

A RAPID METHOD OF DETERMINING THE MOLECULAR MASSES OF LIQUIDS BY MEANS OF THEIR SURFACE TENSIONS.

BY C. E. LINEBARGER.

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INTRODUCTORY.

UNTIL within the last few years our knowledge of the molecular condition of liquids was very limited. Such facts as the existence of allotropic modifications of elements and of isomorphous forms of compounds, the rotation of the plane of polarized light, the abnormal vapor-densities of certain substances in the vicinities of their boiling points seemed to indicate that in liquids two or more gaseous molecules coalesce to form complex molecular groupings.¹ Indeed, de Heen² developed a theory of liquids on the hypothesis that liquid molecules are made up of a number of gaseous molecules, thus making a distinction between "liquidogenic" and "gasogenic" molecules. On the other hand, it has been assumed by some that the differences between gases and liquids are due solely to the greater propinquity of the molecules in the liquid condition, no polymerization of the gaseous molecules taking place. But nothing really definite about the question was advanced until Guye,³ in studying the relation of his critical coefficient to the molecular mass of a liquid at its critical point, found that it was necessary to double the molecular masses of methyl alcohol and water in order to make them conform to the general rule he had established. This is the first time that a definite numerical value was assigned to the molecular mass of a liquid, and it was thereby rendered evident that both of the above suppositions in regard to the molecular condition of liquids correspond to fact; some liquids are polymerized and some are not.

¹ Naumann: *Ann. Chem. (Liebig)*, 155, 325, 1870; Henry: *Ann. de la Soc. Scientifique de Bruxelles*, 1873-1879, 267; Spring: *Bull. del'Acad. de Belgique* [3], 11, No. 5, 1886; Dupré: *Théorie mécanique de la chaleur*, 147; Amagat: *Ann. chim. phys.* [5], 11, 356; Ramsay: *Proc. Roy. Soc.*, 1880, April 22 and December 16; Ramsay and Young: *Proc. Roy. Soc.*, 1885, Nov. 19, and *Phil. Mag.*, 1887, 129.

² de Heen: *Ann. chim. phys.* [6], 5, May, 1885, and *Physique Comparée et la Théorie de Liquides*, 1888.

³ *Ann. chim. phys.* [6], 21, Oct. 1890; *Compt. rend.*, 110, 141 and 1128, 1890; *Bull. Soc. Chim.* [3], 3, 51; *Arch. de Genève*, [3], 23, 197; Thesis: *Le coefficient critique et la détermination du poids moléculaire au point critique*. Paris, 1897.

The next stage in the investigation of the subject was naturally the determination of the classes of liquids that are made up of simple molecules and of the classes of liquids that consist of complex molecules, or, in other words, the determination of which liquids are "normal" and which are "associated;" also the question as to the amount of association presented itself.

This investigation was taken up by Ramsay and Shields,¹ who, by the application of a method based upon determinations of surface energies, examined more than fifty liquids; this work may justly be considered classic and is the source of most of our definite knowledge of the size of liquid molecules.

The division of liquids into two classes according to their molecular polymerization having thus been rendered familiar and definite by the work of these two English chemists, many properties of liquids were subjected to examination in order to ascertain whether they might reveal any indications of molecular polymerization. Guye² has been particularly active in this direction; thus, he found evidence of molecular association in certain liquids, as shown by their latent heats of vaporization attaining a maximum, their curves of vapor-tensions intersecting one another, etc. Also, Linebarger,³ in examining Pictet's Law (commonly but erroneously known as Trouton's Law) and in determining the specific gravities, viscosities, and other physical properties of mixtures of liquids found that certain abnormalities could be best accounted for by the assumption of the presence of polymerized molecules. Moreover, in studying the vapor-tensions of mixtures of volatile liquids, Linebarger⁴ was led to the discovery of a method of determining the absolute molecular mass of a liquid at a definite temperature, Ramsay and Shield's method giving only the average molecular mass throughout a certain range of temperature.

Mention must also be made of an extremely simple method proposed by Traube⁵ for ascertaining whether the molecules of a liquid are in a state of association or not; it is based upon a

¹ *J. Chem. Soc.*, 63, 1089, 1893, and *Ztschr. phys. chem.*, 12, 433, 1893.

² *Arch. de Genève* [3], Jan., Feb., and May, 1895; *Bull. Soc. Chim.*, 13, 34, 1895.

³ *Am. J. Sci.*, 49, 381, 1895; *Am. Chem. J.*, 18, 429.

⁴ *J. Am. Chem. Soc.*, 17, 615 and 690, 1895.

