5. It is inferred that those explanations of the excess of C_v for metals over $3R$ which assume departure by the atoms from simple harmonic oscillation, are probably not valid at all temperatures. This inference is based upon the apparent failure of C_v for typical non-metals to exceed $3R$, and upon the unexplained lack of generality in certain anticipated relations between the excess heat capacity and other properties of the metals.

6. A correspondence between electropositive character and the "excess" heat capacity is shown to exist for many of the metals. This is taken as support for the hypotheses that the excess heat capacities are due to the presence in the metals of loosely bound electrons, and that at moderately high temperatures this excess represents approximately the rate of gain of thermal energy by the electrons. Variation among the metals of the number of electrons involved in the effect is assumed to be responsible for some of the apparent exceptions to the correspondence mentioned above.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE DETERMINATION OF SURFACE TENSION WITH VERY SMALL VOLUMES OF LIQUID, AND THE SURFACE TENSIONS OF OCTANES AND XYLENES AT SEVERAL TEMPERATURES

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Occasionally it is necessary to determine the surface tension of a liquid of which only a very small volume is available. This determination may be most conveniently carried out in a small U-tube of which one arm is a fine capillary, and the other a somewhat wider tube, not much over 2 mm. in internal diameter.[1] The method requires special precautions, and has special advantages, which are discussed below.

In 1910 the capillary constants of octanes and xylenes were thus measured by the late Clarence L. Speyers under the direction of one of us. The results have not heretofore been published, because of question as to the precise magnitude of the correction to be applied to the height of liquid in the wider of the tubes. Very narrow tubes are adequately treated by

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[1] This method was perhaps first used by Frankenheim [*Pogg. Ann.*, **72**, 177 (1847)]. Later it was also used by Schiff [*Ann.*, **223**, 47 (1884)], who perceived some of its advantages. Neither of these experimenters applied satisfactory corrections to the results. The description in Ostwald-Luther's "Physiko-Chemische Messungen," **1910**, vol. 3, pp. 235–237 is also incomplete. Very recently a modification of the method has been used by Y. L. Shekhtman, *Bull. acad. sci. russie* [VI] **13**, 657–662 (1919); see also *C. A.*, **17**, 1909 (1923).

the equation of Poisson (which has been extended somewhat by the late Lord Rayleigh[2]) or that of Hagen and Desains; and very wide tubes, which cause but slight capillary rise, are treated adequately by the equations of Laplace and Lord Rayleigh.[2] The problem presented by the intervening region has not as yet been solved mathematically, and even the extent of the range over which uncertainty may exist was not known until recently.

In 1921 an investigation was published[3] which, while discussing sundry possible errors in the method of capillary rise, dealt especially with the performance of tubes which were neither very wide nor very narrow. This investigation showed that where the quantity r/a (when r is the radius of the tube and a the square root of the capillary constant) is less than 0.5, the equations of Hagen and Desains and of Poisson[4] are sufficiently accurate for the purpose. It showed further that when r/a is greater than 3.5, the equation of Lord Rayleigh for wide tubes is accurate, but that between these limits (which correspond with most organic liquids to tubes about 2.5 and 18mm. diameter) no mathematical equation applies. An empirical method dependent upon the relation of h/a to r/a (when h is the observed capillary rise) was suggested, and the advantage of the earlier use of two narrow tubes of different diameter was emphasized.[5]

This method was adopted primarily because it requires very little liquid. This is not its only advantage, however. In addition, it avoids entirely the difficulty of the precise measurement of a very large meniscus, necessary if the attempt is made to refer the capillary directly to a plane surface. Again, it makes possible the correction of both meniscuses by means of the equations of Poisson (especially as corrected by Rayleigh) or of Hagen and Desains, because even the wider of the two tubes need not be so wide as to overstep the limit of accuracy of these equations. Taking all these circumstances together, we are inclined to think that for practical purposes the method as described in the following pages is one of the most convenient and satisfactory ways to determine surface tension by means of the capillary rise, even when much liquid is available.

