and propyl formates, where it approaches the observed value with increased temperature.

3. Methyl, ethyl and propyl formates show varying values of t_c with the temperature. In one of these (it is probably true for all) it is shown that apparently a reaction which is reversible is caused by increased temperature, which can be reversed by sudden cooling, but which persists on slow cooling, leading at the lower temperatures to a higher drop weight (and also t_c) than the unheated sample. It is only after some days that this heated sample again returns to its original, unheated value. This reaction is probably what causes the drop to be heavier than it should be at the higher temperature, and to lead to the value of t_c which is larger at 60° than at 0° by 6° in the maximum. We cannot say then that these three formates are either associated or normal; but simply that increased temperature causes a reaction of an unknown nature to take place.

4. Surface tensions in dynes per centimeter, calculated from the drop weight by multiplication by the ratio of the benzene constant for capillary rise to that for drop weight, are found to agree exceedingly well with those of Ramsay and Aston. The agreement of methyl formate with the figures of Ramsay and Shields is not so good, nor that of amyl formate with those of Homfray and Guye (although this is probably due to the impurity of the sample used with drop weight), while the values for ethyl acetate vary considerably from those of the workers on capillary rise, although these do not agree well among themselves.

5. The values of t_c calculated from the modified Walden relationship agree as well with those from the k_B formula as can be expected, except for ethyl, methyl and propyl formates, where since the k_B values are variable, no agreement can be expected.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 194.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. VIII. THE RELATIONSHIP EXISTING BETWEEN THE WEIGHT OF THE DROP, THE DIAMETER OF THE TIP FROM WHICH IT FALLS, AND THE SURFACE TENSION OF THE LIQUID.

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It has been shown in previous papers that *for any one tip the laws of Tate, viz.: the weight of a falling drop is proportional to the surface tension of the liquid; and the weight of the drop decreases with increased temperature,* are true. The object of this paper is to present the results of a study of Tate's other law—*that the weight of a falling drop is proportional to the diameter of the tip from which it falls.*

In Table I are given the experimental results obtained with the Morgan drop weight apparatus, at the constant and uniform temperature of 27.8° ± 0.02°, using 16 tips, from 3.05 to 7.86 mm. in diameter, the liquids being carbon tetrachloride, ether, benzene, pyridine, and quinoline. The benzene here was Kahlbaum's "thiophene free," the pyridine, ether and quinoline from the same source, but the two latter were always freshly distilled just before the determination, while the carbon tetrachloride was from Baker, and also freshly distilled.

TABLE I.—DROP WEIGHTS IN MILLIGRAMS.[1]

Diameter of tip. Mm.	Benzene.	Quinoline.	Pyridine.	Ether.	Carbon tetrachloride.
3.05	17.355	28.063	22.699	9.843	15.515
3.93	21.564	34.572	28.324	12.284	19.664
4.00	21.934	35.165	28.811	12.497	19.998
4.51	24.268	38.487	31.811	13.814	22.438
4.70	25.245	......	......	......	23.525
4.98	26.753	42.480	35.137	15.243	25.066
5.31	28.526	......	......	......	27.004
5.50	29.528	46.916	38.762	16.826	28.224
5.50	29.532	46.920	38.766	16.827	......
5.69	30.532	48.540	40.074	17.501	29.556
5.85	31.349	49.692	41.197	18.004	30.698
6.20	33.287	52.680	......	......	32.632
6.55	35.351	55.698	46.147	20.658	34.672
6.84	37.157	58.111	48.200	21.740	36.620
7.39	40.749	63.124	52.350	24.008	......
7.86	43.830	67.638	56.079	26.094	......

The diameters of the above tips were measured by aid of a dividing engine,[2] reading to 0.001 millimeter, each value given in the Table being the mean of a number of measurements, of several diameters; but as the cross-section at the end was never perfectly circular, and in many cases the edges, viewed under the microscope, were not perfectly sharp, the accuracy is not as great as was desired. The results, in general, however, it is thought, are burdened with an error of less than 0.01 mm.

The drops which formed on the three smallest tips were entirely different in appearance, especially toward the end of their life, from what was expected. In place of rising over the edge, as will happen when such

[1] At the suggestion of the Editor the experimental results, consisting of 389 individual determinations, are given in this form. Each of the above values is found from the mean of several 30-drop determinations with the mean of several 5-drop blanks, the extreme variation for the 25 drops being never more than a few tenths of a milligram.