⁵ *Ber. d. chem. Ges.*, 1894-1896.

determination of the density of the liquid under investigation.

The discovery of a method of determining the molecular masses of liquids opens up a broad field of investigation. The discoverer of a new liquid ought no longer to be content with a determination of its vapor-density or cryoscopic behavior in order to ascertain its molecular mass in the gaseous or dissolved state; he ought also to determine its surface tension, its density, or its vapor-tension in solution in order to ascertain whether it is associated or not. The method of vapor-tensions in solution, although it is the only one as yet devised that gives indications of the exact size of a liquid molecule at a given temperature, is rather long and is restricted to volatile liquids capable of analysis in the presence of the solvent. The chemist is therefore confined to the methods by Ramsay and Shields, or Traube. As stated above, Traube's method depends simply upon a determination of density; it does not seem to have attracted much attention, probably because it has merely an empirical basis. But a density determination is also required in Ramsay and Shields' method, so that the two methods may be employed together, the one serving as a control of the other.

The method of determination of molecular masses of liquids from their surface energies, as carried out with the apparatus used by Ramsay and Shields, does not seem to have been generally introduced into laboratories of organic chemistry for the probable reason that it requires careful and skillful manipulation and considerable time. There appears to be a need for an apparatus that can be handled rapidly, does not require much skill in using, is always ready for work, and gives reliable results. It is believed that the apparatus to be described in the following sections meets these requirements.

II. DESCRIPTION OF APPARATUS.

The apparatus (Fig. 1) consists of the following pieces: A column of brass tubing *AA* with iron tripod base; a short horizontal arm *B*, to which is attached a brass gibbed plate *SS* supporting the capillary tubes by means of the clamps *CC* and *DD*, and also the micrometer screw *EF*; a retort ring *AH* bearing the beaker *II*; a compression device consisting of a screw *L*

pressing into a rubber ball K , which is connected by means of rubber tubing and a glass Y tube N to the upper extremities of the capillary tubes; a vertical rod MM passing through the arm B (to which it may be clamped by a thumb-screw not shown in the figure) and provided with rings to support the rubber tubes connected with the capillary tubes, the latter being thus relieved of the weight of the former; a test tube O , into which the capillary tubes pass, supported by the cover of the beaker II ; two thermometers, one to take the temperature of the bath-liquid contained in the beaker, the other that of the liquid undergoing investigation in the test tube O .

Some of these pieces require a more detailed description.

The immovable part of the gibbed plate has a scale fastened along its side divided into fortieths of an inch, while its movable part has a pointer playing over this scale. Back of the gibbed plate is fixed the bearing P , in which the screw EF turns; the clamps CC are attached to the fixed portion of the gibbed plate, also another pointer for the milled head of the screw.

The micrometer screw demands a specially detailed description, inasmuch as the accuracy of the results obtainable by the apparatus depend mainly upon the accuracy of its construction. The one I use has forty threads to the inch, is about four inches long, and of good diameter, so as to give absolute motion, the adjustable split bearing P taking up all lost motion. Great pains were taken in turning it, and I have been unable to detect any irregularities in its construction; indeed, the screw furnished by the makers is even more accurate than is really necessary. The milled head E (about thirty-five mm. in diameter) is divided into 100 parts, thus giving a direct reading of $\frac{1}{100}$ of an inch, and even less than that, since it is easy to estimate fractions of a division.

Three capillary tubes were employed in working with the apparatus:

- A with a bore of about one and a half mm.
- B " " " " " five-tenths mm.
- C " " " " " one-tenth mm.

From the nature of the method it is not at all necessary to know the exact dimensions of the tubes; all that is required is

that the bore be approximately circular and the edges sharp. To prepare the capillary tubes, a stock of tubing is examined and tubes of the desired dimensions selected. Pieces are broken off from these tubes until it is found that the ends present plane surfaces perpendicular to the axis of the tube. If the clamps happen to be too large for the tubes, a filling of sheet lead may be employed.

The liquid serving as bath and contained in the beaker may be water or glycerin; it is heated by means of a Bunsen burner and kept in motion by means of a stirrer (not shown, however, in the figure). Besides this kind of a bath much use was made of a vapor jacket for keeping the temperature uniform during a determination. The test tube *O* was fitted into a considerably larger tube by means of a cork, through a second perforation of which passed a long glass tube acting as a condenser. On boiling liquids or mixtures of liquids in the larger tube, their vapors rise and heat the inner tube with its contents to a desired constant temperature for any length of time.

III.—METHOD OF MAKING A DETERMINATION.