The Apparatus and Method

The simplified method, which has proved highly convenient in the present work, is as follows.

[2] The Rt. Hon. John William Strutt, 3rd Baron Rayleigh, *Proc. Roy. Soc.*, **92A**, 184 (1915).

[3] Richards and Carver, THIS JOURNAL, **43**, 827 (1921).

[4] Lord Rayleigh has somewhat improved the equation of Poisson (see Ref. 2), and has extended its range of accuracy as far as $r/a = 1$ or $= 1.5$.

[5] A somewhat similar empirical method has since been published by Sugden [*J. Chem. Soc.*, **119**, 1483 (1921)] who gives tables recording the relation of r/b to r/a, (b designating the radius of curvature of a meniscus, which is related to the other quantities concerned).

Capillary tubes (found later to have diameters, respectively, of 2.174 mm. and 0.3394 mm.) were joined to make a capillary U-tube. These tubes had been very carefully selected with the help of measurements of short mercury columns at different positions. They had nearly circular cross sections, and after having been selected were carefully calibrated by the measurement of mercury columns, which showed them to be very nearly equable throughout their length. The fine capillary was etched with a number of lines which served to identify the different parts of the tube, and the distances between these lines were measured by means of a cathetometer.

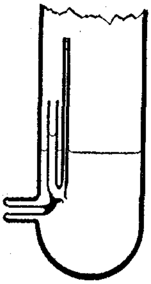

Fig. 1.—Apparatus for measuring the radii of the capillaries. From the capillary rise of water in the two tubes within this apparatus the radii of the tubes were computed. Subsequently the capillary U-tube was removed to a much smaller enclosing tube (1/3 actual size).

The capillary U-tube was provided with a small opening below and was fused in a vertical position to the inside of a suitable glass cylinder (45 mm. in internal diameter) as illustrated in Fig. 1. The cylinder had been selected with care as regards the distribution of the glass in its walls, to avoid optical difficulties. The U-tube was so near to one of the walls that the free surface in the large vessel was in no direction less than 35 mm. in diameter.

After having been scrupulously cleaned the apparatus was filled with water to the height necessary to raise water in the finer tube into the best part of that tube. The heights of liquid in the two capillaries were measured from many positions, using very pure water which had been freed from air by repeated freezing in a vacuum. The temperature was constant (about 18.4°) and the pressure 28 mm. of mercury, air having been almost removed. In this way the following series of measurements was obtained.

Evidently the measurement of the *difference* in height between the two capillary columns was more accurate than that of either of the heights individually.

The averages thus given are, of course, uncorrected for the heights of the meniscuses. They give at once an approximate means of determining the radii of the tubes and therefore a means of determining, according to the equation of Poisson, the accurate values of the corrected capillary rises, and from these the exact values of the radii. The calculation follows. Since the meniscus in the small capillary rose 87.91 mm. above the plane surface, the value for its radius must be about 14.91/87.91 = 0.170 mm., whereas (the other capillary rise being 13.39 mm.) the radius of the larger tube must be about 14.91/13.39 = 1.11 mm. (because the capillary rise of water in a tube of 1.0000 mm. radius at 19° is 14.91 mm.[6]). The

TABLE I

CAPILLARY RISE IN TWO TUBES ABOVE A PLANE SURFACE

Trial	Height in fine capillary above plane surface Mm.	Height in wide capillary above plane surface Mm.	Difference in heights in capillaries Mm.
1	87.93	13.41	74.52
2	87.90	13.40	74.50
3	87.89	13.37	74.52
	Av. 87.906	13.393	74.513

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[6] The Capillary Constant (a^2) of water at 20° in the presence of air was found by us to be 14.880 (Ref. 3, p. 845) and by Harkins and Brown [THIS JOURNAL, **41**, 507 (1919)]

approximate radii of the respective tubes are sufficient for the calculation of the small corrections of the meniscuses. Using the equation of Poisson ($h_1 = h + r/3 - 0.1288\ r^2/h$) the correct values thus found for the capillary rise h_1 are, respectively, 87.97 and 13.75, which give the radii of the tubes 0.1697 and 1.087, respectively. A repetition of this calculation with the new, more accurate radii gives heights of 87.97 and 13.74 and radii of 0.1697 and 1.088, respectively—figures which do not change on further successive approximations.

