X.—*The Nature of Solutions, as elucidated by a Study of the Density, Electric Conductivity, Heat Capacity, Heat of Dissolution, and Expansion by Heat of Sulphuric Acid Solutions.*

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PART I.—GENERAL AND INTRODUCTORY.

IN the early part of 1887, I began an investigation on the nature of solutions, by making a number of determinations of the heat of dissolution of solutions of calcium chloride and nitrate, with the view to settling whether the curves representing these results exhibited any sudden changes indicative of the existence of liquid hydrates, or not. The subsequent publication of Mendeléeff's examination of the densities of alcohol (Trans., 1887, 778) and sulphuric acid (*Zeit. physikal. Chem.*, 1, 275), and of Crompton's examination of F. and W. Kohlrausch's determinations of the electric conductivity of solutions of the latter substance (Trans., 1888, 116), showed that sudden alterations in curvature might be established more satisfactorily by plotting out the rate of change—that is, the first differential coefficient—than by a mere inspection of the original curve, or by attempting to apply

equations to it. Mendeléeff stated that the rate of change of the densities is represented by a series of straight lines, meeting at points corresponding with hydrates of definite molecular composition, whilst Crompton found that, in the case of the electrical conductivities, two differentiations had to be applied before a rectilinear figure was obtained. These results are tantamount to the densities, s , of p per cent. solutions being represented by a series of different parabolas of the form $s = A + Bp + Cp^2$, while the conductivities, k , are represented by a series of the form of $k = A + Bp + Cp^2 + Dp^3$, any one equation holding good between two definite hydrates. Crompton's results added confirmation to the particular hydrates indicated by Mendeléeff.

On examining by differentiation my results with the heat of dissolution of the calcium salts, I found that they yielded rectilinear figures only after a double application of the process, and the hydrates thereby indicated were very numerous; further confirmation of these hydrates was obtained by determining the densities of the solutions, which were found, in accordance with Mendeléeff's statement, to yield a series of straight lines after the first differentiation (see Proc., 1888, 35).

These cases, however, were so complicated that I proceeded to investigate the presumably simpler case of sulphuric acid. The nature of the heat of dissolution curve was found to be the same as in the case of the calcium salts, but the hydrates thereby indicated were far more numerous than those which Mendeléeff had mentioned, and, on examining his density results more closely, I found, with surprise, that the values which he quoted* by no means warranted the conclusion that the first differential consisted of straight lines. These values appeared to me to be too meagre to settle the question at issue, so I made a series of fresh determinations, repeating them at four different temperatures. The results confirmed the existence of those hydrates which the heat of dissolution had indicated, and showed that the curves required a second differentiation before they yielded a rectilinear figure.

From these densities the expansion by heat was deduced, and further confirmation of the hydrates thus obtained. The heat capacities of the weak solutions had also been determined in order to calculate out the heat of dissolution results, and these also afforded similar evidence of an independent nature.

The present communication is confined to the results with sulphuric acid.

* Not determined by Mendeléeff himself, but collected by him from various sources.

Methods of Differentiation employed.

The results obtained, and generally also the curves representing them, were examined by the same process of differentiation as that adopted by Mendeléeff.

When the difference between the densities, &c., of two solutions is divided by the difference in the percentage composition of these solutions, the value obtained gives the mean rate of change in the densities between the two percentages taken, or, as it has to be less perfectly expressed, the mean rate at a point intermediate between these percentages. This constitutes direct differentiation from the experimental values themselves.

Differentiation, however, is a very dangerous and, at the best, a very imperfect tool. The differential is, strictly, the tangent of a curve, and the method here adopted assumes that the curve, which would represent the results, is a straight line between every two experimental points. The method would yield absolutely true results only if these differences were infinitely small; whereas if they be reduced too much—generally below 1 per cent.—the experimental errors attain such relatively large proportions that the results are useless.

The actual differences between the experiments will also affect the form of the differential to a certain extent, and irregularities will be caused if the differences are not the same throughout.

When the experiments themselves form a curved figure consisting of a series of different curves, they will, when differentiated, yield a series of other curves or straight lines, between each of which there will generally be one differential point conforming with neither of the adjacent curves, it being derived from two experiments belonging to two different primary curves. The existence of an undoubtedly non-conformable point is strong proof of a change in the vicinity,* but, when doubtful, it only adds to the difficulty of interpreting the results.

When a second differentiation has to be performed, it is hardly ever possible to apply it to the experimental values themselves, as Crompton did in the case of the conductivities, for the quantities dealt with would be of about the same magnitude as the experimental errors themselves. In such cases we must diminish the error by drawing a smoothed curve through the first differential points, taking readings from this curve and differentiating these. Except in the case of the densities,† I have performed the first differentiation on the smoothed

* Any error in an experiment will affect the two differential points derived from it, in opposite directions.

† To plot the densities out so as to allow 0·0001 gram to 0·01 inch, the whole curve would have to measure about 2000 inches, a wholly impracticable length.

curve representing the experiments, as well as on the experimental values themselves.

In differentiating the smoothed curve, we have the advantage of being able to take as many points as we like, and at equal distances apart; but, on the other hand, the drawing being subject to the "taste" of the draughtsman, it is never safe to dispense entirely with direct differentiation, especially as changes in curvature will be less marked in the original curve than in the first differential figure, and may be overlooked, if we trust entirely to the former. It requires no little practice, and the most careful attention to the magnitude of the experimental errors, to draw the smoothed curve on which to perform the differentiation. The curves representing the present results have been drawn with the help of a long thin steel or wooden lath. Such a lath, when bent under the four points of pressure exerted by one's two hands, does not form a curve of any particular nature, and does not necessarily give a curve which will differentiate eventually into a straight line; but I find that if the experiments form a figure on to which the bent steel *cannot* be fitted, that figure certainly does *not* consist of a single parabolic curve.*

The scale which I have used, wherever practicable, is such that the experimental error is represented by one-tenth to one-twentieth of the distance between the points, the maximum error corresponding to about one-tenth of an inch. Readings from these curves were taken with an accuracy of one-hundredth of an inch or less. Drawings on several different scales, and with several different points as origins, were made in all cases, and the labour entailed in the treatment of the results has by far exceeded that of the determinations themselves.

In cases where the experimental error was comparatively large, the results have been divided into two independent series, and each of these differentiated separately; the results being then plotted out together. In such a case it must be remembered that we may get two non-conformable points in the vicinity of a change. Sometimes the somewhat less exact method of taking the mean of every two consecutive differential points has been adopted.

Considerable difficulty has been experienced in finding any satisfactory method of depicting the curves in print. The size of the original working drawings is such that their reproduction here would

* Though differentiation will alone tell us the precise nature of any curve, I would, with the experience I have gained, generally trust as much to the drawing of the original curve as to differentiation, for showing whether that curve is continuous or not, and where the changes occur in it; but such a method would carry conviction to no one who had not made curves their special study to the same extent as I have done.

be impossible, without considerable, and often injurious, reduction; this, and the inevitable inaccuracy of printed plates, made it evident that any one wishing to examine the results in detail would plot the experiments out for himself and draw his own curves, while, to the more casual reader, small illustrations in the form of woodcuts would be more instructive and convenient than plates. Such woodcuts, therefore, have been used almost exclusively; but their size generally precludes the insertion of the numerous experimental points, and also necessitates the use of relative scales for the abscissæ and ordinates different from those which are suitable to the experimental error: they may sometimes, therefore, give an exaggerated impression of the magnitude of the changes, sometimes the reverse: I have supplemented them, however, with a statement of the scales which I have found most suitable in the various cases—Table XXIV at the end of the paper.

I must warn my readers that many of the individual changes in curvature which I mention, are admittedly of a very doubtful nature, especially when considered by themselves. Their existence can only be established by the concordant indications of independent properties, and, even with such accumulation of evidence, some of them must still remain doubtful. This is inevitable, if these changes are really due to the existence of hydrates of different degrees of complexity and stability. A study of any one portion of this paper without reading Part VII, where the results from various sources are collected and discussed, would probably lead to a very incorrect estimate of the value to be attached to the work in general, and to the conclusions which I draw from it.

Before proceeding to the details of the work, I must express my best thanks to Mr. H. Crompton for the help which he has so ungrudgingly given me in it. Not only has he made many important suggestions which will be specially noticed in their proper places, but, throughout the course of the work, he has aided me with his superior mathematical knowledge, and followed every step in the work with an interest which has almost made it his own.

PART II.—DENSITIES.

Method employed.

The piknometer is nearly always an inaccurate instrument, owing to the imperfect fitting of the stopper into the neck of the bottle, but the very nature of this inaccuracy implies that it may by chance be non-existent in some cases. Such an instrument was used in the following work. The concordance of the results obtained with it were found to be as nearly as possible the same as in the case of

Sprengel tubes,* and the errors noticed were less than might be attributed to the balance and thermometer errors, these latter being 0·0001 gram and 0·004° respectively. Consecutive determinations of the water contents (25 c.c.) of the bottle at the same temperature only once showed a difference of as much as 0·00015 gram, and a more trying test of its trustworthiness was found in the comparison of my results with water at every 2° between 6° and 38° (to be given in a subsequent communication) with the smoothed curves representing those of Kopp or Pierre; the average difference was in each case 0·000012 of the volume, or 0·0003 gram, and, not only does this error include that due to differences in the determination of the actual temperature, but it was evident that the greater part of it was due to some constantly increasing source of error, which would either be absent in a series of determinations done at the same temperature, or, if present, would have no appreciable effect on the differences between the consecutive experiments, the only important consideration in the present case.