The first thing to do in using the apparatus is to get the lower extremities of the two capillary tubes at the same level. This may be accomplished in the following simple manner. A spirit-level is placed upon a piece of plate glass, which in turn is set upon the support *H* at the required height and levelled. The pointers of the side scale, as well as that of the screw head, are set at zero, the tubes allowed to rest freely upon the plate glass, and then clamped into position. While this way of fixing the tubes answers well enough for the initial adjustment of the apparatus, it is not sufficiently accurate to insure their being replaced in the same position, if, from any cause, they become displaced. Indeed, it is not at all certain that the tubes are at the same level to within 0.1 mm., when adjusted in the above manner; yet this degree of accuracy is entirely sufficient for the first adjustment, and later it will be shown how they can be gotten into the same position to within 0.01 mm.

The test tube has a mark scratched on its side, which indicates the volume of liquid that is to be taken for a determination

of its capillary constant, it having been found that differences in the distance between the surface of the liquid and the orifices of the tubes have a little influence upon the readings of the instrument.¹ The volume of the liquid may be as small as a couple of cubic centimeters, if a small test tube be used; generally, however, it is advisable to employ from five to ten cc. The test tube is filled with the liquid under examination to this mark and the tube suspended in the bath. The beaker is placed upon a piece of asbestos board or wire gauze set upon the retort ring, which is raised until the capillary tubes are close to the bottom of the test tube. A thermometer is introduced into the liquid, and the bath liquid stirred so as to insure uniformity of temperature.² The rapidity with which the liquid undergoing investigation takes on the temperature of the bath may be hastened by blowing bubbles up through it by compression of the air in the rubber ball *K*.

When the temperature of the liquid is the same as that of the bath, the movable tube (preferably the one with the smaller bore), is raised by turning the screw. This may be done rapidly while bubbles are being forced out of the larger tubes every second or so. At a certain point bubbles may cease to issue from the larger tube and commence to come from the smaller one, an indication that the correct adjustment has been passed. The screw is now turned very cautiously in the opposite direction until bubbles issue at about the same time from both of the tubes. The final adjustment is generally best made as follows :

The air is compressed *very slowly* until it has arrived just at the orifices of both tubes. The pressure is then not increased further, and, as a rule, it will be observed that, if the adjustment is perfect, bubbles will issue of their own accord from both the tubes in a second or so ; sometimes one of the bubbles lags a little behind the other. The success of the operation depends upon the *steady* and *gradual* compression of the air ; if this be subjected to abrupt or irregular changes of pressure, not inconsiderable errors may be committed. It is advisable to make at

¹ This influence is, however, but slight. Readings with ether were found to differ by only $\frac{1}{100}$ of an inch, when the difference between the free surface of the liquid and the lower extremities of the capillary tubes differed by more than four inches.

² The mode of procedure is essentially the same when a vapor jacket is employed.

least two readings, one when the narrower tube is being lowered, the other when it is being raised; indeed, the readings can be made so rapidly that it is a good plan to take a half dozen or so, the tubes being moved alternately up and down.

IV.—DISCUSSION OF SOURCES OF ERROR IN APPARATUS.

In the determination of the capillary constants by means of the apparatus described in the preceding sections, measurements of three kinds have to be made, *viz.*, measurements of specific gravity, of temperature, and of the distance between the lower extremities of the capillary tubes. We pass to the discussion of the errors inherent to each.

I. The determination of the surface tensions by any of the direct methods, such as measuring the height to which liquids rise in capillary tubes, etc., cannot be said on an average to be accurate to more than one part in two thousand, and only in exceptional cases to one part in ten thousand. On the other hand the accuracy of a specific gravity determination can easily attain one part in ten thousand, and in many cases to even one part in a hundred thousand. In the formula to be communicated in the following section, it will be seen that the influence of the specific gravity upon the value of the capillary constant is not very great, so that a determination of the specific gravity to one part in two thousand is perhaps sufficiently accurate for our purposes, although it is of course better to be sure of the fourth decimal place. We may conclude then that the accuracy of a determination of the specific gravity of a liquid where surface tension is to be ascertained, may be counted perfect, if it be made to within one part in ten thousand.

II. For temperatures between 0° and 50° it is an easy matter to keep the temperature of even such a simple bath as the one given in Fig. 1 constant to within 0.05° long enough to adjust the apparatus and make several readings. By the use of the larger baths, or, better still, of vapor jackets, the temperature can be kept sufficiently uniform for the investigation at different temperatures of most liquids. As a variation of temperature amounting to 0.1° changes but little the readings of the apparatus, it may be allowed that the error committed in estimating the temperature is, for the purpose of this investigation, negligible.