[2] Our thanks are due to Dr. C. C. Trowbridge, of the Department of Physics, who placed at our disposal the dividing engine, and aided us materially in preparing for the measurements.

a small tube is jarred, and which was expected in these cases, the drop here continued to hang from the edge without any sign of rising above it, so that up to the time when it was somewhat more than half formed, its appearance was similar to a drop hanging from one of the larger tips, such as have been considered in the other papers of this series. Sooner or later, however, as the drop increased in size, *a change in its profile became apparent, the lower part bulging out beyond the limits which would result from a projection of the circumference of the tip, and forming what might be described as a spherical mass of liquid joined to the tube by a column of smaller diameter. There was, however, no rising of the liquid over the edge.* It is probable that with a still smaller tip, the immediate consequence of this formation of a larger mass of liquid at the bottom of the drop would be to force the liquid up and over the edge of the tip, though in these cases no such result was observed.

Naturally if the drop rises over the edges of the tip, the weight falling will be larger than it should be, for the area from which it falls would be increased by an amount which depends upon the surface tension of the liquid, and hence is not uniform for all liquids. In the same way when this bulging of the bottom of the drop is noticed, the amount of which is apparently also proportional to the surface tension, the falling drop must be heavier than it should be for that diameter, judged by the results obtained from a tip which exhibits no bulging; for here the weight falling would not simply be proportional to the diameter (or area) of the tip, which remains constant, but also to the extent of the bulging, which varies with the nature of the liquid. In both cases it is probable that the weight of the drop, in place of being simply proportional to the surface tension, is proportional to it in a more complex way. It is clear here, at any rate, that the results found on a tip upon which the drop bulges cannot be compared with those found on a tip which produces a normal drop; and further, that on such a tip two liquids cannot be compared, unless, of course, they both bulge to the same extent.

A second thing noticeable in obtaining the above results is the effect of a tip which is too large, *i. e.*, one on which it is impossible to perfectly control the speed of formation of the drop just at the moment of its fall. Naturally, this is to a certain extent a question of the apparatus used, for it is quite evident that when a liquid is passing through but a few centimeters of capillary tubing the perfect control will be lost at a smaller diameter of tip than it would when the liquid passes through a length of several meters of the same tubing, for the viscosity of the liquid would then prevent absolutely and automatically any considerable speed of formation. It would be expected, then, that the largest tip which could be employed on the Morgan drop weight apparatus would be smaller than that which could be used successfully on such a form as that of Morgan and Higgins.[1]

The effect of the so-called lack of control, as far as it refers to a tip which is just too large, is apparently to change what has been practically a static phenomenon into one that is dynamic, resulting in the carrying down of an excessive amount of liquid due to spurting at the final moment of fall. Increase in the diameter of the tip, after perfect control is lost, however, apparently also has the effect of changing the profile of the drop, causing the sides of the drop, which are parallel or nearly so, when the control is perfect, to converge at the bottom, forming an inverted cone quite different in shape from the bag-like form produced under ideal conditions. This, naturally, would cause the drop to break at a different place, and cause the fall of a weight which is not comparable to that falling from a tip giving the normal shape of drop. It would seem, then, from these qualitative observations, that *the drops of various liquids falling from a tip are only to be compared when the drop profiles are similar; and the drop falls of its own weight alone.* It is quite evident, thus, that the important factors as to the tip upon which a liquid will give satisfactory results, are the volume of the drop and its surface tension; for the shape assumed by the drop is dependent not only upon its volume, but also upon the surface forces which would tend to condition the form assumed by this volume. It was for this reason that the above liquids were chosen for the work; for carbon tetrachloride, with its small surface tension and large density, gives, with one or two rare exceptions the smallest possible drop volume, accompanied by small surface tension; ether, with its small surface tension, and also small density, and consequently larger volume, the next larger; then benzene and pyridine, and, finally, quinoline, which with the exception of water and a few other liquids, gives the largest possible drop volume, with large surface tension.