To obtain this accuracy it is necessary to place a small glass plate over the open capillary in the stopper while the bottle is in the bath, and being weighed,† otherwise an appreciable loss occurs through evaporation, even when the liquid is below the bottom of the stopper. The increased accuracy obtained in this way may be judged by the following values, obtained when the bottle was filled with water:—

A. Without the plate—

Extreme diff. of	0·0006	gram in 4	determinations at	8°
„	0·0005	„	5	„
				18

B. With the plate—

Extreme diff. of	0·0001	gram in 3	determinations at	8°
„	0	„	2	„
				18
„	0	„	3	„
				28
„	0·00015	„	5	„
				38

The calorimeter, with its stirrer worked by an electromotor, was used as the bath, a very small flame being placed under it when temperatures above 18° were required; at, and below 18°, the temperature of the laboratory was reduced to that of the determinations. The thermometer was tapped continuously as in calorimetric work.

Experimental Error.

The water contents of the bottle were generally determined at the

* Dr. Perkin's and Dr. Nicol's results were taken for this comparison.

† A cap cannot be used while the bottle is in the bath, as it increases the evaporation, or rather, distillation, from the capillary.

beginning and end (sometimes more frequently) of a series of determinations, and any slight variation noticed was assumed to have taken place regularly. The tare of the bottle was taken before and after each day's work, and rarely showed any alteration. Thus each determination is practically dependent on one weighing only, and the error of the first differential deduced from two determinations is generally of the same magnitude as that of a single determination, since there is generally a difference of 2 per cent. between the strength of every two consecutive solutions, and the actual differences and their errors will be divided by 2. An error of one estimation figure in the reading of the thermometer (0.1 mm. or 0.004°) will, in an extreme case (with acids of high strength and high coefficient of expansion), cause an error of 0.0001 gram; the balance error may be placed at a like amount; so that 0.0002 gram, or 0.000008 of the density, may be taken as a safe limit of error in the majority of cases, both for the determinations themselves and for the differential points deduced from them. With solutions above 78 and below 10 per cent., the differences were less than 2 per cent., and the error in the differentials here will be proportionately larger.

The glass plate on the stopper of the bottle was not adopted till after the series at 18° had been finished, so that the error with these results will be somewhat greater,* and another source of inaccuracy in this case was, that the contents of the bottle were determined once for all, it not having been ascertained at that time that a change of a few degrees will effect an alteration in the capacity of a well-seasoned glass bottle (see *Phil. Mag.*, March, 1890). It would, however, be excessive, I think, to place the error of the determinations at 18° at twice the value of those at the other temperatures.

Temperature of the Determinations.

The exact temperatures at which the densities were determined were 7.978° , 17.925° , 28.064° , and $38.203^\circ \pm 0.002$. All these were ascertained by a direct comparison of the experimental thermometers with a "natural standard," the zero point of which had been recently determined; the "constant difference" of this instrument was taken to be the distance between the boiling point and freezing point, taken immediately *after* boiling, and Poggendorff's correction was applied to the readings.

To reduce my determinations of the water contents of the bottle to true densities, Kopp's determinations of the latter were taken; these are 0.999890, 0.998712, 0.996353, and 0.993070 at the four tempera-

* It would not, on an average, be nearly so much greater as the above quoted determinations with the more volatile water would imply.

tures respectively. By mistake, the density at 17.925° was taken as 0.998695 in the calculations, but this error will scarcely affect the densities themselves, and will not affect the differentials at all.*

Preparation of the Solutions.

I am indebted to the kindness of Dr. Messel for a liberal supply of the pure acid, prepared by repeated crystallisation. Mr. Crompton was good enough to estimate its strength volumetrically, starting with pure silver. His results, deduced from the examination of two weaker solutions prepared from the strong acid, were—

$$\begin{aligned} \text{A. } \left\{ \begin{array}{l} 99.953 \\ 99.816 \\ 99.704 \\ 99.857 \end{array} \right\} &= 99.8325 \text{ per cent. H}_2\text{SO}_4. \\ \text{B. } \left\{ \begin{array}{l} 99.753 \\ 99.962 \\ 99.854 \\ 99.897 \end{array} \right\} &= 99.8665 \text{ per cent. H}_2\text{SO}_4. \\ \text{Mean} &= 99.8495 \text{ per cent. H}_2\text{SO}_4. \end{aligned}$$

The value was taken as 99.85 per cent.

The second half of this lot of acid (which had been supplied in two bottles) appeared, from a comparison of about 20 density determinations at 18° , to be 0.007 per cent. stronger than the first half (the one analysed), and, as this small difference could not have been distinguished with certainty by further analysis, it was determined by these density results themselves.

Subsequent work has led me to conclude that the strength of the acid used in the present work is somewhat greater than I have taken it to be. In plotting out the freezing points of a series of acids containing somewhat more water and more anhydride than H_2SO_4 itself, we get a figure consisting of two nearly straight lines rising up so as to meet at a very sharply marked angle, and the point at which they meet must correspond, for reasons which I need not enter into at present, to the definite compound H_2SO_4 itself; the point of intersection of these lines may be ascertained to within ± 0.01 per cent. or less. In this way I have determined, by means more reliable than any analysis, the strength of a large quantity of acid used in subsequent work, and I have compared this acid with that used in the present work, the contents of the second bottle above mentioned being taken for this purpose. The comparison, made by taking the densities of 52 and 66 per cent. acids at 28° , gave

* It has been corrected in Table VII.

99.92700 and 99.92914, mean = 99.92812 per cent., as its strength, instead of 99.857, given by the analyses. This result was further confirmed by determining its freezing point, which gave 99.932 ± 0.01 per cent. as the strength.*

As all the present results had been calculated out long before this later work had afforded this more certain means of ascertaining the strength of the acid, and, as the error would not appreciably affect these results when differentiated, I did not think it worth while to alter them, except in a few cases, where the introduction of the correction will be specially mentioned. In all the other cases the percentages quoted are 712/1000000 too low.

The accurate dilution of very strong sulphuric acid is not an easy matter. Three main series of solutions were prepared as follows:—

Series A. By exposure to moist air for a month, with subsequent addition of water. Used for about every other determination of the heat of dissolution.

Series B. By addition of ice. Used in the majority of the density determinations at 18°.

Series C. By the very cautious addition of water. Used in the other density and heat of dissolution determinations.

The solutions were made up in quantities of 100 to 200 grams, using a balance reading to 0.0001 gram, so that their relative composition is accurate to about one unit in the fourth decimal place of the percentage, provided no loss of anhydride occurred in making them.

In the case of all three sets, the solutions from 58 to 16 per cent. were made from a 58 per cent. solution; those from 16 to 4 per cent., from a 16 per cent.; those from 4 to 1, from a 4 per cent.; and the weaker ones from a 1 per cent. solution. To ensure uniformity in the whole series, including the last determination—that is, the one with water itself—this water was boiled in platinum at the same time as that used for diluting the acid, and kept for the same time in bottles of the same glass as those containing the acid. Although this water evidently contained air, not the slightest difference (that is, less than 0.000004) could be detected between its density and that of freshly-boiled water.

Results obtained.

The densities (not specific gravities) at 18° are given in Table I: the full series, with differences not less than 1 per cent., are first entered, and then the more numerous ones with strong and weak

* Some acid prepared by W. Kohlrausch (*Ann. Phys. Chim.*, **17**, 69) by crystallisation gave almost exactly the same results as my stock acid, 1.8342 against my 1.834185 at 18°. Perkin found the density of some supplied to him by Messel to be 1.83748 at 15°, my acid being 1.83726 at this temperature (*Trans.*, 1886, 783).

solutions: the differentiation of alternate experiments (A and B) are given in the last four columns.* Table II contains the results at 8°, 28°, and 38°, the differentiation of alternate experiments being here given (in the few instances where it is adopted) separately.

FIG. 1.—Densities of Solutions of Sulphuric Acid.
Percentage Strength.

Fig. 1 is a sketch of the densities at 18° and 38° plotted against percentage composition. The general change in curvature at about 80 per cent., and the existence of a maximum at 97.5 per cent. are noticeable, being ignored by most text-books.

Fig. 2, A (p. 80), gives a small size illustration of the first differential obtained directly from the results at 8°. Plates 1 and 2 (p. 184) show this, as well as the results at the other temperatures, on a scale more appropriate to the experimental error and inclination of the various parts of the figures.

At 28° and 38° it was found impossible to extend the determinations below a 20 per cent. acid, owing to the liberation of air-bubbles, and the densities at these temperatures, even from 30 per cent. downwards, may be affected (though apparently with regularity) from this cause.

* Where two solutions of nearly the same strength have been examined, the results with each have been differentiated separately with those of the next stronger and next weaker solutions; we thus get two pairs of partially independent differential points at nearly the same percentages. This is a more accurate method than taking the mean of the two experiments themselves. Those solutions marked by an asterisk belonged to different sets of preparations from the others.

In each of the plates (1, 2, and 3) the experimental error of 0.0002 gram, or 0.000008 of the density, would alter the position of the points by about one hundredth of a big division of the paper. Greater errors evidently exist in some cases, and are probably due to errors in the composition of the solutions. By the omission of the doubtful determinations we get the points, marked by crosses (the "alternate determinations" of the table), each of which, it must be remembered, is a substitute for the two points on either side of it, and considerable assistance in determining where such mean points should be taken, is afforded by the fact, that the solutions used at 18° were, in nearly all cases,* different from those used at the other temperatures.

Starting at the 100 per cent. end, we have, in each case, a rapid rise, represented by a line of a strongly-curved nature, as far as about 94 per cent.; this is then followed by a long, and comparatively flat stretch as far as 84 per cent., it being so flat in the case of the results at 18°, that it is within experimental error a straight line. Then follows a more or less sharp curve, which gives place to a gentler curve: the differential reaches a maximum point at about 73 per cent., and then proceeds to fall, but not regularly, for it forms a most unmistakably wavy line, exhibiting two troughs at about 42 and 3 per cent. respectively, after which it rises again in a very abrupt manner.