III. The possible error that may be committed in the readings of the apparatus can best be judged by considering the readings themselves. A number of series of readings for different liquids at various temperatures are accordingly given just as they were taken directly from the apparatus.

The readings are not to be taken as material for the calculation of the surface tensions of the liquids, as in some cases they do not represent the true distances between the lower extremities of the capillary tubes, the positions of these having been altered purposely several times. The unit of a reading is a fortieth of an inch.

Nitroethane ¹ at 16.95°. Tubes A and B.	Nitroethane ¹ at 46.6°. Tubes A and B.
23.27	21.23
23.26	21.26
23.28	21.21
Nitromethane ¹ at 24.5°. Tubes A and B.	Nitromethane ¹ at 41.5°. Tubes A and B.
24.28	22.86
24.26	22.87
24.23	22.80
24.25	22.81
24.29	22.85
24.26	
24.26	
Benzene at 20.0°. Tubes A and B.	Benzene at 20.5°. Tubes B and C.
22.86	30.55
22.88	30.54
22.85	30.59
22.86	30.56
22.87	30.55
Toluene at 25.0°. Tubes A and B.	Toluene at 46.6°. Tubes A and B.
24.42	22.65
24.44	22.63
24.41	22.62
24.40	22.63
24.43	22.64
Another series made ten days later.	22.64
24.43	22.66
24.45	22.64
24.42	
24.43	
24.45	

¹ Made by Mr. L. W. Jones, of the University of Chicago.

Methyl nitrate at 0.2°. Tubes A and B.	Carbon bisulphide at 19.5°. Tubes A and B.
18.29	19.35
18.28	19.32
18.25	19.30
18.26	19.33
18.28	19.34
Ethyl ether at 0.1°. Tubes A and B.	Ethyl ether at 25.0°. Tubes A and B.
17.90	13.55
17.92	13.53
17.92	13.52
17.95	13.54
17.93	Another series made over a month later.
	13.54
	13.55
	13.53
Toluene at 78.4°. Tubes B and C.	Monochlorbenzene at 77.8°. Tubes B and C
24.73	23.34
24.77	23.38
24.75	23.32
24.71	23.35
24.74	23.34
Ethyl iodide at 25.0°. Tubes A and B.	Ethyl alcohol at 51.0°. Tubes A and B.
8.89	18.65
8.87	18.62
8.88	18.64
8.88	18.61
8.87	18.63
Another series made twenty days later.	
8.87	
8.86	
8.88	
Water at 40.0°. Tubes A and B.	Water at 20.0°. Tubes A and B.
77.10	76.09
77.13	76.13
77.14	76.10
77.09	76.16
77.11	76.23
77.16	76.14
77.13	76.16
77.12	76.18
	76.15
	Another series made a fortnight later.
	76.12
	76.18
	76.21
	76.19
	76.14
	76.18

These series of numbers have been taken from my note books almost at random, and are but a small portion of the number of readings I have made. They show that for most liquids differences in the readings amounting to more than $\frac{5}{4000}$ of an inch seldom occur, and when a series of readings are made and their average taken, the error almost vanishes. Only in case of water were greater differences of readings observed; yet, since water has such a large capillary constant, the error committed is very slight. It was observed that the nearer the extremities of the capillary tubes were, and, consequently, the smaller the numerical value of the reading, the more concordant were the readings.

While the three sources of error just discussed seem to be almost negligible, there is another, inherent, not in the apparatus, but in the method, which stands seriously in the way of obtaining reliable absolute determinations of the surface tensions of liquids. This source of error lies in the determination of the "apparatus constant," which may vary from one liquid to another. A more detailed discussion of it will be given in the next section, after the way in which the "apparatus constant" is determined is described.

V.—CALCULATION OF RESULTS.

Having now shown the degree of accuracy attainable in the readings of the apparatus under discussion, I will pass to the consideration of the manner in which the results obtained by this indirect method may be converted into those arrived at by direct methods. As stated above, two things besides the temperature are measured in this method: (1) the specific gravity of the liquids taken, and (2) the vertical distance between the lower ends of the two capillary tubes when air under the same pressure issues in synchronous bubbles from their orifices. It is not difficult to determine the specific gravity to within $\frac{1}{5000}$, although an accuracy of $\frac{1}{10000}$ is quite sufficient. The distance between the ends of the two tubes can be measured to about a hundredth of a millimeter, except in the case of water, where the degree of accuracy of measurement is only within a tenths of the same unit of length. It is now our task to pass from the data obtained from measurements of these quantities to the capillary constants measured in dynes per centimeter.