In order to test the apparatus, observations were made also with alcohol and benzene. The results for the ratio of the radii were sufficiently concordant to show that the apparatus functioned in a very satisfactory manner.

The approximate diameters of the two capillaries having thus been determined, the subsequent method of calculation is as follows.

Let h_1 be the corrected rise in the smaller capillary, and h_2 the corrected rise in the larger capillary; $H = h_1 - h_2$, and $G = h_2/h_1 = r_1/r_2$.

Then $h_1 - h_1G = H; h_1 = H/(1 - G)$.

Since $\gamma = \frac{h_1 r_1 g d}{2}$; therefore $\gamma = \frac{H r_1\, g d}{2(1-G)} = KHd$, where d is the density of liquid minus that of air, g the gravitational constant (980.4, at Cambridge, Massachusetts) and K is a constant for any given apparatus at any given temperature.

In this equation, K (which is equal to $\frac{r_1\, g}{2(1-G)}$) may be determined empirically (if the diameters of the capillaries are known accurately enough to determine the corrections to be applied respectively to the two meniscuses in order to obtain H) from the observed differences in height. Since the corrections are small, the approximate mode of calculating these diameters, as given above, amply suffices.

If h and h' are the observed heights of the two capillaries above a plane surface, in the tubes having respective radii of r_1 and r_2, according to the equation of Poisson, $h_1 = h + r_1/3 - 0.1288\ r^2/h$, and $h_2 = h' + r_2/3 - 0.1288\ r_2^2/h$. Therefore, $H = h_1 - h_2 = (h - h') + \frac{r_1 - r_2}{3} - 0.1288\text{-}\left(\frac{r_1^2}{h} - \frac{r_2^2}{h'}\right)$.

Now $(h - h')$ is the observed difference in height of the two capillaries, and $(r_1 - r_2)/3$ is a constant with any given apparatus (in this case —0.306). Hence the differences in the corrections to the observed heights

to be 14.894. Giving the latter somewhat the greater weight, we may assume that 14.89 is very near the truth. When air is removed (as in the present case) the value was formerly found by us to be 0.02 less, giving 14.87. Since in this neighborhood the temperature coefficient of the capillary rise is about —0.025, the capillary constant of water in the absence of air at 18.4° is not far from 14.91. Domke found it to be 14.90 at 18.2° (corrected to vacuum conditions). The effect of air upon the capillary constant of water is chiefly due to its density; its effect on the surface tension of water is very small. (See Ref. 3, p. 846.)

with different liquids are dependent entirely on the last term of the equation, which is very small (in the present case varying between +0.011 with water at low temperature to about 0.028 with the organic substances concerned).[7] In the present series of experiments, therefore, we have for water at 18.4°: $H = h - h' - 0.295$ mm.; and for the organic liquids: $H = h - h' - 0.28$ mm., approximately—(varying somewhat with the magnitude of h' which is easily found with sufficient approximation from the other data).

Evidently the effect of an error in the diameter of the capillaries is very small, if the equation is used in the form $\gamma = KHd$, and K is determined empirically from a known substance, as Ostwald and Luther have pointed out.[1] With the present apparatus, using water as the known substance, an error of 1% in r_2 would cause an error of less than 0.005% in the final result. If the standard substance has a capillary constant not far from that of the substance to be determined, the error becomes practically zero. The use of such a standard substance is doubly desirable if any doubt exists as to the uniformity of the capillary tubes, because such usage causes the meniscuses of the two substances to fall in the same places, and thus eliminates possible error from this source.