Now, even the most general characteristics of this first differential are absolutely conclusive as to its not being rectilinear, and not being a single or simple curve, and, consequently, that the densities themselves cannot be represented by any single curve. No amount of smoothing could mask the wavy character of three quarters of the figure, or could reduce it to uniformity with the flat portion from 84 to 94 per cent., and with the abrupt curvature exhibited at both extremities.

Although the figure may be continuous, it can only be drawn in separate sections or curves; but to determine the exact nature, or even number, of these constituent curves, is a difficult problem. A good deal, but, as will be shown below, not so much as might be expected, depends on the amount of smoothing allowed. In the present drawing this smoothing is sufficient to render the whole figure continuous, and to allow considerable latitude beyond the known experimental error: no greater amount of smoothing is legitimate in the first instance, and could be justified, only in the event of the present drawing leading to contradictory, or to no conclusions.

The constituent curves of the figures have been extended beyond the points up to which they are applicable, simply in order to show

* Except at 5, 7, 9, and the odd percentages from 79 upwards.

more clearly which portions have had to be drawn separately. These constituent curves, in some instances, cut each other on being produced, but, in the majority of cases, they appear to meet tangentially. Curve VIII, Plate 2, between 50 and 60 per cent., is of a very doubtful character, chiefly owing to the error in the 60 per cent. solution: it does not, however, appear possible to draw curves VII and IX so as to meet without increasing the error of the points very considerably; they apparently cease to be applicable at about 50 and 60 per cent. respectively, and hence curve VIII has been drawn to represent the points between these two percentages. With Fig. D especially, this curve is very doubtful, since there may be another error at 58 per cent.; there is also some doubt as to the drawing of curve VII.

The two series of determinations at 18° , with totally different sets of solutions (A and B, Table I), when plotted out separately, show a concordance which affords strong additional proof of the correctness of the results.

The more numerous results with weak solutions (F and G, Pl. 2) show some remarkably abrupt changes, the exact position and nature of which must, however, be doubtful, owing to the magnitude of the error consequent on the proximity of the determinations.

The results with very strong solutions at 18° and 8° (F and G, Pl. 1) show the existence of a change of curvature at about 97.5, which did not appear in the 1 per cent. series owing to lack of sufficient points.* The alternate determinations only have been differentiated in this case; but, even then, the error is three times as great as with the 1 per cent. series.

The direct first differentiation having failed to reduce the densities to a rectilinear figure, the effect of a second differentiation was examined, the operation being performed on the first differential curves. Table III contains the numerical results.† A general review of them is given in Fig. 4, B (p. 87), while A, B, and E, Pl. 3, represent them in greater detail, and on more appropriate scales. The results at the other temperatures closely resemble those at 18° , which alone are represented in the plate. The constituent lines are prolonged in the drawings to render the points of junction clearer.

The second differential diagram is certainly composed of lines

* If, however, a sufficient number of readings be taken from the continuous and apparently regular first differential curve for the 1 per cent. series between 94 and 100 per cent., a second differential is obtained which consists of two straight lines meeting at about 97.5 per cent., showing a change here, in a similar, though not so precise a manner, as when we start with a curve containing all the experimental points.

† In the values in this, and some of the other tables, the decimal point has been moved six places to the right, to economise space.

which are straight within experimental error,* though it is not possible to affirm that they are absolutely straight, or that they may not be united with each other by short curved reaches. Each portion of the first differential figure which had to be drawn separately yields an independent straight line for the second differential, the only exceptions being (1), in the case of curves VII and XII at 8° (not shown here), which, on the second differentiation, yielded (though doubtfully) two straight lines meeting at 40 and 88 per cent. respectively; (2), in the case of both extremities of the figures, where the second differentials are undoubtedly curved: but by being so they really afford strong confirmation of their rectilineal character; for the ends of the 1 per cent. first differential series are, as a matter of fact, made up of one or two points taken from different contiguous curves, and, when we take for the second differentiation points sufficiently close to each other, we find that these end curves split up into straight lines. The results are shown by Fig. E, Pl. 3 (p. 184), and by the discontinuous lines in Fig. F, Pl. 3; the irregularity in the line 1 of the latter is probably due to error.

The following table gives the percentages at which the changes of curvature occur. The determination of their exact position is a matter of considerable difficulty; if the curves constituting the first differential are tangential to each other, the second differential lines will meet at the point of change, but if they are not tangential, but

TABLE A.—*Position of the Changes in the Density Curves for Sulphuric Acid.*

At 38°.	28°.	18°.	8°.	Mean.
93·5 (94·5)	94·0 (94)	97·2 (97·2)	97·7 (96·8)	97·5 (97)
— (89)	— (88·5)	93·6 (94)	94·0 (95)	*93·8 (94·1)
84·4 (84)	84·5 (85)	— (89)	88·0 (?) (88·7)	88·0 (?) (88·8)
78·2 (78)	77·5 (79·8)	84·5 (84·3)	84·5 (83·5)	*84·4 (84·2)
72·8 (71)	73·3 (69·5)	78·0 (77·5)	79·0 (79)	78·2 (78·6)
59 (58·5)	57 (62?)	72·8 (71)	73·3 (71)	73·05 (70·6)
49 (none)	50 (49·5)	58 (59)	58 (?) (60)	*58·0 (59·3)
— (42)	—	51 (51)	51 (51)	50·3 (50·5)
32 (31)	29 (28·5)	— (38·5)	40 (?)	40·0 (?) (40·3)
		29·5 (29)	30 (34?)	*30·1 (30·6)
		18·5 (19)	18·5 (19)	18·5 (19)
		8·8 (9·5)	10·5 (9·5)	*9·7 (9·5)
		4·0	3·75	*3·9
		1·05	1·05	1·05
		0·35	0·25	*0·30

* The error may be best estimated from the portion marked XII, Pl. 3; the points in it should lie on an horizontal line, since they are derived from the first differential, which was here drawn as a straight line.

cut on prolongation, the second differential lines will not meet at these points, and may not meet at all. The majority of the curves appear to be tangential to each other, but this is not always so, and, consequently, the meeting points of the second differential lines may give erroneous results. The position of the changes has, therefore, been determined from an inspection of the first differential diagram. Those which I consider to be best established are marked by an asterisk.

The values given in brackets are of some interest. The differentiation of all the densities for different temperatures was worked out at first entirely independently of each other. Each set of results standing by itself, there were no grounds for regarding any particular points as anomalous, and, consequently, the drawings were made with much less smoothing than at present. Yet the position of the changes deduced from them agrees in almost every particular with those deduced from the later drawings. The former values are those given in brackets. The indication of changes at 88 and 40 per cent. (where, however, other results prove such changes), and the low position of the change at 73 per cent.,* are the chief points where any material differences exist.

An investigation of a portion of the results at 18°, to test the possibility of drawing the first differential in sections other than those here given, was made by drawing the portion between 35 and 81 per cent. in sections of which the middle points coincided with the points of change given in the table. Omitting three determinations, which are evidently erroneous, it was found that the average error of the differential points according to this second drawing was 0·000008, as against 0·000004 according to my original drawing, and that the arrangement of + and - errors told against its correctness even more than the increased magnitude of the error. Its adoption would suppose the existence in 23 determinations of 16 errors greater than the liberal estimate of 0·000008 given on page 75 as a maximum. A similar comparison was also made by deducing equations from the points themselves instead of taking drawn curves, but the increase of error was even greater according to this method. The portion of the figure examined, it must also be noticed, is one in which the changes are admittedly but feebly marked, if not as regards their existence, at any rate as regards their exact position.

The conclusions which I draw from these density results, taken by themselves, may be briefly stated as follows :—The direct first differential coefficient forms a continuous but complicated figure, which

* The determination of the position of the change here is difficult, owing to the general change in the direction of the differential in its neighbourhood. This portion has been plotted out on many different scales, and the mean result taken.

can only be drawn in separate sections: it does *not* follow from this that each of these sections represents a definite and distinct curve; but, in the fact that each of these sections—differing considerably from each other as to their curvature—on further differentiation gives a straight line, and, in the fact that the results at different temperatures all indicate changes at the same points, we have strong presumptive evidence that such is the case, but this presumption can only be converted into proof by finding that other independent properties, and curves of a different nature, exhibit similar changes at these same points.

My conclusions as to the nature of the first differential of the densities are in direct opposition to Mendeléeff's. He first represented it as a continuous curve (*Ber.*, 1886, 379), but subsequently (*Zeit. physikal. Chem.*, **1**, 275) represented it as rectilineal, Fig. 2, D (p. 81), being a carefully enlarged reproduction of his later drawing. Above it, Fig. 2, C, I have plotted the values which he quotes, and of which Fig. D was given as a representation. That these points show the existence of more or less abrupt changes of curvature in certain regions is evident, but I am unable to see how they can be made to harmonise with Fig. D.*

Mendeléeff's values (deduced from the observations of other physicists) are given in Table IV, together with a slight modification of them, introduced so as to make them more strictly comparable with my own (the want of analogy being merely due to the fact that the actual differences are greater than with mine), and these are plotted in Fig. E, Plates 1 and 2, where they show such a very good general concordance with my own results† that they may be taken together with the latter as affording a further illustration of the effect of temperature on the figure.

Contraction on Mixing Sulphuric Acid and Water.

At the suggestion of Professor Foster, I calculated, from the densities at 18°, the contraction which occurs on mixing the acid and water in various proportions (Table V).

* Mendeléeff inferred from his mathematical theory of the effect of hydrates in solution that the first differential would be rectilineal, and *subsequently* quoted experimental results in support of this conclusion (see *Trans.*, 1887, 779). A study of his drawing of his own results with alcohol leads to the same conclusions as in the case of his sulphuric acid diagram.