Inasmuch as our knowledge of the form of the bubbles just on the point of issuing from the orifices of the capillary tubes is not at all precise, there appears to be no immediate way of finding a relation on theoretical grounds between the data furnished by this indirect method and those given by direct methods. Jäger¹ obtained the relationship employed by him in the following manner: "Wie sich unsere Annahme für die Formulirung des Einflusses, welchen die Röhrenweite auf den bewussten capillaren Druck hat, als richtig erwies, so zeigt sich, wie wir später sehen werden, dass es vollständig genügt, wenn wir

$$\alpha F(s) = \alpha(1 + \beta s)^2$$

setzen, wobei β eine Constante bedeutet, die sich ebenfalls leicht ermitteln lässt, wenn zwei Flüssigkeiten, deren α und s bekannt sind, zu Gebote stehen. Verwenden wir nämlich zu unseren Messungen stets dieselben beiden Capillarröhren, so wird für die eine Flüssigkeit die Gleichung (1)

$$\alpha(1 + \beta s) \varphi(r, r') = hs,$$

für die zweite,

$$\alpha'(1 + \beta s') \varphi(r, r') = h's',$$

somit

$$\frac{\alpha(1 + \beta s)}{\alpha'(1 + \beta s')} = \frac{hs}{h's'}.$$

Aus dieser Gleichung kann der Werth von β ermittelt werden da alle übrigen in ihr vorkommenden Grössen bekannt sind."

In order to obtain the value of β , he made use of Brauner's³ and Wolf's⁴ directly determined data for water and ethyl ether. By transforming the immediately preceding equation into

$$\alpha = \frac{\alpha'hs(1 + \beta s')}{h's'(1 + \beta s)},$$

he obtained therefrom on putting

$$\frac{\alpha'(1 + \beta s')}{h's'} = c,$$

$$\alpha = c \frac{hs}{1 + \beta s};$$

¹ *Loc. cit.*

² a = capillary constant; s = specific gravity.

³ *Ann. der Phys. Pogg.*, 70, 515.

⁴ *Ann. der Phys. Pogg.*, 70, 575.

and substituting for specific gravity = s , the specific volume = $v = \frac{1}{s}$, he finally obtained

$$\alpha = c \frac{h}{v + \beta},$$

an equation used throughout his work in transforming his results.

It is hardly necessary to mention that the degree of accuracy that can be attributed to an indirect method of measuring a physical constant of Nature depends upon the accuracy of the results obtained by direct methods; hence the importance of choosing the most exact directly determined data for the calibration of an indirect method. Ramsay and Shields¹ have elaborated the method of measuring the heights to which liquids rise in capillary tubes, and have carried out series of determinations of the capillary constants of various liquids in contact only with their own vapor and glass, which are justly regarded as of the greatest trustworthiness, and may be confidently taken as standards.

If Jägers equation,

$$\frac{\alpha(1 + \beta s)}{\alpha'(1 + \beta s')} = \frac{hs}{h's'}$$

be correct, it ought to be possible to obtain the same value of β , when the data for α and α' , s and s' , and h and h' are taken for any pair of liquids. On carrying out the calculations, however, I found, on employing the data given by Ramsay and Shields,² for the specific gravities and capillary constants, and the readings of my apparatus for the differences of level between the extremities of the two capillary tubes, that the values of β varied considerably for different pairs of liquids. Furthermore, it was found that, if β and c be calculated for any two liquids, and then from the equation

$$\alpha = c \frac{hs}{1 + \beta s},$$

the value of α be deduced for a third liquid, differences between the values thus obtained and those given by Ramsay and Shields amounting to five or ten per cent. were obtained in some cases,

¹ *Ztschr. phys. Chem.*, 12, 433, 1893.

² *Loc. cit.*

although once in a while a pretty good correspondence was observed. Jäger's equation appears to be merely approximate and does not stand a rigid scrutiny. Jäger himself seems to find the justification of his formula in its yielding results corroborative of certain theoretical views he advances, and in the agreement between his observed values and those calculated for the same temperatures, by means of temperature coefficients; but as the temperature coefficients were derived from his own data, which differ but rarely more than five or ten per cent. from those communicated by Ramsay and Shields,¹ and he does not attain to a much closer correspondence than that between his observed and calculated values, the correctness of the formula does not seem to be any the better established.