The effect of changing temperature on the radius of the capillary, and therefore upon K, is small, but for the sake of completeness it may be considered. G, of course, is not affected by change of temperature if the two capillaries are made of the same kind of glass. Each radius, and therefore also K, had the linear temperature coefficient of soft glass, about 0.0000094.

The constant K in the empirical equation $\gamma = KHd$ must now be computed. This computation might be based upon the determinations of water already given, but there are two reasons for another procedure. In the first place the temperature reading during these experiments, although sufficiently accurate for the approximate evaluation of the radii, was not very precisely known. In the next place the apparatus was somewhat differently arranged (in a wider and less carefully studied enclosing tube) in the preceding experiments than in the following ones. For these reasons it is better to determine K with the arrangement actually used in the surface-tension measurements, that is to say, by means of one of the series of measurements recorded in Table II. Of these series, that of water is the best for the purpose, because the value of its surface tension is best known. Unfortunately, however, even of this substance the surface tension is known accurately only at 20°. The older determination

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[7] With the organic liquids yet another term in this equation should be considered for the greatest possible precision. (See Lord Rayleigh, *Proc. Roy. Soc.*, **92A**, 189 (1915).) This term ($0.1312\ r^3/h^2$) in the present case is beyond the limit of accuracy of the experimental work and has therefore been omitted.

of its surface tension by Volkmann,[8] although carefully performed, has probably yielded too low results all along the line.

On plotting the results for H (corr.) for water (from Table I) at three temperatures, that at 20° is found to be not far from 73.50. If we assume as a standard value the known surface tension of water at 20° to be 72.80 dynes/cm., and substitute these values of H and K in the expression $K = \gamma/Hd$, we have K at $20° = 0.991$. This is, of course, dependent on the graphic computation of H. A more accurate interpolation may be obtained from the surface tension itself, since its variation with temperature is more nearly linear than that of H. Accordingly, the surface tensions at the three Centigrade temperatures (t_1, t_2, t_3) were calculated with the help of this provisional value of K from the equation $\gamma = K_{20°}(1 + [t° - 20°]\ 0.00009)\ Hd$, which takes account of the fact that K has a small temperature coefficient. From the three values of γ thus found, an equation of the type $\gamma_t = \gamma_0 + at + bt^2$ was constructed, which is nearly linear, b amounting to only 0.00023. With the help of this equation the value of γ (and from it that of K) at 20° was adjusted more accurately, by shifting the whole curve very slightly.

Such an equation, of course, has no physical significance; and if there were any reason for suspecting great eccentricity in the behavior of the surface tension of water, its use would not be permissible. However, the work of Volkmann (already alluded to) shows that no great eccentricity exists, the temperature coefficient being nearly constant between 0° and 35°. The use of the equation is not necessary for the method in hand; if the value of $h - h'$ at 20° had been observed, these complications would have been avoided.

The final values for K at different temperatures found by this method of successive approximations were as follows: at 0°, 0.9904; at 34.3°, 0.9907; at 60.0°, 0.9910.

Thus, for example, the equation for the calculation of surface tension at 0° is $\gamma = 0.9904\ Hd$.

Having thus been standardized, the apparatus was used for the measurement of the surface tensions of several liquids at three temperatures each. For use at 0° the capillary U-tube was removed from the wide tube which had served for the approximate determination of the radii, and fixed within another tube (12 mm. in external diameter—just large enough to hold it snugly) which had been carefully selected with regard to its optical performance. A small standardized thermometer was inserted beside the U-tube. Connection with the mercury pump and gage made possible the removal of the air from the capillaries. Very little liquid was needed. The walls of the upper part of the containing tube were "wetted" with the liquid under investigation, since the vapor above the meniscuses must

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[8] Volkmann, *Wied. Ann.*, **56**, 457 (1895).

be saturated to prevent evaporation, which ruins the meniscus. The measurements of the differences of capillary rise between the two tubes of the U were made by means of an accurate cathetometer, using a fine standardized meter scale at exactly the same distance from the telescope, in connection with the filar micrometer in the eyepiece. The larger of the meniscuses was read as easily as the smaller one. On comparing this method with the measurement of a large flat surface, the gain in this sharp definition of both meniscuses is seen to exceed by far the loss due to the diminution in the vertical rise measured, since the column actually measured was about $^5/_6$ as great as that which would have been measured if the finer capillary had been referred to a plane surface, whereas the gain in definition was at least 200%. Moreover, in narrow tubes optical defects in the glass walls of the tube are much less likely to occur than in wide tubes.