A reproduction of Mendeléeff's first curvilinear drawing of the sulphuric acid differential will be found in the *Phil. Mag.*, **28**, 33; it forms a striking contrast with his second drawing, and also with the experimental points.

† The point at 57·5 per cent. alone seems to be somewhat erroneous.

FIG. 2.—Differentiation of the Densities of Sulphuric Acid Solutions.
Percentage H_2SO_4 .

FIG. 2.—Differentiation of the Densities of Sulphuric Acid Solutions.
Percentage H_2SO_4 .

The figure which these results form is, as in the case of the densities, too large for convenient manipulation. Fig. 3, A represents it

FIG. 3.—Contraction on Formation of Sulphuric Acid Solutions.
Per cent. H_2SO_4 .

on a small scale. It is a continuous, though irregular, curve, attaining a maximum at 68 per cent., and exhibiting a few more or less sudden changes of curvature, of which one at about 5%, and one somewhere below 1 per cent., are the most marked.

The first differential obtained directly is illustrated by Fig. 3, B, and, like that of the densities, can only be drawn in separate sections. A second differentiation was performed on this figure (Table VI), and the results are depicted side by side with the second differential of the densities in Plate 3. The general similarity,* though not identity, of these two figures is very striking, and, having been obtained from two figures (the first differentials) which differ entirely in their general character, afford very strong evidence that the rectilineal nature of the figure, and the position of the changes which they both indicate, are true characteristics of the properties in question, and not the chance outcome of the taste of the draughtsman.

The extension of the curvature of the end portion of the contractions from 0 per cent. to solutions of greater strength than in the case of the densities, is but the result of fewer points having been taken in the former: the curve here, and that at the 100 per cent. end, splits up into separate lines when all the determinations are plotted out, but the results are not illustrated here. The drawing of the portion X is very doubtful. The similarity of the two figures would be somewhat increased by taking the contractions on the formation of 1 c.c. (Columns 5 and 10, Table VI), instead of on 1 gram: the results would at 0 per cent. occupy the same position as those for 1 c.c., whilst at the 100 per cent. end they would occupy the position indicated by Fig. F in Plate 3.

The position of the changes of curvature indicated by the contractions and densities at 18° are as follows:—

Densities.	Contractions.	Densities.	Contractions.
97·2	97·6	51·0	47·0
93·6	93·6	29·5	31·0
84·5	85·5	18·5	19·0
78·0	78·8	4·0	3·9
72·8	74·0	1·05	0·95
58·0	60·0		

The concordance between the two sets of results is very good, and would, no doubt, have been better, had the contractions been plotted out on as many different scales, and been worked up with the same care as the densities.

Two points of importance may be noticed. (1.) The constituent

* In working out these results I was (and still am) in ignorance that such a similarity should exist.

curves of the first differential of the contractions are different in nature from the corresponding ones of the densities, since they do not meet tangentially. (2.) The maximum of contraction does not occur, as is generally supposed, at the dihydrate, 73 per cent., but at about 68 per cent., and does not coincide with the position of any sudden change of curvature.* It will also be noticed that the changes in the first differentials are more clearly marked with the contractions than with the densities, but I doubt whether this advantage would not be more than compensated by the increased calculations, and consequent chances of mistakes, which the former necessitate.

Construction of a Table of Densities.

The determinations which had been made of the densities of sulphuric acid afforded the means of constructing a fuller and more accurate table than any which existed. The special advantages which they offered for this purpose were (1) that the composition of the acid had been determined by a more certain method than mere analysis; (2) that the very numerous solutions taken were of a composition very near to round percentage values; (3) that such small corrections as were necessary to reduce them to such, could be applied with the greatest accuracy, now that the rate of change with the composition (that is, the first differential) was accurately known.

The various steps in the construction of this table (Table VII) were as follows:—

(1.) The densities at 17.925° were corrected so as to refer to water as 0.998712 (p. 71).

(2.) The percentage strength of the solutions was altered in accordance with the determinations based on the freezing points by being raised 712 millionths (p. 73).

(3.) The few obvious errors which the first differential diagram had revealed were corrected.

(4.) The values for round percentages at 7.978° , 17.925° , 28.064° , and 38.203° were deduced from the experimental values by the help of the first differential figures (Plates 1 and 2).

(5.) To detect and correct any arithmetical errors which had been made in doing so, each of the four sets of results was differentiated, and the resulting figures compared with those in Plates 1 and 2.

(6.) The results at the two higher temperatures did not include determinations above 9.6 per cent. at less than 1 per cent. intervals, nor did they extend down to percentages below 20. The former were supplied by plotting out the densities from 96 to 100 per cent., and taking readings at the required points from the curves thus obtained. The

* The position of this maximum is known to alter with the temperature.

densities below 20 per cent. were supplied by a more doubtful process :—The differences between the densities at 17.925° and 7.978° (an interval of 9.947°) were plotted out, and two curves drawn by their means; a smoothed curve (1) utilising only the differences between 29 and 20 per cent., together with that of 0 per cent.; an irregular curve (2) following the irregularity of the points from 29 per cent. downwards; the differences (d) between these two curves (0.00009 of the density at most) were taken at intervals throughout. Then the differences between the densities at 38.203° and 17.925° (an interval of 20.278°) were plotted out, these giving a curve 1' similar to 1: by assuming the differences between curves 1 and 2 to be proportional to the intervals of temperature, we get the curve 2' for these last determinations by multiplying the differences, d , by $\frac{20.278}{9.947}$ and adding the result on to the readings of curve 1'; in this way the densities at 38.203° were deduced from those at 17.925° , and the densities at 28.064° from those at 7.978° . The values thus obtained cannot be very exact, but, I think, they are probably right to the fourth decimal place.

(7.) The densities of each solution at the four temperatures were plotted out on a scale which showed 0.00002 of the densities and 0.02° (the largest scale which could be conveniently adopted); from the smoothed curve representing them, the rate of change was determined, and used for the arithmetical reduction of the densities at 7.978° to 8° , 17.925° to 18° , 28.064° to 28° , and 38.203° to 38° . The values for the other temperatures (every degree from 40° to 0°) were got by taking readings directly from the curves: these would be less accurate than the former.

(8.) As the extrapolation of these curves was extended as much as 8° below the last determination, the values at these extreme temperatures cannot be regarded as more than approximate. Their accuracy was improved by differentiating all the values at 0° , comparing the differential with the figures in Plates 1 and 2, and introducing such corrections as increased the smoothness of the curve.

(9.) Finally, as a check on the readings taken from the curves, the values for each solution at different temperatures were differentiated, and such slight corrections made as would render them more regular.

The accuracy of the values may be thus summed up:—

The percentages represent the truth within about $1/10,000$ th of their total value: their relative accuracy, however, is probably 100 times greater.

The density values at and near 38° , 28° , 18° , and 8° are more accurate than at other temperatures, but, with certain exceptions, the

actual errors are probably nowhere greater than one or two units in the fifth decimal place. The exceptions are, (1) all the solutions at temperatures below about 5° or 6° , (2) solutions of a strength of 30 per cent.* downwards at temperatures above 20° . Here the errors may affect the fourth decimal place.

About one quarter only of the full table is reproduced here; some of the values which are utilised in Part VI are not contained in it, and these are given in Table VII, A.

PART III.—ELECTRIC CONDUCTIVITY.

Crompton's examination of F. and W. Kohlrausch's determinations of the electric conductivity of sulphuric acid solutions (Trans., 1888, 116) led him to conclude that these results, when differentiated a first time, gave a continuous but irregular curve; and, when differentiated a second time, a series of straight lines, meeting at the percentages of 84.4, 73.1, 47.6, 18.5, and 3.5, corresponding to the hydrates with 1, 2, 6, 24, and $150\text{H}_2\text{O}$, thus confirming the four changes indicated by Mendeléeff's density curve, and showing, in addition, a fresh change at $24\text{H}_2\text{O}$.

I certainly think that these results, if taken by themselves, would scarcely warrant such conclusions, though perhaps they might in some points add confirmation to Mendeléeff's hydrates, assuming, as Crompton did at the time, that these were already well established. Crompton's results, I found, were also vitiated in parts by various arithmetical mistakes, and I have therefore reproduced his table here (Table VIII) in a corrected form.

Fig. 4, A gives an illustration of my drawing of the direct first differential, drawn, as in the case of the densities, with a bent ruler and having the separate sections prolonged. Fig. 4, B represents the second differential, deduced also directly from the experimental values. This appears to me to be made up of three straight lines and two curves, and the breaks indicated by it correspond in one case only (the monohydrate) with any mentioned by Crompton.

The portion VI does not contain sufficient points to admit of a second differentiation, but the position of the first differential point at 99.7 per cent. indicates the possibility of another change between 99 and 100 per cent.† Besides the breaks shown by the direct

* The actual determinations at 38° and 28° extended down to a 20 per cent. solution, but the possible liberation of air bubbles rendered the results below 30 per cent. somewhat doubtful (see p. 74).

† The values at the higher percentages (marked by an asterisk in the table) were selected by Crompton from W. Kohlrausch's determinations. I have examined the other determinations made by the same physicist, but without gaining any further information from them.

FIG. 4.—Conductivity of Sulphuric Acid Solutions.

Direct First and Second Differentials.

Per cent. H_2SO_4 .

second differential, there appears to be another at about 3·5 per cent., since, by differentiating the first differential *curve I*, I always got a second differential consisting of two straight lines meeting at this point, as shown by I',* Fig. 4, B.

Considering the paucity of the determinations, and the severe strain put upon them by two direct differentiations, I think that they are fairly conclusive in favour of the second differential being rectilinear, and Crompton has done good service by drawing our attention to this fact.†

The positions of the various changes which I consider to be shown are the following, although the indications can in no case be taken as proof:

99·5, 96·8, 94*, 84*, 63 (or perhaps 73‡), 37·5, 9·5*, and 3·5 per cent.