The bulging effect was very noticeable on the 3.05 mm. tip in the cases of benzene, ether, pyridine, and quinoline, but was not so apparent on the two next larger. Carbon tetrachloride also bulged on the 3.05 tip, but its variation on the next two was not so striking. Benzene, ether, and pyridine seemed to bulge on the three smallest tips to practically the same extent, and thus should be comparable in a way on each tip.

On the tips from 4.51 to 5.50 mm. inclusive, the behavior of ether, benzene, pyridine and quinoline seems to be perfect, no bulging being noticeable, and the drop profile being the same in general, while perfect

[2] Much of the difficulty experienced by Morgan and Thomssen with beveled tips, and also with the first sharp-edged ones, it is thought now was due to the use of capillary tubing of too large a bore. This not only gave trouble, owing to the threads of liquid which could not be drawn back in the tube, but also introduced difficulty in control.

control is still possible. The control of carbon tetrachloride seemed poor on the 4.69 mm. tip, and continued to get worse and worse, as the diameter of the tip increased, the drop becoming more and more abnormal in shape. With this liquid no special precautions were taken as to control, so that the results given can be corroborated by any one—this will explain any apparent difference in the above results and those obtained, only after much practice, by Morgan and Thomssen. The control of ether is lost before that of benzene, and that of pyridine before that of quinoline, which was satisfactory certainly on all tips up to that of 7.39 mm.

In order to show the effect of too small, as well as of too large a tip, the drop weight in milligrams has been divided in each case by the diameter of the tip in question; these values are given in Table II. It is to be remembered here that unfortunately the error in measuring the diameter is not the same in all cases, some tips being sharper as to edge, and more perfectly circular in section than others. This would account for small variations in the value.

TABLE II.

Values of $\frac{\text{drop weight in mg.}}{\text{diameter in mm.}}$.

Diameter.	Benzene.	Quinoline.	Pyridine.	Ether.	Carbon tetrachloride.
3.05	5.703	9.201	7.442	3.227	5.087
3.93	5.487	8.797	7.207	3.126	5.004
4.00	5.484	8.791	7.203	3.124	5.000
4.51	**5.381**	**8.534**	**7.044**	**3.063**	**4.975**
4.70	**5.371**	.....	.....	.....	**5.006**
4.98	**5.372**	**8.530**	**7.056**	**3.061**	5.033
5.31	**5.372**	.....	.....	.....	5.086
5.50	**5.369**	**8.530**	**7.048**	**3.059**	5.144
5.50[1]	**5.370**	**8.531**	**7.049**	**3.059**	.....
5.69	**5.366**	**8.531**	**7.043**	3.076	5.194
5.85	5.359	**8.494**	**7.042**	3.078	5.248
6.20	**5.369**	**8.497**	.....	.....	5.263
6.55	5.397	**8.504**	7.045	3.154	5.293
6.84	5.432	**8.496**	**7.047**	3.178	5.354
7.39	5.510	8.547	**7.084**	3.249	.....
7.86	5.576	8.605	7.135	3.320	.....

The numbers in heavy type here indicate the tips which should give comparable results by any treatment. It will be noted that in general the values are too large for the smaller tips, then remain constant with an increase in the diameter, and then increase again; exactly as was forecasted from the qualitative observations. For carbon tetrachloride, apparently, but few tips could be used which would lead to identical

[1] Tip used by Morgan and Thomssen. The other though of the same diameter had no flaws, and the edges were sharper.

results (without very special precautions as to control), *viz.:* those which are just smaller or just larger than 4.5 millimeters in diameter. There are but few liquids, however, which could give as much difficulty as this, for it is due to a very small drop volume, accompanied by very small surface tension; one example of this, perhaps the only one, is nickel carbonyl. *It will be observed that on the 4.51 mm. tip we could expect to obtain comparable results for all liquids, for even quinoline with its large drop volume shows no bulging upon it. We may conclude from Table II, then that Tate's other law—that the weight of a drop falling from any tip is proportional to the diameter of the tip—holds rigidly between certain definit limits, for all the liquids examined—and the only reason that it does not hold for all liquids on all tips is that the bulging of the drop on the smaller tips, and the opposite change of profile on the larger ones, causes the drop which forms and falls to obey laws which are not general, but which hold only for related liquids, i. e., for those with which the bulging, or change of shape in the opposite direction, would have the same weight-increasing effect.*

For *benzene*, using the values of w/r which are in heavy type, we find the relationship between drop weight and diameter; in other words, the analytical expression of Tate's first law, to be

$$w = 5.37 \times 2r, \quad \text{or}$$
$$w = 1.709 \times 2\pi r,$$

where w is in milligrams, $2r$ lies between 4.51 and 6.20 millimeters, and the temperature is 27.8°.