No difficulty was found in supercooling benzene to 0° without solidification in the capillary tubes; but *p*-xylene always solidified, making its determination at 0° impossible.

Before each reading, the apparatus was tilted, back and forth, so that the capillaries above each meniscus should be "wetted." This is a precaution of great importance. The apparatus was then placed in the ice-bath until the thermometer registered 0°; and just before each reading, the level of the ice was lowered in order that the meniscuses might be seen. The difference in height of the meniscuses was observed from several directions so as to minimize the effect of possible imperfections in the glass—both cathetometer and capillary U-tube having been adjusted in a vertical position (the latter by means of a plumb line). The fact that these measurements in different positions always agreed within 0.1% furnished evidence that the glass was not optically defective in serious degree.

More recent investigations, already mentioned, have treated this matter more precisely; and if the work herein described were to be repeated today, no observations would be made through wide auxiliary enveloping tubes. An adaptation of the present method for use in a thermostat with optically perfect windows[9] has recently been devised, and will form the subject of a future contribution. Nevertheless, although the apparatus used in the work herewith detailed was not as satisfactory as it could now be made, it was unquestionably accurate enough to give results which must be a close approximation to the truth.

The observations at 0° having been completed, the apparatus was modified for use at higher temperatures. The 12mm. tube containing the capillary U was fused into a larger tube, so that the former could be surrounded by a vapor suitable for the maintenance of constant temperature. Ether

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[9] See for example, Richards and Coombs, THIS JOURNAL, **37**, 1660 (1915).

vapor (at about 34°) and chloroform vapor (at about 60.5°) were employed; the thermometer indicated exactly the temperature at the time of the capillary reading. At each of these temperatures three readings of capillary rise were made with each of the liquids under investigation. The averages are recorded in the table. Benzene gave fluctuating results at 60°, possibly due to evaporation; these results were not certain enough to be recorded.

The density of each of the liquids at each of the temperatures used was carefully determined by two pycnometers and reduced to the vacuum standard. The corrections in the surface-tension equation for the density of the *vapor* are usually small; they were computed with sufficient accuracy and duly applied.

Preparation of Materials

Pure water was repeatedly frozen in a vacuum to free it from air. Benzene was freed from thiophene and recrystallized four times.[10] After long standing over sodium it was distilled, being adequately protected from moisture. It was probably nearly if not quite free from water, but saturated with air. Its density was determined as follows: at 0° (supercooled) 0.9004; at 20°, 0.8788; at 40°, 0.8569; at 60°, 0.8353 (all values being reduced to the vacuum standard).

The octanes were kindly made by Dr. Latham Clarke, formerly of this University.[11] Although they had been prepared with great care, doubt exists as to the extent to which they may have been contaminated with isomers. At least the samples used by us were free from sulfur and halogens. Since densities, compressibilities and surface tensions were all determined upon the same samples, the results are comparable with each other even if other hydrocarbons existed in them. After standing a long time over mercury and repeated distillation over sodium; their boiling points were: *n*-octane, 124.5° (760 mm.); monomethyl-2-heptane, 116.0° (760 mm.); di*iso*propyl ethane (*sym.*), 108.4° (760 mm.).

Kahlbaum's *o*-, *m*- and *p*-xylenes were dried over anhydrous copper sulfate and repeatedly fractionated. Their densities at 20° were, respectively, 0.8811, 0.8656 and 0.8611; the boiling points were: *o*-xylene, 143.9° to 144.2° (763 mm.); *m*-xylene, 138.8° to 139.2° (761.2 mm.); *p*-xylene, 136.2° to 136.4° (736.7 mm.). The *p*-xylene had a constant freezing point very near 13.2° until practically all of it was solidified. The density of supercooled *p*-xylene was determined very accurately at 0° to be 0.8779. At 20° the value was 0.8611; at 40°, 0.8444; and at 60°, 0.8274—all reduced to the vacuum standard.

