\mathrm{T} - h,$$

where $g$ and $h$ are functions of the volume only. Then, by eliminating T, and putting for E its value $-v\dfrac{dp}{dv}$, we see that we have a linear differential equation for $p$ of the first order, the independent variable being $v$. The integral of such an equation must be of the form

$$p = k\psi + \chi,$$

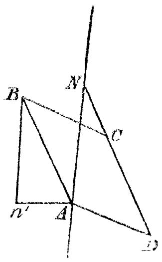
where $k$ is the constant of integration, while $\psi$ and $\chi$ are functions of $v$ only; we see also that we must have $\psi'/\psi = -g/bv$. This equation determines a system of adiabatics by giving successively different values to $k$, and by taking two neighbouring values, say $k$ and $k + dk$, we obtain two adiabatics as near together as we please. Let now the pair of adiabatics be crossed by two isothermals at temperatures T and T + $d$T, then the area of the infinitely small parallelogram formed must be independent of T by the Second Law of Thermo-dynamics.

Fig. 6.



Let ABCD in fig. 7 denote a magnified picture of this small parallelogram; then, by shearing the figure after the manner of Maxwell in obtaining his fourth thermodynamical relation (*loc. cit.*, p. 166), we obtain

Fig. 7.



PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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area ABCD = increase of pressure when we pass from lower to higher adiabatic at constant volume.

× increase of volume when we pass from higher to lower isothermal along adiabatic.

$$= -\psi\, dk \times \left(\frac{dv}{d\mathrm{T}}\right)_k d\mathrm{T}.$$

Now, whatever the variations of pressure volume and temperature, they are subject, if small, to the relation

$$dp = b\, d\mathrm{T} + \left(\mathrm{T}\frac{db}{dv} - \frac{da}{dv}\right) dv.$$

Let us denote differentiation with regard to $v$ by accents, then we may put this

$$dp = b\, d\mathrm{T} + (b'\mathrm{T} - a')\, dv.$$

Also any adiabatic alteration will be subject to the relation

$$dp = (k\psi' + \chi')\, dv.$$

Hence,

$$b\, d\mathrm{T} + (b'\mathrm{T} - a')\, dv = (k\psi' + \chi')\, dv$$

$$\left(\frac{dv}{d\mathrm{T}}\right)_k = \frac{b}{k\psi' + \chi' + a' - b'\mathrm{T}} = \frac{b}{k\psi' + \chi' + a' - b'\dfrac{p + a}{b}}$$

$$= \frac{b}{k\psi' + \chi' + a' - \dfrac{b'a}{b} - \dfrac{b'}{b}(k\psi + \chi)} = \frac{b}{k\left(\psi' - \dfrac{b'}{b}\psi\right) + \chi' + a' - \dfrac{b'}{b}(\chi + a)}.$$

Therefore

$$-\psi(v)\left(\frac{dv}{a\mathrm{T}}\right)_k = \frac{b\psi}{k\left(\psi\dfrac{b'}{b} - \psi'\right) + \dfrac{b'}{b}(\chi + a) - \chi' - a'}.$$

Now this quantity is to be independent of T so long as we keep $k$ unaltered, hence we have

$$k\left(\frac{b'}{b^2} - \frac{\psi'}{b\psi}\right) + \frac{b'}{b^2\psi}(\chi + a) - \frac{\chi' + a'}{b\psi} = \text{function of } k \text{ only.}$$

This can only be the case if the expressions $\dfrac{b'}{b^2} - \dfrac{\psi'}{b\psi}$, $\dfrac{b'}{b^2\psi}(\chi + a) - \dfrac{\chi' + a'}{b\psi}$ are functions of $k$ only. But both these expressions, from their form, can be seen to be functions of $v$ only; hence they must be numerical constants. Let

$$b'/b^2 - \psi'/b\psi = \mathrm{C}, \text{ say,}$$

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then

$$b'/b - \mathrm{C}b = \psi'/\psi.$$

Substituting for $\psi'/\psi$, we may write this

$$b'/b - \mathrm{C}b = -g/bv,$$

so that

$$g = \mathrm{C}b^2v - b'v.$$

As long as there is no assumption made about the connection between $g$ and $b$, this equation simply gives $g$ in terms of $b$. The adiabatics we have drawn, however, were the result of further assuming that $g/b$ is equal to a constant; and if this condition is introduced, we find that the form of $b$ is restricted. Let us denote by $\gamma$, the constant value of $g/b$, then

$$b'/b^2 + g/b^2v = \mathrm{C}, \quad \text{or} \quad b'/b^2 + \gamma/bv = \mathrm{C}.$$

Put $1/b = u$, and we have

$$du/dv - \gamma u/v = -\mathrm{C}.$$

This equation is easily integrated, and we obtain

$$u = \frac{1}{\mathrm{R}}(v + ev^{\gamma}),$$

so that

$$b = \frac{\mathrm{R}}{v + ev^{\gamma}},$$

where R and $e$ are constants at our disposal.