How well this expression of Tate's law holds for benzene; *i. e.*, how well the values of w thus calculated agree with those directly observed is shown in Table III.

TABLE III.

w FOR BENZENE CALCULATED FROM $w = 5.37 \times 2r$ AT 27.8°.

Diameter.	Wt. 1 drop calc.	Wt. 1 drop obs.	Δ.
4.51	24.219	24.269	0.050
4.70	25.239	25.245	0.006
4.98	26.743	26.753	0.010
5.31	28.515	28.526	0.011
5.50	29.535	29.530	0.005
5.69	30.555	30.532	0.023
5.85	31.415	31.349	0.066
6.20	33.294	33.287	0.007

A glance at the column of differences here shows the worst disagreement between the calculated and the observed values of drop weight to be about 0.2 per cent. Since the measurement of diameter can be considered accurate to only about 0.01 mm., however (*i. e.*, to 0.25 per cent. on the 4.51 mm. tip, and 0.17 per cent. on the 5.85 one), this agreement is as close as could possibly be hoped for.

To show that the same kind of a relationship between drop weight and diameter of tip holds also for each of the other liquids; and further, to show the relationship existing between the weights of different liquids falling from the same tip, the indirect method already used in the previous papers is best employed; *i. e.*, that based upon the Ramsay and Shields form of equation

$$w\left(\frac{M}{d}\right)^{2/3} = k(t_c - t - 6).$$

It is quite evident here that in comparing different tips with the same liquid, that the w values must be related to one another as are the k values found for benzene on the two tips. For example, for benzene, we would have, at the same temperature of observation, t,

$$w'\left(\frac{M}{d}\right)^{2/3} = k'_B\ (288.5 - t - 6),$$

and

$$w''\left(\frac{M}{d}\right)^{2/3} = k''_B\ (288.5 - t - 6).$$

i. e., $w' : w'' : : k'_B : k'_B : .$ For different liquids on the same tip, then, using the value of t_c as given in the previous papers, and calculated for any one tip from its k_B value, *viz.*: 521.3° for quinoline, 346.6° for pyridine, 195° for ether, and 283.2° for carbon tetrachloride, constants, k, should be calculated for each liquid, *if the w values are properly related*, which are the same as the k_B value for that tip. In this way we can find the limits of diameter between which the drop weight method can be used for the purposes already discussed in the previous papers. Naturally, we would expect here only to get satisfactory results for those tips which in Table II gave uniform values for the $w/2r$; but the comparison is somewhat more satisfactory than that, owing to the fact that here there is no term of doubtful accuracy; the drop weight, and consequently the k value, can be determined in general with a much smaller percentage error than is found in the measurement of diameter, even under ideal conditions.

In Table IV are given the values of k for each of the liquids, using the values of t_c given above. In this table only those tips are considered which give satisfactory results as to the value of k, the diameters, as will be observed, being those already fixed by the ratio $w/2r$.

TABLE IV.—k VALUES NECESSARY TO GIVE ABOVE VALUES OF t_c.

	Diameter of tip, mm.						
Liquid	*4.51*	*4.70*	*4.98*	*5.31*	*5.50*	*5.50*	*5.69*
Benzene	1.908	1.985	2.103	2.243	2.322	2.321	2.400
Quinoline	1.906	.....	2.104	.....	2.324	2.323	2.404
Pyridine	1.906	.....	2.105	.....	2.323	2.323	2.401
Ether	1.909	.....	2.107	.....	2.326	2.325	[2.419]
Carbon tetrachloride	1.908	[2.000]	[2.131]	.....	.....	.....	.....
Average	1.907	.....	2.105	.....	2.324	2.323	2.402

It will be noted here that a tip of the diameter of 4.51 millimeters leads to satisfactory results with all liquids, from carbon tetrachloride, with its minimum drop volume and very small surface tension, to quinoline with its very large drop volume and large surface tension. In other words, even a liquid such as quinoline, giving an exceedingly large drop volume, can be used on this tip without danger of the results being affected by a bulging of the drop.[1]