It accordingly became peremptory to devise another formula which should be in better accordance with Ramsay and Shields'² measurements. But here a difficulty arose. Ramsay and Shields determined the capillary constants of liquids that had been freed from air; the liquids were in contact only with their own vapor and glass. There is no doubt but that the surface tensions of liquids can be measured accurately by means of their rise in capillary tubes only when no air is present; R. Schiff³ had already made this observation before Ramsay and Shields. Just what influence the presence of air has upon the capillarity of liquids we do not know; the greater or less volatility of a liquid makes the degree of dilution of air in contact with its surface correspondingly greater or less. In the apparatus described in this article, the liquid under examination is saturated with air, and the pressure of the air varies with the specific gravity of the liquid. The difficulty at issue lies in the question as to whether the indirect determinations made with liquids in contact with air are comparable to more than a gross approximation with those obtained by the direct method as employed by Ramsay and Shields. This difficulty seemed at first to be unsurmountable, but, finally, a simple relation was discovered which shows an excellent correspondence between Ramsay and Shields' data and mine.

¹ *Loc. cit.*

² *Loc. cit.*

³ *Ann. Chem. (Liebig)*, 233, 47.

The relation in question is

$$\gamma = chs + s^2 \dots \dots \dots (A)$$

wherein γ represents the capillary constant in dynes per centimeter, c the "apparatus constant," h the distance between the ends of the tubes, and s the specific gravity. The value of the constant was obtained in the following way. The data for γ and s were taken from Ramsay and Shields' and Ramsay and Aston's papers, and those for h from my own measurements. These were set in equation (A) and the value of c calculated therefrom. The greatest pains were taken in the purification of the liquids examined, so that they had no doubt the same properties as those used by the investigators just named. The data and results of the calculations are given in Table I. for the tubes *A* and *B*, and in Table II. for tubes *B* and *C*.

TABLE I.

Values of "Apparatus Constant" for Tubes A and B.

Name of liquids.	<i>T.</i>	<i>s.</i>	γ .	<i>h.</i>	<i>c.</i>
Water	20.0°	0.9984	70.72	55.60	1.248
"	30.0°	0.9958	69.10	54.85	1.247
"	40.0°	0.9923	67.50	53.90	1.245
Methyl alcohol...	20.0°	0.7905	23.03	23.16	1.227
Ethyl " ...	20.0°	0.7900	22.03	21.97	1.236
Acetone ...	16.8°	0.7798	23.35	22.95	1.238
"	46.4°	0.7656	19.68	20.00	1.250
Ethyl ether.....	20.0°	0.7143	16.49	17.91	1.245
" "	30.0°	0.7000	15.27	16.87	1.252
Ethyl iodide.....	19.1°	1.937	30.00	10.88	1.248
Carbon bisulphide	9.7°	1.2773	32.73	19.90	1.224
Benzene.....	11.2°	0.8871	29.21	25.86	1.239
"	46.0°	0.8500	24.71	22.75	1.241
Chlorbenzene.....	9.5°	1.1182	33.71	23.46	1.238
"	45.6°	1.0795	29.30	21.25	1.227
Toluene	15.2°	0.8682	28.18	25.21	1.253
"	46.6°	0.8380	24.60	22.65	1.259

Average = 1.243

TABLE II.

Values of "Apparatus Constant" for Tubes B and C.

Names of liquids.	<i>T.</i>	<i>s.</i>	γ .	<i>h.</i>	<i>c.</i>
Acetone	16.8°	0.7998	23.25	27.72	1.023
"	46.4°	0.7656	19.68	24.22	1.029
Chlorbenzene.....	45.6°	1.0795	29.30	25.71	1.014
"	77.8°	1.0444	24.65	23.38	1.011
Ethyl ether	20.0°	0.7143	16.49	22.08	1.036
Benzene	11.2°	0.8871	29.21	31.44	1.019
"	46.0°	0.8500	24.71	27.86	1.013
Toluene	15.2°	0.8682	28.18	30.60	1.032
"	46.6°	0.8380	24.60	27.75	1.028
"	78.4°	0.8080	20.93	24.75	1.014

Average = 1.022

A glance at the tables shows that the "constants" are indeed quite constant. In Table I., the average of the numbers in the last column is 1.243; the greatest variation on one side is 0.019 for carbon bisulphide at 9.7°, and on the other side, 0.016 for toluene at 46.6°. Generally, the differences from one liquid to another are not larger than they are for the same liquid from one temperature to another. Likewise, in Table II., the average value of the constant is 1.022, with differences of 0.014 for ether at 20.0° on the one hand, and 0.011 for chlorbenzene on the other.