Those marked by an asterisk are, I think, the best established.

I am glad to be able to state, with Mr. Crompton's authority, that he agrees with me in the criticism which I have here given of these conductivity determinations, and that he considers that the interpretation which he originally put on them must naturally fall through, now that it appears that Mendeléeff was mistaken in his statements as to the densities, for Crompton never regarded the conductivity results as sufficient to stand by themselves, but only as affording additional proof to a theory which had (as he then imagined) been already satisfactorily established by other facts.

PART IV.—HEAT CAPACITY.

The unit heat capacity of a body is measured by the number of units of heat required to raise a unit mass of it 1°; its specific heat is the ratio between its heat capacity and that of some standard substance under the same conditions, the variable standard, water, being generally selected. The two terms are precisely analogous to "density" and "specific gravity;" the former measures a property of the substance, the latter measures the difference between the properties of two substances.

The unit of heat being the amount necessary to raise 1 gram of water from 0° to 1°, it is most important in ordinary calorimetry to

* Placed one division of the paper higher than it should be. The numerical values are given in Table IX.

† The curvature of line II might, perhaps, be reduced to straightness, if we had sufficient points to indicate changes at 9 and 19 per cent., such as my density results show.

‡ According to the first differential, the position of this change might be 63 or 73 per cent., the second differential favours the former view; but a small error in one determination only would alter the case.

know the heat capacity of water at different temperatures. Such determinations as have been made of it show, unfortunately, very large discrepancies, Regnault's results, which are known to have been miscalculated, being generally taken. The value at 18°, deduced from the four most concordant sets of determinations available,* is 1·006; in the present work I took 1·005 by mistake.

The most accurate method of general applicability known for the determination of the heat capacity of weak solutions, consists in dissolving some strong solution of the same substance in water at two different temperatures. The difference in the heat evolved is equal to the difference between the total heat capacities of the reagents (water and strong solution) and that of the resulting weak solution.

$$H - H' = (U - V)(t' - t).$$

To apply this, various quantities of a sulphuric acid solution of 58 per cent. strength† were dissolved in water at 15° and 21° (t and t'): the rise of temperature noticed being r and r' in the two cases, W being the weight of solvent water, w that of the strong solution, w' the weight of the apparatus, and c , c' , c'' and c_i the heat capacity of the water, the strong solution, the resulting weak solution, and the apparatus respectively, we get—

$$[(W + w)c'' + w'c_i]r' - [(W + w)c'' + w'c_i]r = [(Wc + w'c_i + wc') - (w'c_i + (W + w)c''] (t' - t),$$

whence

$$c'' = \frac{(Wc + wc')(t' - t) + w'c_i(r' - r)}{(W + w)(r' - r + t' - t)}.$$

A drawback to the general use of this method is, that the heat capacity of the strong solution must first be known; but it need be known approximately only, since an error of 1 per cent. in its value will introduce an error of only 0·0005 in the heat capacity of a 5 per cent. solution, and will affect all the results regularly in inverse proportion to the strength of the solution obtained.

The method assumes that the heat capacity of the liquids concerned is the same at the lower as at the higher temperature. This is not the case; but the difference is very small. Judging by Marignac's results, the difference at temperatures 6° apart would be only about $\frac{1}{5000}$ th for most 5 per cent. solutions, and the error

* Regnault's recalculated by Bosscha, Baumgartner's, v. Münchhausen's and Henrichsen's. (See Landolt and Börnstein, *Tabellen*, 176.)

† A solution of this strength gives a resulting solution of the maximum strength with the smallest possible rise of temperature.

thereby introduced would be almost entirely counterbalanced by the heat capacity of the water varying in the same direction as that of the solution.

The determinations were made in the same way as those mentioned in Part V. As it was practically impossible to take exactly the same weight of the strong solution at the two temperatures, the results obtained were plotted out into curves, and the readings of these curves, at points near those at which the actual experiments existed, were taken. Two determinations at least were made near each point.

Two opposite thermometric errors of 0.0005° in the determination of r and r'^* would cause an error of 0.00017 in the heat capacity found. With sulphuric acid, the rapid increase in the heat evolved with the amount of strong acid used renders it impossible to plot out the values for this evolution on a sufficiently open scale, and the error may be doubled from this cause alone. This source of error was reduced in the present case by taking the readings for r (and r'), not only from the curves directly representing them, but also from curves in which the values for r/w were plotted out. The error, therefore, in the heat capacities might probably amount to 0.00025 ,† and, judging by the regularity of the results themselves, it never appears to exceed this.

The determinations were extended to a 12 per cent. solution by a second series of determinations, in which the strong acid was dissolved in a 4.6 per cent. acid, instead of in water. The heat capacity of this solvent acid had been determined by the first series, and the two series were made to overlap.

Results obtained.

The results with the weaker solutions are given in Table X, the experimental values being quoted in the first four columns. The values for r and r' for a round number of grams of solution, w , as determined from the curves directly representing these quantities, are given in the sixth and eighth columns, whilst the mean of these values and those deduced from the r/w and r'/w curves are given in the seventh and ninth columns. With the stronger solutions (Table XI) the values for r and r' were deduced solely from the r/w and r'/w curves.‡

* These, of course, are not dependent on the differences between two experimental values *only*.

† The average difference between Thomsen's duplicate determinations is about 0.003 .

‡ Anyone plotting out these values will notice irregularities in the case of r/w

Fig. 5, A illustrates the diagram representing these results. It consists of four distinct curves, of which II and III are the best established; these bend in opposite directions, and do not appear to meet at all. The same want of continuity seems to exist between curves I and II, whilst there are not enough determinations (only two) to settle the nature of curve IV (the dotted line), and whether it touches curve III, or not. There are 4, 9, 11 (three of series 1 and

FIG. 5.—Heat Capacity of Sulphuric Acid Solutions.

eight of series 2), and 2 experimental points on these four constituent curves respectively. The break at 4 per cent. depends on a

for about 3 grams, and r'/w for about 8.5 grams, which are somewhat too great to be attributed to error. In my drawing I have erred on the safe side, by smoothing out these irregularities. The values in brackets in the table show what differences their not being smoothed out would make.

difference of 0.0013, or five times the experimental error, besides, of course, being established by the general direction of the curves on either side of it: the exact position of the change near 1 per cent. cannot be determined, and, indeed, the recognition of any change at all here is a difficult matter; it is best done by carefully drawing curve II, and producing it to 0 per cent., when it will be found that all the points below 1 per cent. lie above the prolongation.*

The first differential obtained directly (Tables X and XI) is shown in Fig. 6, B: the changes are fairly well marked, but the nature of the constituent curve is somewhat doubtful, owing to the curvature being very small in comparison with the experimental error. A second differentiation (Table XII and Fig. 6, C) reduces these curves to straight lines. Fig. 6, A represents the first differential obtained from the smoothed curve, Fig. 5, A (Table XIII): it differs from the direct first differential in representing the constituent portions I and III as straight lines, instead of curves; this is but a natural result of the process of smoothing, and of the smallness of the differences on which the curvature in this case depends.

FIG. 6.—Heat Capacity of Weak Sulphuric Acid Solutions.

First differential from the curve and from the experiments. Second differential from the latter.

* In this, and other cases, it is sometimes advantageous to draw some particular curve on a more open scale than could be done accurately by plotting out the experiments themselves. This may be effected by drawing the curve first on a small scale, taking readings from this, plotting these out on a large scale, and drawing a smoothed curve through them.

Whether the heat capacities require one or two differentiations to reduce them to straight lines, must, therefore, be regarded as somewhat uncertain, the evidence being in favour of the latter view.

The positions of the changes are—

9·85, 4·0, and 1·0 per cent.,

of which the first two are very clearly marked.

A point of some interest arises as to these curves. The heat capacity must be a continuous function of the strength of the solution, and hence the drawings here made of the results cannot be correct at the points near 1 and 4 per cent., where the curves are represented as not meeting each other. I think it probable that the main curves, I, II, and III, are connected by short curves of a totally different nature, resulting from, and representing, a state of passage between the different conditions which exist in the main curves. This is supported, perhaps, by the fact that there is one experimental point at 4·1 per cent, exactly between the two curves. No such intermediate condition is noticed in the density or heat results, but in the heat capacity we are studying a property of a nature totally different from that in these other cases; the density is a property under *fixed* conditions, and the heat of dissolution is a measure of a portion of the potential energy in the substance, also under *fixed* conditions, whereas the heat capacity is the work which has to be expended on the substance in order to *alter* its conditions.

The smallness of the difference between the sum of the heat capacities of the strong acid + that of the water (or 4·6 per cent. acid), and that of the resulting weak acid, is noticeable, and might excuse a superficial observer in concluding that no chemical action occurred. In series I we find—

Per cent. H_2SO_4 .	c'' .*	$c + c'$ †	Diff.
2·67	0·98084	0·98396	—0·00312
5·06	0·96125	0·96510	—0·00385

while in series II the cases of maximum difference are—

Per cent. H_2SO_4 .	c'' .*	$c + c'$ †	Diff.
8·42	0·93631	0·93611	+0·00020
9·55	0·92668	0·92739	—0·00071

Calculating pure H_2SO_4 (heat capacity 0·3332) and water as the constituents, the differences, though greater, are still small—

* Heat capacity of resulting solution.

† Heat capacity of components.