The preparation of ethyl benzene has been already described. Its boiling point was 136.0 at 760 mm.[10]

The Results

The results are recorded in Tables II and III. Table II gives the observed heights, densities, pressures and temperatures, and also the surface tensions calculated from these data.

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[10] Richards and Barry, This Journal, **37**, 997 (1915).

[11] See Richards and Jesse, *ibid.*, **32**, 289 (1910); also L. Clarke, *ibid.*, **31**, 585 (1909).

TABLE II

DATA AND RESULTS FOR SURFACE TENSIONS

Substance	Pressure mm. Hg	Temp. (t°)	h obs.	H corr.	d obs. at t° (in vac.)	d corr. for vapor	Surface tension (dynes/cm.)
Water	20	0	76.94	76.64	0.9999	0.9999	75.89
	96	34.32	72.11	71.81	.9942	.9941	70.72
	760	60.65	69.25	68.95	.9830	.9822	67.11
Benzene	355	0	36.05	35.76	.9004	.8997	31.87
	760	34.95	31.93	31.65	.8624	.8609	26.99
n-Octane	80	0	33.79	33.50	.7198	.7197	23.88
	104	34.47	30.12	29.83	.6922	.6915	20.44
	566	60.00	27.30	27.03	.6707	.6691	17.92
Monomethyl-2-heptane	96	0	32.61	32.32	.7157	.7156	22.90
	104	34.27	28.95	28.66	.6881	.6878	19.52
	572	61.04	26.10	25.81	.6658	.6642	16.99
sym-Di*iso*propyl ethane	93	0	31.36	31.07	.7153	.7152	22.01
	77	34.47	27.70	27.41	.6861	.6858	18.62
	760	61.20	24.87	24.59	.6622	.6606	16.10
o-Xylene	13	0	36.90	36.60	.8968	.8968	32.51
	98	34.47	33.61	33.32	.8692	.8689	28.67
	225	60.80	31.12	30.80	.8468	.8461	25.85
m-Xylene	13	0	36.04	35.74	.8823	.8823	31.23
	103	34.47	32.71	32.42	.8534	.8531	27.40
	221	60.80	30.15	29.86	.8304	.8297	24.55
p-Xylene	145	22.90	33.55	33.26	.8589	.8587	28.27
	290	34.75	32.27	31.98	.8492	.8489	26.89
	350	60.60	29.85	29.57	.8269	.8261	24.21
Ethyl benzene	13	0	36.21	35.91	.8855	.8855	31.50
	90	34.27	32.75	32.47	.8609	.8606	27.68
	218	60.50	30.24	29.95	.8395	.8388	24.89

Table III gives (in the second and third columns of figures) the constants for equations of the type $\gamma_{t^\circ} = \gamma_{0^\circ} + at + bt^2$. These constants

TABLE III

TEMPERATURE COEFFICIENTS AND TOTAL SURFACE ENERGIES[12]

Substance	γ at 0° dyne/cm.	a	$b \times 10^4$	γ at 20° dyne/cm.	E_{0°	E_{20°
Water	75.89	−0.1585	+2.3	72.80	119.2	119.0
Benzene	31.87	....	...	28.9	...	...
n-Octane	23.88	− .1004	+0.18	21.88	51.3	51.2
Monomethyl-2-heptane	22.90	− .1008	+ .66	20.91	50.4	50.1
Di*iso*propyl ethane	22.01	− .1012	+ .76	20.02	49.7	49.2
o-Xylene	32.51	− .1135	+ .688	30.27	63.5	63.1
m-Xylene	31.23	− .1128	+ .50	28.99	62.0	61.8
p-Xylene	...	....	...	28.62	...	...
Ethyl benzene	31.50	− .1143	+ .84	29.24	52.7	62.3

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[12] No values of *a*, *b* or *E* are given in this table for benzene and *p*-xylene, because only two points were observed on the benzene curve, and the extrapolation needful to determine the value for *p*-xylene at 0° is too great for reasonable accuracy.

are computed from the values at 0°, 34° and 60° given in Table II. They make possible the computation of γ at any given temperature between 0° and 60°. The values of γ at 0° are recorded in the first, and at 20° in the fourth column of figures.