We are now in position to calculate the exact size of each of the tips used in the previous papers of this series, where only approximate values from a direct measurement with a micrometer were made. The values given are now found to have been throughout about 0.1 mm. too large. The tip used by Morgan and Thomssen, for example, from the relationship $k_{B-4.51} : k_{B, M \& T} :: 4.51 : 2r$ is found to be 5.50 millimeters, which also agrees with the recent, direct, measurement; by a similar proportion that of Morgan and Daghlian is found to be 5.64, and that of Morgan and Schwartz 5.53 millimeters.

It is also necessary here to see if by any chance a liquid already studied has suffered owing to a lack of control. As was mentioned in an earlier paper, ethylene dibromide is a liquid somewhat of the type of carbon tetrachloride, so that the results of Morgan and Thomssen on the 5.50 mm. tip may be slightly high. This would not, as has already been explained, affect the definition of the normal molecular weight, but the determination of the exact value of t_c, *i. e.*, that found on a tip on which the control is certainly perfect, where the value might be slightly different, must be left for future work. The only other liquid which could possibly be affected by more perfect control is bromine, which forms a drop of small volume but has sufficient surface tension to make the drop appear normal in profile, on the tip used by Morgan and Daghlian. If the control was not perfect here it was not noticeable to the eye, so that a smaller tip could only give a very slightly smaller result, if it changed it at all.

[1] *Water on this tip leads to a drop weight which is just what it should be, according to the relationship $w' : w'' :: k'_B : k''_B$, where w'' is the weight on a very much larger tip, k''_B being its k value for benzene. This shows that even water, forming as it does the largest known drop volume, also behaves normally on this small tip, and does not show any effect of a bulging of the drop. It would appear, then, that a tip of this diameter, 4.51 millimeters, is a universal tip on this apparatus, holding for all liquids. On larger ones, carbon tetrachloride, and perhaps a few others which are similar, would lead to results that are too large, owing to the lack of perfect control of the drop; but no other would probably fail to hold a smaller tip than 5.7 mm., on which the control of ether first becomes poor. In short, then, this 4.51 tip is not too small for the liquid giving the largest possible-drop volume, nor is it probably too large for any known liquid at temperatures at which it would be likely to be used. Further, in case it were too large, the visible lack of control would warn the observer, and a smaller tip, the standard, benzene, value for which could be calculated from the above benzene values, and the measured diameter of the tip, assuming that benzene does not bulge, could be used.*

The constants for the larger and smaller tips, which were not included in Table IV, are given in Table V. Here for each tip is also given the k value as calculated for benzene on the assumption that it always follows the law observed for the values given in Table IV.[1] These are the values which could be used as the standard, for example of a smaller tip, in the case that a liquid were used which gives such a small drop volume, if such there be, as to fail to give a good result on the 4.51 mm. tip. It will be noted from the Table that the relationship is just what was forecasted from Table II. As control is lost, the drop weight, and consequently the k value, becomes too large. Thus the control of benzene is lost before that of pyridine, which does not hold on as large a tip as quinoline, all of which is in perfect accord with the data in Table II.

TABLE V.—VALUES OF k NECESSARY TO GIVE ABOVE t_c VALUES.

	Diameter of tip, mm.								
Liquid	*3.05*	*3.93*	*4.00*	*5.85*	*6.20*	*6.55*	*6.84*	*7.39*	*7.86*
Calculated k. [$k = 0.4224 \times (2r)$]	1.288	1.660	1.690	2.471	2.619	2.767	2.889	3.122	3.320
Benzene	1.364	1.695	1.724	2.465	2.617	2.779	2.921	3.303	3.446
Quinoline	1.390	1.712	1.741	2.461	2.609	2.758	2.878	3.126	3.350
Pyridine	1.360	1.697	1.726	2.469	.....	2.765	2.888	3.137	3.360
Ether	1.360	1.698	1.727	2.488	.....	2.855	3.005	3.318	3.607
Carbon tetrachloride	1.319	1.672	1.701	2.589	2.752	2.925	3.089	.....	.....