Per cent. H_2SO_4 .	c'' .*	$c + c'$.†	Diff.
3	0.97812	0.98475	—0.00663
6	0.95452	0.96469	—0.01017
9	0.93137	0.94454	—0.01317
12	0.90862	0.93438	—0.02576

Fig. 5, B (p. 91) represents the heat capacities of strong solutions used in the subsequent heat of dissolution determinations, as deduced from Berthelot's table (*Mec. Chim.*, 1, 496), which collects the values of Thomsen, Marignac, and Pfaundler. Beyond illustrating the general irregularity of this property as a function of percentage composition, and the probability of the more marked changes occurring at about 10, 50, and 73 per cent., they can afford no definite information as to the nature of the figure, through lack of sufficient points.

PART V.—HEAT OF DISSOLUTION.

In 1875 Berthelot (*Ann. Chim. Phys.* [5], 4, 446) published his determinations of the heat evolved when solutions of different strengths of the commoner acids and alkalis are diluted with an excess of water, and concluded that there were signs of changes near certain points, indicating in an approximate manner the existence of hydrates in solution. His determinations were numerous, but would not seem to be accurate enough for settling the question,‡ even if sufficient data had been quoted to permit of their recalculation into a form suitable for mathematical analysis.

Thomsen afterwards (*Thermochem. Untersuch.*, 3, 1—114) went afresh over the same ground,§ and also investigated the cases of many salts as well. His conclusions—that the action was regular, and that hydrates higher than those known in the solid form did not exist in solution—were in direct opposition to Berthelot's, and have gained a ready acceptance amongst chemists.||

Thomsen's conclusions are indeed remarkable. The points determined on each curve rarely exceeded six¶ (sometimes there were only

* Heat capacity of resulting solution.

† Heat capacity of components.

‡ The initial temperatures sometimes varied 4° or 5° , and the heat capacities used were very uncertain.

§ He had previously (*Ber.*, 1870, 496) investigated sulphuric acid, as also had Hess, Graham, Abria, Favre and Silbermann, and especially Pfaundler (*Ber.*, 1869, 122).

|| "The generally adopted 'hydrate theory' of solution can scarcely be expected to survive the dissemination of Thomsen's researches" (P. Muir, *Elements of Thermal Chemistry*, 167).

¶ And these points were least suited for showing irregularities, since they corresponded to simple molecular proportions (see a remark of Crompton's, *Proc.*,

three or four), a number scarcely sufficient for determining even the general character of the reaction, and yet, in many of the cases where they appeared sufficient, they showed that this general character was eminently irregular. In 10 cases out of 53, the value of the reaction changes its sign, in two others the irregularity is palpable, and, even in those actions of greatest apparent regularity, it is found that no simple equation can represent all the results. The equations which express the results with strong solutions generally give values too low when extended to weaker ones* (see *Chem. News*, 54, 215); nor can they be extended in the opposite direction with any better success. Thus, Thomsen has extended his curve in the case of copper chloride so as to give the heat of dissolution of liquid $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; if he had extended it further still, so as to get the value for CuCl_2 itself, he would have recognised the inadmissibility of such a process; for the value obtained (9233 cal.) gives, as the heat of formation of liquid dihydrate from its liquid components, 1434 cal., whereas this quantity should be nearly identical with that of its formation in the solid state from the solid components, which direct experiment gives as 3540 cal.† With calcium chloride the case is still more striking. Thomsen's determinations give—

$$\text{CaCl}_2 \cdot 10\text{H}_2\text{O} + m\text{H}_2\text{O} = \frac{m}{m + 5.08} 2,508,$$

from which the heat of dissolution of liquid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ should be 11801 cal., instead of 6640 cal., as my direct determinations prove it to be, and that of liquid CaCl_2 should be -3460 cal., a negative quantity, whilst even the *solid* salt gives a positive evolution of as much as 19250 cal.

Thomsen's results with sulphuric acid are of special importance, not only from his having studied this acid more fully than any other substance (12 points were determined!), but that the seeming regularity of these results is for ever being urged against the hydrate theory of solution. The language in which he expresses his con-

1888, 38, of which Thomsen's values for SO_3 and $\text{SO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ form excellent illustrations; the former lies within experimental error on the extension of his curve for $\text{H}_2\text{SO}_4 + n\text{H}_2\text{O}$, the latter is very far removed from it).

* Thus Thomsen's equation for sulphuric acid is inapplicable beyond $19\text{H}_2\text{O}$, that for nitric acid beyond $5\text{H}_2\text{O}$, and that for hydrochloric acid seems to be inapplicable everywhere.

† If the heat of fusion of the hydrated salt is (as Person concluded from the instances which he examined) equal to the sum of those of the anhydrous salt and water present, the identity would be absolute. I think it probable that in many cases this equality does not hold good (indeed there are instances in which it certainly does not), but the discrepancy could hardly make as much difference as in the instances quoted above.

clusions as to the curve representing them is of a most positive and uncompromising character. "One sees," he says (III, 8), "that the fixed points can be united by a regular curve, and that throughout, there are nowhere any signs of an irregularity, such as would indicate the formation of definite hydrates." He then gives the equation for the hyperbola representing this curve, and a table showing the near agreement of the found and calculated values for $\text{H}_2\text{SO}_4 + x\text{H}_2\text{O}$, when the values for x are 1, 2, 3, 5, 9, 19, and 1600, and then proceeds, "One sees that the differences are very small, and are positive or negative indiscriminately.* There is, therefore, no doubt but that the heat evolved on diluting liquid sulphuric acid with water is a continuous function of the water used, and excludes absolutely the acceptance of definite hydrates as existing in the solution."

The concordance of the found and calculated values for these seven points is, indeed, remarkably good, but, even if it were absolute, it could scarcely warrant such a conclusion, especially when it is remembered that the portion where this agreement exists is but little more than *one per cent. of his whole curve*,† and that throughout the remaining *ninety-nine hundredths* of it there is no agreement at all, the differences reaching as high a value as 683 cal.

If any conclusions at all can be drawn from Thomsen's work, they must certainly be in favour of the probable irregularity of the actions in question.

* If the differences between the calculated values and the experimental points are tabulated for *all* of the latter, the indiscriminate arrangement of the + and - errors is by no means apparent. They are—

$x =$	1,	2,	3,	5,	9,	19,	49,	99,	199,	399,	799,	1599
Diff. =	-3,	+14,	-30,	-27,	+66,	-59,	-544,	-683,	-636,	-467,	-180,	+17

Had Thomsen extended his determinations to more dilute solutions, he would have found still greater differences. My value for $x = \alpha$ (determined by the extension of an experimental curve which reached as far as 0.04 per cent., or 15,000 H_2O) compared with the value calculated by his equation, gives a difference of +3233 cal.

† Measured along the abscissæ, which represent the number of molecules of water added to H_2SO_4 : the concordance is exhibited as far as the 19th H_2O : the curve extends to 1599 H_2O . Measured along the curve itself, the relative proportions of the regular and irregular parts would depend on the scale used: with the scale adopted by Thomsen in Fig. AB, Table I, vol. iii, the regular part would measure 1.8 per cent. of the whole figure.

It is but fair to state that Thomsen afterwards (*loc. cit.*, p. 56) suggests that this aberration, which must invalidate his conclusions, may be due to the contraction on mixing, but he offers no evidence in favour of such a view, and no explanation of why the effect of this action should be appreciable only in those cases (weak solutions) where it occurs to the smallest extent.

Graphic Representation of Results.

The question as to the plotting of the results becomes of paramount importance when a mathematical analysis of the curves obtained has to be performed.

The drawings which I give in Fig. 7 refer to calcium chloride, and are better for the purpose of illustration than the more complicated results with sulphuric acid; the heat curves, however, are very similar in the two cases.

Fig. 7.

When the densities are plotted against percentage composition (A), or when the molecular volumes are plotted against molecular composition (B), rectilinear or parabolic figures are obtained in each case, differing only in distribution of the experimental points along them (the same six experiments are plotted in all the figures); but, if we plot the densities against molecular composition (C), or the molecular volumes against percentage composition, we get a complicated hyperbolic figure, most unsuitable for mathematical analysis. Yet such is the method of plotting which has heretofore been adopted in the case of all heat results; the heat of dissolution, or formation, of a *fixed* weight of the dissolved substance (the so-called "molecular" heat of dissolution, but molecular in a sense different from that of molecular volume, since it bears no reference to the molecular composition of the *solution*) being plotted against the molecular com-

position of the solution. Fig. 7, F (p. 97) represents the heat of dissolution thus plotted; if inverted it will represent the heat of formation (F^m) as plotted by Thomsen.

As any quantity expressing the heat of dissolution in a manner corresponding to "molecular volume" has no meaning (such as molecular weight $\div$ heat of dissolution), we must abandon the representation according to molecular composition altogether. I plotted out in the first instance the heat of dissolution of various solutions containing gram-molecular proportions of the salt, against percentage composition (E). On differentiating this, however, no satisfactory results could be obtained, another apparently continuous curve being produced. Mr. Crompton then suggested that, instead of plotting the heat of dissolution of gram-molecular proportions, we ought to take the heat of dissolution of 100 grams of the solution (Fig. D). Satisfactory results were obtained in this way. Similar results would no doubt be arrived at by taking the heat of formation of 100 grams of the solution; such a curve, instead of falling from a maximum down to zero, would start at zero (at the point where no water was present), rise to a maximum, and then fall back again to zero.

Method of Experimenting.

Two classes of determinations were made:—

1. "Mixing" experiments, in which 420 c.c. of the solutions were mixed with successively equal volumes of water. A detailed description of the new mixing calorimeter devised for this purpose, and the method of using it will be found in the *Phil. Mag.*, March, 1890.

2. "Dissolution" experiments, in which 4 to 30 grams of a strong solution were dissolved in 600 c.c. of water (*ibid.*).

Calculation of the Results.