Table III gives also the values for the "total surface energy" for unit area, calculated from the equation, $E = \gamma - T(d\gamma/dT)$.

Conclusions

The comparison of these results with those of others is not without interest. As already stated, the results for water are higher all along the line than those of Volkmann, because a higher and more accurate value at 20° was used to standardize the present values. The curve is nevertheless essentially parallel with Volkmann's curve as far as 40°. Above 40°, Landolt and Börnstein (1912) accepted the work of Brunner.[13] This investigation, having been performed nearly 80 years ago, was doubtless defective in many respects. It showed a distinctly more rapid decrease in surface tension with increasing temperature than do the results herewith communicated.

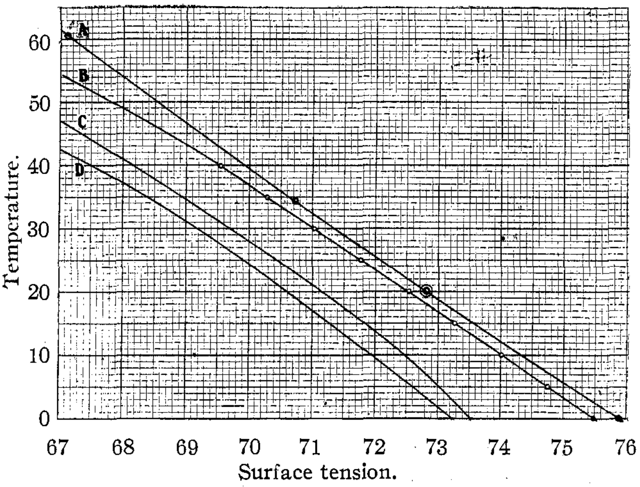

Fig. 2.—The effect of temperature on the surface tension of water. Curve A: Represents the results recorded in this paper ($\gamma = 75.89 - 0.1584t + 0.00023t^2$). Curve B: Above 40° represents the results of Brunner (as accepted by Landolt and Börnstein's Tables). Curve B: Below 40° represents the results of Volkmann. Curve C: Represents the results of Weinstein. Curve D: Represents the results of Ramsay and Shields.

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[13] Brunner, *Pogg. Ann.*, **70**, 481 (1847).

The determinations of Ramsay and Shields, and Weinstein[14] of about thirty years ago are also inaccurate, for the reasons already given.[3] The results of all these investigations are plotted in Fig. 2. Frankenheim's[1] very early results (1847) lie between those of Volkmann and those of Weinstein.

The diagram shows that the curves are by no means identical in character. Evidently further work upon the temperature coefficient of the surface tension of water is needed. We are inclined to think that the present results, at least between 0° and 30°, are to be considered as giving the most satisfactory estimate of the temperature coefficient now at hand.

The values for benzene are chiefly interesting because they are consistent with the recent work of Harkins and Brown and ourselves and thus give further evidence that the method is satisfactory. Exact comparison is complicated by presence of air in some of the cases, and the partial absence of air in others—for air has appreciable effect on the capillary constant of benzene.[3]

Few other determinations of the surface tension of the octanes have been found.[14a] The figures show no unexpected peculiarities; in every case, of course, the surface tension diminishes with increasing temperature. On comparing, at similar temperatures, the three octanes with one another, we see that as usual the surface tensions follow the same order as the boiling points. In relation to compressibility, as usual also, the compressibility is seen to be greater the less the surface tension (the compressibilities of the three octanes being, respectively, 0.000088, 0.000091, 0.000095 between 100 and 500 megabars).[15] These results are entirely in accord with the theory of atomic compressibility.