The slightly low results for quinoline, as contrasted with the values calculated from the formula $k = 0.4224 \times 2r$ for benzene, on the 5.85, 6.20, 6.55 and 6.84 mm. tips, are probably due to a slight trace of water in the quinoline, for these tips were the last ones studied, and since the quinoline showed no trace of color, it was not redistilled before the determinations, and the calculations were not made until all was finished. The values for pyridine, on the other hand, appear to be in remarkable agreement with the calculated values on the 5.85, 6.55 and 6.84 mm. tips. The results for benzene and pyridine are always more to be relied upon than those for other liquids, for these when once obtained in the pure state undergo no change on standing, while the others must always be redistilled just before each determination. The pyridine, on all the larger tips, was determined here according to the procedure advocated in an earlier paper, *i. e.*, the remaining drop was always drawn back after each one fell, so that every drop was as normal as a first drop, and exhibited no trace of a pulling away from the edge of the tip, which is often noticed when successive drops are formed without this precaution. The only condition necessary in the determination of a liquid at a temperature as near the boiling point as 27.8° is to that of ether, is the assur-

[1] $k = 2r \times 0.4224$, r in millimeters.

ance that the blank in every way duplicates exactly the conditions holding during the determination of the weight of the larger number of drops. In most of the cases above this liquid was also studied at 0°, to confirm the value at the higher temperature, with the result that a practically identical value of k was found at both temperatures.

Naturally, for the general drop weight method, the results in this table have little importance, for the tips lying in diameter between 4.51 and 5.50 mm. are the ones that would be used with it, and on them as has been shown already (Table IV), all liquids, with but a few exceptions, which can be recognized as such by the eye, as soon as the first drop forms and falls, give perfectly satisfactory results.

Since we find constant calculated values of k for the liquids on the tips with diameters between 4.51 and 5.50 mm., we would naturally expect to get a value of surface tension, from the proportion $\gamma : w : : K_B : k_B$, (where k_B is the drop weight constant for the tip, as found for benzene) which is constant for each liquid, independent of the size of the tip, so long as it is within the above limits. Using for K_B the value 2.1012, as found from the surface tension results of Ramsay and Shields, we obtain the values given in Table VI.

Combining the relationship

$$w = 5.37 \times 2r$$

or

$$w = 1.709 \times 2\pi r,$$

which we found for benzene with the above proportion, *viz.*:

$$k_B : K_B : : w : \gamma,$$

we find the relationship between drop weight, diameter, and surface tension for any liquid at 27.8° to be

$$w = 0.06397 \times (2r)\pi\gamma,$$

where γ is given in dynes per centimeter. The values of γ resulting from the application of this formula to the drop weight results of the various liquids are given in Table VII; these values, naturally, should differ from those in Table VI only by an amount equal to the error in the original equation for the variation in the drop weight of benzene with the diameter of the tip. Of course it is to be remembered here that the result

TABLE VI.—SURFACE TENSIONS IN DYNES PER CM. AT 27.8.°

$$\gamma = w\ 2.1012/k_B$$

Diameter of tip.	k_B.	Quinoline.	Pyridine.	Ether.	Carbon tetrachloride.
4.51	1.908	42.39	35.04	15.22	24.71
4.70	1.985	.....	.....	.....	.....
4.98	2.103	42.44	35.10	15.23	.....
5.31	2.243	.....	.....	.....	.....
5.50	2.322	42.47	35.09	15.23	.....
5.50	2.321	42.47	35.09	15.23	.....
5.69	2.400	42.49	35.08	[15.32]	.....
Average................		42.45	35.08	15.23	24.71

in VI could be obtained at any temperature at which w is known, while results from the equation used in VII could be found only from a drop weight at 27.8°.

TABLE VII.—SURFACE TENSIONS IN DYNES PER CM. AT 27.8°.

$\gamma = w/0.063972 \times (2r)\pi$.