If we confine ourselves to volumes which lie between 70 and 4, the values of $b$ may be roughly reproduced by means of the above formula, taking care to give suitable values to R and $e$. But if, in such a formula, we were to attempt to extrapolate to large volumes, the result would be that we should obtain values of $b$ totally at variance with experiment. This shows us once more the need of restricting our formulæ entirely to those portions of the field that have been experimentally investigated.

## APPENDIX.

### *Experiments with Liquid Ether.*

In experimenting with liquid ether, the apparatus and method of working were similar in every respect to what has already been described.

The volume of 1 grm. of the ether was, as before, not directly determined, but was

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inferred from a knowledge of temperature and pressure. It was more easy to obtain well-defined heaps of silica in the liquid than in the gas.

The following results were obtained :—

| Pressure. | Volume of 1 grm. | Wave-length in millims. | (Velocity in centims. per second)$^2$. |
|---|---|---|---|
| Temperature 100° C. | | | |
| 4,859 | 1·638 | 37·67 | 43·786 × $10^8$ |
| 15,834 | 1·6225 | 38·20 | 45·026 |
| 28,665 | 1·610 | 40·43 | 50·436 |
| Temperature 120° C. | | | |
| 7,496 | 1·735 | 32·42 | 32·431 × $10^8$ |
| 15,823 | No data | 33·50 | 34·707 |
| 28,644 | ” | 35·25 | 38·341 |
| Temperature 150° C. | | | |
| 13,281 | 1·931 | 23·33 | 16·794 × $10^8$ |
| 15,861 | 1·913 | 24·53 | 18·567 |
| 18,550 | 1·903 | 25·00 | 19·285 |
| 21,595 | 1·894 | 25·47 | 20·017 |
| 28,712 | 1·870 | 27·34 | 23·064 |
| Temperature 175° C. | | | |
| 19,998 | 2·218 | 15·27 | 7·195 × $10^8$ |
| 21,625 | 2·208 | 15·61 | 7·519 |
| 23,565 | 2·176 | 16·64 | 8·544 |
| 28,753 | 2·110 | 18·54 | 10·606 |
| Temperature 185° C. | | | |
| 23,356 | 2·490 | 10·93 | 3·686 × $10^8$ |
| 24,677 | 2·424 | 12·52 | 4·859 |
| 25,898 | 2·376 | 13·23 | 5·401 |
| 27,250 | 2·330 | 14·42 | 6·416 |
| 28,753 | 2·299 | 15·19 | 7·120 |
| 30,431 | 2·262 | 15·97 | 7·869 |
| 32,313 | 2·229 | 16·84 | 8·750 |
| Temperature 190° C. | | | |
| 25,074 | 2·730 | 8·35 | 2·151 × $10^8$ |
| 25,867 | 2·668 | 9·81 | 2·969 |
| 27,250 | 2·546 | 11·61 | 4·159 |
| 28,753 | 2·463 | 12·81 | 5·063 |
| 30,431 | 2·398 | 14·04 | 6·082 |
| 32,313 | 2·342 | 15·18 | 7·110 |
| 36,681 | 2·256 | 17·12 | 9·044 |
| Temperature 195° C. | | | |
| 25,898 | * | 7·14 | 1·573 × $10^8$ |
| 27,250 | 3·285 | 7·22 | 1·608 |
| 28,753 | 2·779 | 9·58 | 2·832 |
| 30,431 | 2·601 | 11·28 | 3·926 |
| 32,313 | 2·501 | 12·79 | 5·047 |
| 34,441 | 2·426 | 14·07 | 6·108 |
| 36,681 | 2·366 | 15·31 | 7·233 |
| 39,700 | 2·307 | 16·50 | 8·400 |
| Temperature 200° C. | | | |
| 30,431 | 3·282 | 8·20 | 2·075 × $10^8$ |
| 32,313 | 2·803 | 10·28 | 3·261 |
| 34,441 | 2·632 | 11·90 | 4·370 |
| 36,681 | 2·520 | 13·46 | 5·590 |
| 39,700 | 2·415 | 15·00 | 6·943 |
| Temperature 205° C. | | | |
| 30,398 | * | 6·67 | 1·373 × $10^8$ |
| 33,282 | 3·314 | 7·62 | 1·792 |
| 34,409 | 2·931 | 9·84 | 2·988 |
| 36,681 | 2·721 | 11·62 | 4·166 |
| 39,658 | 2·565 | 13·13 | 5·319 |
| Temperature 210° C. | | | |
| 32,282 | * | 7·10 | 1·555 × $10^8$ |
| 34,409 | 3·535 | 7·88 | 1·916 |
| 36,681 | 3·122 | 9·83 | 2·981 |
| 39,658 | 2·788 | 11·57 | 4·131 |

Treating these data as before, the isochoric lines for $V^2/v$ are found to be straight. The investigation was not pushed further, however, as the formulæ involved appeared to be even more complicated than in the case of the larger volumes; but the above experimental data have been given for the sake of anyone who feels interested in the subject.

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* Volume not read; curve nearly horizontal.