Renard and Guye[16] determined the surface tension of *m*-xylene and found it to be 28.88 at 10° and 26.07 at 38°—results which are distinctly too low (like all their other results) for the same reason that Ramsay and Shields' results are too low. Xylenes have been studied also by Feustel,[17] and Dutoit and Friederich.[18] The latter give for *m*-xylene the values 28.97 at 15.7° and 22.71 at 74.9° instead of our values 29.47 and 23.03 (extrapolated), respectively. The results for the three xylenes at 20° have already been recorded approximately.[19] The results herewith given differ scarcely at all from the earlier estimates. In the earlier publication

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[14] Ramsay and Shields, *Z. physik. Chem.*, **15**, 98 (1894); **15**, 89 (1894). Weinstein, "Metronomische Beitrage, No. 6," Norm.-Eich.-Komm., **1889.**

[14a] The values found by Harkins and Cheng [THIS JOURNAL, **43**, 48 (1921)] are somewhat lower than ours. No details of preparation, nor boiling points, are given.

[15] Richards, Stull, Mathews and Speyers, *ibid.*, **34**, 988 (1912).

[16] Renard and Guye, *J. chim. phys.*, **4**, 92 (1906).

[17] Feustel, *Ann. phys.*, **16**, 61 (1905).

[18] Dutoit and Friederich, *Arch. sci. phys.*, [4] **9**, 105 (1900).

[19] Richards (Faraday Lecture), *J. Chem. Soc.*, **99**, 1203 (1913).

it was pointed out that the properties of the xylenes, like those of the octanes, are entirely in accord with the theory of atomic compressibility.

Ethyl benzene is not very different from *m*-xylene as regards its physical properties, but the correspondence between them, as regards these properties, is not so close as between the individuals of any pair of the three xylenes. This would indeed be expected, because of the difference in structure.

"Total surface energy" is seen to vary very little with changing temperature.

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Summary

This paper recounts experimental work performed in 1910, which has awaited publication until more exact knowledge of the problem of medium-sized capillary tubes had been secured. The method consisted in the measurement of differences of capillary rise in two narrow tubes of different diameters. Now that the means for calculating the correction to the rise in the wider of these tubes is certain, this method becomes a very convenient one for the purpose, possessing many advantages. The tube was standardized by means of pure water. With it the surface tension of water, three isomeric octanes, *o*-, *m*- and *p*-xylene and ethyl benzene were determined, each at three temperatures. Equations are given for the calculation of the surface tension at any intervening temperature. The total surface energies are recorded; they change but slightly with changing temperature. The results are essentially in accord with the theory of atomic compressibility.

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NOTES

Density and Hydration in Gelatin Sols.—In a recent article, Svedberg and Stein[1] determined "*d*," the change in density when 5 g. of gelatin was suspended in 100 cc. of various solutions. The following quotation gives their method of calculation.

> "The volume of the pycnometer was determined in the usual way. The density difference, *d*, was arrived at quite directly: the difference in weight between the pycnometer plus the gelatin sol and the pycnometer plus the pure solvent was divided by the volume of the pycnometer. A concrete example taken from the results will make the statement clearer. For 5% gelatin solution in *N* hydrochloric acid we find,

$$\begin{array}{lll} N\,\mathrm{HCl\ solution} + \mathrm{pyc.} & = 50.8212\ \mathrm{g.} & \\ N\,\mathrm{HCl} \quad\quad\quad\ + \mathrm{pyc.} & = \underline{50.4740} & \dfrac{0.3472}{\mathrm{vol.\ of\ pyc.}\ (27.17565)} = d = 0.012776.\text{"} \\ \quad\quad \mathrm{Diff.} & = \ \ 0.3472 & \end{array}$$

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[1] Svedberg and Stein, This Journal, **45**, 2613 (1923).