Introducing $c = 1.243$ from Table I. and $c = 1.022$ from Table II. into equation (A), and treating α as the unknown quantity, I calculated the capillary constants to be those given in Tables III. and IV., respectively, beside which are placed the corresponding data given by Ramsay and Shields¹ and Ramsay and Ashton.

TABLE III.

Comparison of Capillary Constants for Tubes A and B. $c = 1.234$.

Names of liquids.	Temp.	γ .	γ .	$\gamma - \gamma$.
		$\gamma = chs. + s^2$.	Ramsay & Shields.	
Water.....	30.0°	68.82	69.10	-0.28
"	40.0°	67.42	67.50	-0.08
Methyl alcohol.....	20.0°	23.39	23.03	+0.36
Ethyl alcohol	20.0°	22.17	22.03	+0.14

¹ *Loc. cit.*

Names of liquids.	Temp.	γ .	γ .	$\gamma - \gamma$.
		$\gamma = chs. + s^2$.	Ramsay & Shields.	
Acetone.....	16.8°	23.34	23.35	-0.01
“	46.4°	19.59	19.68	-0.09
Ethyl ether.....	20.0°	16.42	16.49	-0.07
“	30.0°	15.18	15.27	-0.09
Ethyl iodide	19.1°	29.90	30.00	-0.10
Carbon bisulphide... ..	9.7°	32.22	32.73	-0.49
Benzene.....	11.2°	29.31	29.21	+0.10
“	46.0°	24.75	24.21	+0.04
Chlorbenzene	9.5°	33.86	33.71	+0.15
“	45.6°	29.68	29.30	+0.38
Toluene.....	15.2°	27.96	28.18	-0.22
“	46.6°	24.25	24.60	-0.35

TABLE IV.

Comparison of Capillary Constants for Tubes B and C. $c = 1.022$.

Names of liquids.	T .	γ .	γ' .	$\gamma - \gamma'$.
		$\gamma = chs + s^2$	Ramsay & Shields.	
Acetone.....	16.8°	23.32	23.35	-0.03
“	46.4°	19.64	19.68	-0.04
Chlorbenzene	45.6°	29.56	29.30	+0.26
“	77.8°	26.01	25.66	+0.35
Ethyl ether.....	20.0°	16.42	16.49	-0.07
Benzene.....	11.2°	29.28	29.21	+0.07
“	46.0°	24.88	24.71	+0.11
Toluene.....	15.2°	27.93	28.18	-0.25
“	46.6°	24.46	24.60	-0.14
“	78.4°	21.09	20.93	+0.16

It is at once apparent that only in a few instances the differences between Ramsay and Shields' results and mine amount to more than a few tenths of a per cent., and in some cases the correspondence is as good as perfect. Furthermore, the differences that are found seem to be very nearly the same when either pair of tubes is employed; this indicates that the differences are due rather to the possible differing degrees of purity in the liquids employed by each of us than to a fault in the apparatus itself. However that may be, the data show that it is possible to obtain with the apparatus in question results, which by means of the formula (A), are comparable with those obtained by Ramsay and Shields or Aston. One cannot withstand the temptation to quote Jäger's words:¹ “.....unsere

¹ *Loc. cit.*

methode is vollständig geeignet, richtige Resultate zuergeben. Fasst man noch die leichte, sichere und wenig zeit beanspruchende Handhabung, welche unser Apparat erfordert, ins Auge, so wird man wohl leicht zur Ueberzeugung gelangen, dass unter den gegenwärtigen Methoden für den praktischen Gebrauch kaum eine bessere zu finden sein dürfte." As to what pertains to the experimental handling of the apparatus, my experience with it enables me to subscribe to the above. But a restriction has to be made in regard to the conversion of the indirect results into direct ones. Jäger's formula has been shown above to be only approximately correct, and the one I propose has but an empirical basis. Although it has been found to stand the test of comparison with ten liquids of different properties, when two sets of tubes were employed, it is not allowable to claim that it will furnish reliable results for any liquid whatsoever. In other words, the instrument cannot be depended upon to give absolute data, since the "apparatus constant" may differ from liquid to liquid. Still it is not at all probable that the variations in the value of the "apparatus constant" will be very great in any case, and, as a variation of as much as ten per cent. has but a relatively small influence upon the surface tension, the method may be considered to give results accurate enough for the calculation of molecular masses, since Ramsay and Shields do not claim for their method an accuracy of more than six or seven per cent.