To be comparable, all the results must be calculated out for the same final dilution: this must be not less than that obtained in the determination with the weakest solution used (0.04 per cent.). Theoretically the dilution should be infinite, and the heat evolved for infinite dilution is in this case easily obtained by plotting out the results (for dilution down to 0.04 per cent.) against percentage composition, and extending the curve as far as 0 per cent. All the present results are expressed for infinite dilution.

Let t and t' be the initial and final temperatures in any determination, where w grams of solution is mixed with W grams of water, the water equivalent of the apparatus being $w'c$, and the heat capacity of the resulting solution being c'' , then, the heat developed by diluting

100 grams of the solution to the same extent as in the actual experiment (D^{100} observed) will be—

$$D^{100} = \frac{100[(W + w)c'' + w'c_1](t' - t)}{100}.$$

To reduce the values for D^{100} in the various mixing experiments to what they would be if the final strength of the solution was the same as in the last determination of the series, we must add to each the heat evolved on diluting the (about) 200 grams of weak solution obtained, with a further equal volume of water (determined in the next experiment), then that evolved on diluting the resulting (about) 400 grams to a similar extent, and so on, till the last stage of dilution is reached. These values are then plotted out, and the heat evolved on diluting the last solution with infinity of water is found, and the whole results recalculated with this as the zero point. Thus the heat of dissolution of any solution to infinity (D_{∞}^{100}), or even to a state of considerable dilution, depends not only on the actual determination with that solution, but on all the other determinations with weaker solutions increased in geometrical proportion. "The correction" for infinite dilution to be applied to the observed values in the case of sulphuric acid is particularly large: with an 18 per cent. solution it amounts to 656 cal., that is, twelve times the quantity measured (47 cal.) in the actual determination.

It is evident from this, how inadvisable it is to extend the mixing experiments to solutions of greater strength than is absolutely necessary.

With the dissolution experiments, the "correction to infinity" is relatively small, since the strength of the solution obtained in any determination is far less (2.5 to 0.25 per cent.) than in a mixing experiment; but even here it attains very large proportions, sometimes amounting to nearly 3000 cal., and sometimes exceeding the evolution measured in the determination itself. The correction* has to be deduced from the curve representing the results of the mixing experiments, very carefully enlarged in the manner indicated on p. 92.

The so-called "molecular" heat of dissolution is deduced from that of 100 grams by multiplying the latter by the molecular weight of the anhydrous substance, and dividing by the percentage composition of the solution.

* $D_{\infty}^{100} = D^{100} \text{ obs.} + \left(D_{\infty}^{100} \frac{W + w}{w} \right)$, in which D_{∞}^{100} is the heat of dissolution of 100 grams of a solution of the strength of that resulting in the determination, and W and w the weights of water and strong solution taken respectively.

Experimental Error.

The average difference in the readings of the heat evolved as given by the two thermometers used together in the mixing calorimeter, was 0.0008° ,* which would represent a difference of only 0.13 cal. in the two values for D^{100} in the one determination; but the values for D_{∞}^{100} would contain an accumulation of similar errors from all the determinations with weaker solutions, so that it is impossible to estimate the probable accuracy of these latter values, except by comparing them with the dissolution experiments (see below).

In the dissolution experiments, the average difference in the independent duplicates was found to be 7.6 cal. (in the corrected values for D_{∞}^{100}), so that the mean error of a single determination is 5.4 cal., and that of the mean of two determinations is 3.8 cal.,† the probable errors being two-thirds of these quantities. Two, and often three, determinations were made at each point.

This error is certainly very small, since an error of only 0.001° (0.1 mm. of the thermometric column) in the rise of temperature measured would, on the average, make a difference of 4.1 cal. in each result, and the errors entailed in the application of the large correction for dilution to infinity could not, from a *a priori* considerations, be placed at less than double this value. Yet the smallness of the actual error is well established by some 150 determinations in the present case, and in other cases where the correction to infinity is smaller, and the weight of solutions taken can be larger, the mean error deduced from some 200 experiments is less than half the value here given.

Besides the magnitude of the "correction" and the small weights of strong acids which have to be taken,‡ there are other special sources of error in the present case, owing to the rise of temperature and, consequently, the rate of cooling being more than usually great, and owing to the tubes from which the acid has been emptied having to be weighed out on a delicate balance as well as may be, between the one minute intervals when the thermometer is read, and while, often, a drop of the hygroscopic acid is running down the outside of the tube.

In differentiation we depend on the relative accuracy of consecutive observations, and the error in comparing these would not, I think, be much greater than in comparing duplicate experiments with the same solution: the only cause (provided the compositions of the solutions are known correctly§) which could make it larger would be

* Deduced from more determinations than the present paper contains.

† Varying from 6 to 2 cal. with the strength of the solution dealt with.

‡ To reduce the great rise of temperature.

§ Errors in the percentage composition of a magnitude such as are shown to be probable from the irregularities in the first differentials of the densities, would scarcely

the different strengths of the final solutions, and, consequently, their different heat capacities, and the difference in the correction for infinity; but the quantities taken in duplicates generally differed so much, that there would often be a greater difference in final strength with the duplicates than with consecutive determinations. Such a difference in the quantities taken, though it increases the divergence of the duplicate results from the mean, tends to bring that mean nearer the true value.

Results obtained.

Of the two series of mixing experiments (Table XIV), the first and fuller one was, owing to the frequency of the changes exhibited with very weak solutions, alone available for extension so as to get the value for infinite dilution. A curve obtained by plotting out the values for D_{∞}^{100}/p was in this, and other cases, found more adapted for extension to 0 per cent. than the D_{∞}^{100} curve itself. In the calculation of the last determinations in both series, errors were subsequently discovered (indicated in the table), but, as the difference made by them was far within the limits of experimental error, it was not thought worth while to recalculate the results in consequence. The stronger solutions used in these experiments were made up independently of, and therefore had not quite the same composition as, the solutions obtained in the various preceding determinations; to apply the small corrections necessary on this account, the results had first to be calculated on the assumption that the two solutions in question had been identical (values given in the column headed D_{∞}^{100} , approx.), the correction determined from the curve which these values formed, and then the various results recalculated.

Leaving these for the present, the dissolution experiments (Table XV) will be examined first.

On a small scale they form a curve of great seeming regularity, very similar to that shown in Fig. 7, D (p. 97). The difficulty of treating them on a scale commensurate with the experimental error is considerable, owing to the rapidity of the increase and the magnitude of the quantities measured. They were generally treated in three overlapping portions, drawn to different scales, the total length of which was some 13 feet.

The two extreme portions of what I consider as being the smoothed curve representing these results are illustrated, though very imperfectly, by Fig. 8 (next page). The whole figure is continuous throughout,

have an appreciable effect on the heat of dissolution results, since the error thereby caused in the plotting of the results is partially counterbalanced by an opposite error introduced into the calculation of the magnitude to these results.

except in the vicinity of 20 and 50 per cent., where the discontinuity must, I think, be due to some error. Like the density curves, it can only be drawn in separate sections, but, unlike these, the sections all cut each other on prolongation. The average divergence of the experi-

FIG. 8.—Heat of Dissolution of Sulphuric Acid Solutions.

mental points (the means of two or three determinations) from the curve drawn was almost exactly what it should be, according to the estimate of the error deduced above from the difference between duplicates, and varied from 6.5 cal. with the stronger solutions (100 to 80 per cent.) down to 2.1 cal. with the weaker ones* (30 to 5 per cent.). There are, on the average, about six mean experimental points on each section. Of the various changes, that at 9 per cent.

* Somewhat larger errors may be noticed in this and in other cases, where two solutions of nearly the same strength have been used. But in such instances the second determination was made owing to there having been some doubt as to the accuracy of the first: they would, therefore, lead to a wrong estimate of the average error.

On differentiating this smoothed curve (Table XVI), the results

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illustrated by Fig. 9, B (p. 103) were obtained, each separate section of the original figure yielding either a curve, or a straight line, as a first differential. Two details may be mentioned:—(1) that a drawing of the original curve may be made, obliterating the change at 36 per cent., but that the differential from this drawing (given at the end of Table XVI) still shows a change here; (2) that no change at 84 or 73 per cent.—the composition of the mono- and di-hydrate—is noticeable in the experimental curve, and only becomes apparent after differentiation.

The first differential curve was then differentiated (Table XVI), and a discontinuous figure, which was rectilineal throughout, was thereby obtained (Fig. 9, E, p. 103). The comparative magnitude of the changes at the higher percentages is the chief point to be noticed respecting it.

On reconsidering these results, grave doubts were entertained as to the correctness of the conclusions drawn. It seemed possible that there might be some unknown sources of error in the experiments, and that the splitting up of the curve was but a consequence of the manner in which the figure had been drawn.

To settle this point, the results were again plotted out, but on a scale about half as open as before, and the curve was drawn without paying any attention to the position of the changes previously noticed, and purposely smoothing out all seeming irregularities. The only part which could not legitimately be smoothed over was the change at 9 per cent.; the curve therefore starts at this point. The readings of this curve will be found in Table XVII, and the differential deduced from them is illustrated by Fig. 9, C. It certainly offers ample justification for the interpretation given to the large scale drawing; for, in spite of the excessive smoothing, it still shows the majority of the changes which the latter had shown; their exact position has in some cases been slightly altered by the smoothing, and in four cases—namely, at 97·5,* 88,* 84, and 36 per cent.—they have been entirely obliterated, but the general agreement is far better than could have been expected. Table B, p. 109, gives the position of the changes shown by the two drawings.

The application of a direct differentiation to the experimental values proved a matter of great difficulty, and no success was obtained till the error was diminished by treating them in two series (last two columns of Table XV).† The result of this treatment, how-

* Of these two, however, there were some indications; those at 84 and 36 per cent. were very feebly marked even in the large curve.