Diameter of tip.	Benzene.	Quinoline.	Pyridine.	Ether.	Carbon tetrachloride.
4.51	26.75	42.42	35.06	15.23	24.73
4.70	26.75	.....	.....	.....	.....
4.98	26.74	42.46	35.12	15.24	.....
5.31	26.75	.....	.....	.....	.....
5.50	26.72	42.45	35.07	15.22	.....
5.50	26.71	42.44	35.06	15.21	.....
5.69	26.70	42.45	35.05	[15.31]	.....
Average.....	26.73	42.44	35.07	15.23	24.73

These values of surface tension are those which, with the Ramsay and Shields' constant 2.1012, will lead to the values already given of t_c, from which the k values were calculated. The values for benzene are the same as those which would have been found by Ramsay and Shields at this temperature; those for quinoline are practically the values that Bolle and Guye would have found, for their average value of the calculated t_c (see No. IV) is 522.4°, in place of the 521.3° we have used; the pyridine would agree very well with the value Dutoit and Friederich would have found, for their calculated t_c is 346.2° in place of our 346.6°; the value of carbon tetrachloride is that found by Ramsay and Shields, *i. e.*, leads to the same t_c as do their values at other temperatures, while the ether gives the same value as would be extrapolated from the higher temperature values of Ramsay and Shields.

The results of this research may be summarized as follows:

1. The drop weights of benzene, quinoline, pyridine, ether and carbon tetrachloride have been determined with the Morgan drop weight apparatus at 27.8°, on sixteen different, sharp, straight-edged tips, varying in diameter from 3.05 to 7.86 millimeters.

2. On the smaller tips the drop of liquid, instead of rising over the edge of the tip, as might be expected, was found to bulge at the bottom, extending there beyond the continuation of the sides of the tip, thus leading to high results; while on the larger tips, in addition to the loss of the perfect control of the drop, which is first observed, the profile of the drop is found to undergo a change which makes it appear quite different from the normal bag-like one, with its nearly parallel sides, for it converges at the bottom, which causes the drop to break away at a different point, and leads to results which are too high.

3. All liquids, from water, forming the largest possible drop volume, to carbon tetrachloride, which gives practically the smallest, are found

to give perfectly satisfactory results from all points of view, on a tip with a diameter of 4.51 millimeters; while, excluding carbon tetrachloride, and possibly a few other similar liquids, characterized by a very small surface tension and a large density, which then form drops of minimum volume, equally satisfactory results are obtained on all tips with diameters between 4.51 and 5.50 mm.; and higher, for many liquids.

In other words, it is shown that when the drop profile is not abnormal to the eye, and the control of the drop is perfect, Tate's first law—the weight of a falling drop is proportional to the diameter of the tip from which it falls—holds rigidly.

4. Surface tensions in dynes, calculated from the benzene constants and the drop weight from the tip employed (*i. e.*, by aid of the proportion $\gamma : w : : K_B : k_B$) are found to agree on all tips from 4.51 to 5.50 mm., independent of the diameter of the tip, as long as the drop profile is normal and the control of the drop is perfect; in other words, for all liquids except carbon tetrachloride, which gives perfectly satisfactory results on tips around 4.5 mm. in diameter only, owing to its exceedingly small drop volume.

Surface tensions in dynes for these liquids are also calculated at 27.8° by aid of the formula $\gamma = w/0.06397 \times (2r)\pi$, which is also found to lead to results independent of the diameter, and which agree with the values calculated from the above proportion.

5. It is to be concluded from this investigation that the Morgan drop weight apparatus will give satisfactory results when the tip diameter lies between 4.51 and 5.50 millimeters, although if such a liquid as carbon tetrachloride is to be used it would be necessary to reduce the tip diameter to 4.51 mm., which will probably give satisfactory results for every known liquid.

LABORATORY OF PHYSICAL CHEMISTRY.

ANHYDROUS HYDRAZINE. I. A CONVENIENT APPARATUS FOR THE PREPARATION OF ANHYDROUS HYDRAZINE.

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The first compound of hydrazine was prepared in 1875 by E. Fischer[1] by the reduction of a diazonium compound with potassium bisulfite. Curtius[2] obtained the sulfate of hydrazine by digesting an aqueous solution of triazoacetic acid with dilute sulfuric acid. By distilling hydrazine hydrate over barium oxide, Curtius and Schulz[3] attempted to prepare

[1] *Ber.*, 8, 589 (1875).

[2] *Ibid.*, 20, 1632 (1887); Curtius and Jay, *J. prakt. Chem.*, [2] 39, 27, 107 (1889).

[3] *J. prakt. Chem.*, [2] 42, 521–49 (1890).