VI. MODE OF PROCEDURE IN DETERMINING THE MOLECULAR MASSES OF LIQUIDS.

In determining the molecular mass of a liquid it is well to measure its surface-tension at three different temperatures, and for this purpose vapor jackets will be found convenient. Temperatures easy to get are (1) that of the atmosphere 10° to 25° ; (2) that of boiling carbon bisulphide, about 46° ; (3) that of boiling alcohol, about 78° . Of course, other liquids than these may be used, all that is required is that the temperatures obtained are 20° - 30° apart.

The liquid is placed in the test tube *O*, and carbon bisulphide is poured into the jacketing tube. The capillary tubes are im-

mersed in the liquid, and, after the temperature has become uniform, several readings are made, their average being taken. The carbon bisulphide is now boiled and when the temperature has become constant a second series of readings is made. The flame is removed and, after the liquid has cooled down a little, alcohol is substituted for the carbon bisulphide. The alcohol is now boiled and a third series of readings taken when the temperature becomes stationary. All of these operations can be easily made in less than an hour.

It is possible to determine the specific gravity of the liquid at the different temperatures during the above operation, as the capillary apparatus requires but little continuous attention, most of the time taken up in a determination being needed in warming the liquid to a constant temperature. Any of the ordinary methods of density determinations may be employed which can give it to the third or fourth decimal place.

The necessary calculations may be illustrated by a couple of examples, one of a normal liquid, the other of an associated liquid. For the theoretical grounding and fuller explanation of the method, reference must be had to Ramsay and Shields' paper.¹

BENZENE.

$$\gamma = chs + s^2 = (1.243 \times 25.86 \times 0.8871) + 0.80 = 29.31 \text{ dynes at } 11.2^\circ.$$

$$= (1.243 \times 22.75 \times 0.85) + 0.72 = 24.75 \text{ dynes at } 46.0^\circ.$$

$$\gamma(Mv)^{\frac{2}{3}} = (78/0.8871)^{\frac{2}{3}} \times 29.31 = 575.1 \text{ ergs at } 11.2^\circ.$$

$$(78/0.8500)^{\frac{2}{3}} \times 24.75 = 501.8 \text{ " " } 46.0^\circ.$$

$$\frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = \frac{575.1 - 501.8}{46.0 - 11.2} = \frac{73.3}{34.8} = 2.106.$$

The value assigned to the constant by Ramsay and Shields is 2.121, from which the constant just calculated differs by only 0.015; hence benzene is a normal liquid.

¹ *Loc. cit.*

ACETONE.

$$\gamma = chs + s^2 = (1.022 \times 27.75 \times 0.7998) + 0.64 = 23.32 \text{ dynes at } 16.8^\circ.$$

$$(1.022 \times 24.22 \times 0.7656) + 0.59 = 19.55 \text{ dynes at } 46.4^\circ.$$

$$\gamma(Mv)^{\frac{2}{3}} = (58/0.7998)^{\frac{2}{3}} \times 23.32 = 406.1 \text{ ergs at } 16.8^\circ.$$

$$(58/0.7656)^{\frac{2}{3}} \times 19.55 = 351.6 \text{ " " } 46.4^\circ.$$

$$\frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = \frac{406.1 - 351.6}{46.4 - 16.8} = \frac{44.5}{29.6} = 1.840.$$

The smallness of this constant indicates association in acetone. To determine the amount of association, we multiply the molecular mass M , by a factor x , which represents the average number of simple molecules that have coalesced to form a complex molecule. The calculation is as follows :

$$\left(\frac{2.121}{1.840}\right)^{\frac{3}{2}} = 1.25 \text{ between } 16.8^\circ \text{ and } 46.4^\circ.$$

the average molecular mass throughout this range of temperature is accordingly $1.25 \times 58 = 73$.

The apparatus described above was made by Walmsly, Fuller & Co., of Chicago, and has proven satisfactory in every detail. The makers inform me that they are ready to furnish the apparatus provided with a micrometer screw divided according to the metric as well as the English system.

ON THE REACTION BETWEEN CARBON TETRACHLORIDE AND THE OXIDES OF NIOBIUM AND TANTALUM.

BY M. DELAFONTAINE AND C. E. LINEBARGER.

Received April 20, 1896.

EUG. DEMARCAÿ¹ states that if the vapor of carbon tetrachloride be passed over the oxide of niobium or of tantalum heated below redness, the metallic oxides are converted into chlorides. "Dans le cas de l'acide niobique, la réaction se produit déjà, bien qu'avec lenteur à la température de la naphthalene bouillante (280°) et avec une extrême rapidité à 440°."²

Now the chlorides of these rare elements enter into reaction

¹ *Compt. Rend.*, 104, III, 1887.

² *Loc. cit.*