† See footnote, p. 74; there are here so many pairs of differential points deduced from determinations with solutions of nearly the same strength, that I have marked them A and A', &c.; A being a differential deduced from two deter-

ever, is to diminish the curvature of the constituent parts of the differential, and to obliterate two of the more feebly marked changes at 84* and 97·5 per cent. Fig. 9, A (p. 103) illustrates the figure thus obtained.† On applying a second differentiation to this (Table XVIII), a rectilinear figure was the result, closely resembling the second differential obtained from the smoothed experimental curve (Fig. 9, E), except in the parts between 80 and 88 per cent., and between 94 and 100 per cent., where the nature of the first differential was uncertain, and the straight lines here drawn to represent it gave two horizontal lines on the second differentiation. No illustration of this second differential is here given.

The remaining drawing, D, in Fig. 9, is worthy of special attention. It shows the results of pushing the smoothing process still further than was done in what I have termed the ultra-smoothed curve, which gave the differential, Fig. 9, C. If, instead of taking readings from the ultra-smoothed experimental curve at every 1 or 2 per cent., we take them at considerable distances, say, at every 5 per cent., greater smoothing will be produced in the differential obtained from them; but, though the majority of the changes are thereby obliterated, the magnitudes of those near certain points are intensified, and we get Fig. 9, D, which cannot be drawn except as three distinct curves, one of which bends in the opposite direction to the other two.

The mixing and dissolution experiments have to be treated separately, for, where they overlap (5 to 18 per cent.), there is a considerable difference between them. This difference reaches as much as 16 cal., but, as it would be caused by a single error of 0·06 cal. or 0·0003° in the experiment with the weakest solution (0·08 per cent.)—supposing all the other determinations to be absolutely correct—it must be considered to show a remarkable degree of concordance.‡

In dealing with these mixing experiments, the rapid increase in the heat evolved renders it necessary to plot them out to several different scales. The most extensive of these is illustrated by

minations marked A, and A' being one from one determination marked A and one marked A'.

* The irregularity of the points near this percentage indicated the probability of some change. But there were not enough points to define it.

† The line XVIII is, of course, not established, and is only of use in showing the existence of a change above 99 per cent. The drawings of the various smoothed experimental curves do not extend beyond this percentage.

‡ Better concordance might be obtained by re-calculating the mixing experiments, starting with the strongest solution and working downwards, instead of starting with the weakest solution and working upwards, as in the first case. The actual value to be taken for the strongest solution would have to be deduced from the results of the dissolution experiments, a considerable number of these being performed at the point in question.

Fig. 10, A :* the changes which occur in it, of which the best marked one is at 4 per cent., are of the same character as those in the region

FIG. 10.—Heat of Dissolution of Sulphuric Acid Solutions.

of stronger solutions. The general change in direction at the extreme end is very remarkable: it is illustrated on an enlarged scale in Fig. 10, B. The curve here is of such a nature that it cannot be drawn conveniently with a bent ruler; and more satisfactory results were obtained by plotting out the values for D_{∞}^{100}/p , as shown in Fig. 11.

This figure is well worthy of attention. The results of the second series of experiments are distinguished from the others by crosses; the point at 0.88 per cent. appears to be somewhat anomalous; but, whether we include it or omit it (as has here been done in making the present drawing), it will be apparent that the inclination of the curve becomes very abrupt somewhere about 0.4 per cent.,† and that

* The highest determination, that at 18 per cent., is too far from the next lower one (9 per cent.) to be of any service in drawing the curves.

† It may be here noted that this remarkable change could not have been revealed by Thomsen's determinations, since his results ended with a 0.34 per cent. solution. The importance of extending any series of determinations to the greatest dilution possible is rendered very evident by the present results.

There are two slightly different drawings of this curve below 0.16 per cent.; both are treated in Table XX.

Fig. 11.—Heat of Dissolution of Sulphuric Acid Solutions.

about 0.1 per cent. it alters its direction again, bending in the opposite direction.

If this form of plotting the results be extended to stronger solutions, the curve again bends upwards, presenting on the whole the same general appearance as Fig. 7, E (p. 97), the values for D_{∞}^{100}/p being of the same nature as those for the so-called molecular heat of dissolution.

The differentiation of the mixing experiment curve (Table XIX)* is illustrated in Fig. 12 (next page). The first differential, A, is composed of well-marked curves; whilst the second one, B, is rectilinear within experimental error. The comparative magnitude of the changes with very weak solutions may be judged by the portions III and IV, which are reproduced as dotted lines in Fig. 9, B and E. On a larger scale, a certain amount of curvature in the second differential line I is noticeable, but this is probably due to error. A difference in the nature of the curvature of line V in the first differential, as shown by the mixing or dissolution experiments, will also be noticed, and is no doubt due to the rapid accumulation of small errors in the former.

The number of changes which existed with weak solutions showed that it would be useless to perform a direct differentiation of the experimental values, owing to the comparative paucity of the determinations.

* The values for the weakest solution were deduced from readings of the D_{∞}^{100}/p curve.

FIG. 12.—Heat of Dissolution of Sulphuric Acid Solutions.
First and Second Differential from the Smoothed Curves.

The positions of the various changes shown by the heat of dissolution results are collected in the following table, B. The ultra-smoothed curve gives approximations only: the results obtained from an examination of the smoothed experimental curve (together, sometimes, with that of the first differential deduced from it) are more trustworthy than those from the direct first differential. The mean does not include the values in the first column.

The concordance of the position of the changes, as determined by the two methods of analysis, is very good; yet, the heat results generally cannot be regarded as very satisfactory when considered by themselves, and, looking at the number of determinations which were made, and the care which was taken about them, they proved somewhat disappointing.

Perhaps such a result should have been anticipated, owing to the thermometer being an instrument 50—100 times less delicate than

TABLE B.—*Position of the Changes in the Heat of Dissolution Curves.*

From the 1st diff. of the ultra-smoothed curve (approximate).	From the smoothed curve.	From the direct 1st diff. curve.	Mean.
—	99·5	99·2†	99·35
Possibly 97·5	97·3	—	97·3
94	93·5	93·8	93·83
87	88·9	89·0	88·95
—	84·0	—	84·0
76*	79·0	79·0	79·0
—	73·0	73·0	73·0
61	58·3	60·0	59·15
49	49·5	49·0	49·25
—	35·5	39·0	37·75
28	28·0	28·5	28·25
20	19·3	19·0	19·15
9·5	8·7	9·3	9·0
	4·07		4·07
	1·13		1·13
	0·40		0·40
	0·11		0·11

the balance on which the densities depend, and to the fact that the results of the individual determinations cannot be utilised directly, as the densities can, without the application of complicated calculations and corrections. Many of the changes are so feebly marked that much uncertainty must prevail as to their existence and position; it was only by the expenditure of an amount of time and trouble, of which the present account can give but a faint idea, that any definite conclusions could be arrived at. It is not difficult to see the reason of this. The magnitude of the individual changes appears to bear no relation to the magnitude of the total heat evolved, or to the rapidity with which this increases with the strength of the solution. These last two peculiarities of the reaction have the sole effect of rendering the experimental error almost double what it would be in any ordinary case, and of necessitating the adoption of methods (differentiation in alternate series) which tend to obliterate the sharpness with which the changes of curvature are marked.

Table C (p. 110) contains the values for the so-called molecular heat of dissolution (D_x^m). The strengths entered are either such as correspond to the hydrates which exist according to the present work, or such as will permit of a comparison of my own determinations with those of Thomsen and Pfaundler (*Thermochem. Untersuch.*, 3, 54, and

* Very uncertain. There might be a change on each side near 76 per cent., instead of one at 76 per cent.

† Probably rather higher.

TABLE C.—*Molecular Heat of Dissolution (D_x) of Sulphuric Acid Solutions at 17·91°.*

Composition.		Molecular Weight.	D_{100}° .	D_x° .		
Molecular.	Per cent. H_2SO_4 .			Pickering.	Pfaundler.	Thomsen.
H_2SO_4	100	97·82	21563	21093	21165	19981
H_2SO_4	99·473	98·32	21215	20858	—	—
"	97·030	100·81	19627	19787	—	—
"	94·233	103·81	17885	18565	—	—
"	91·592	106·80	16280	17387	17395	—
"	89·095	109·79	14840	16293	—	—
"	84·488	115·78	12460	14426	14332	13602
"	78·407	124·76	9995	12470	—	—
"	73·142	133·74	8363	11187	—	—
"	64·483	151·70	6193	9395	9518	10563
"	57·656	169·66	4828	8191	8255	8844
"	52·137	187·62	3918	7351	7367	—
"	49·757	196·60	3552	6933	—	6873
"	47·582	205·58	3252	6686	6652	—
"	37·701	259·46	2088	5418	—	5029
"	29·526	331·30	1399	4635	—	—
"	22·279	439·06	941	4132	—	—
"	18·492	528·86	748	3937	—	—
"	10·003	977·86	381·5	3732	—	3725
"	8·585	1139·5	{ 330 <i>d</i>	3760 <i>d</i>	—	3297
"			{ 313 <i>m</i>	3566 <i>m</i>	—	—
"			{ 188·5 <i>d</i>	3536 <i>d</i>	—	—
"	5·215	1875·9	{ 182·9 <i>m</i>	3431 <i>m</i>	—	—

(d) From "dissolution" experiments.

(m) From "mixing" experiments.

TABLE C—continued.

Composition.		Molecular Weight.	D_4^{100} .	D_4^m .	
Molecular.	Per cent. H_2SO_4 .			Pickering.	Pfaundler.
H_2SO_4 , 119 H_2O	4·377	2235·1	$\begin{cases} 151\cdot0d \\ 152\cdot7m \\ 147\cdot7d \end{cases}$	$\begin{cases} 3598d \\ 3411m \end{cases}$	(3411)
" 130 "	4·021	2432·6	$\begin{cases} 138\cdot5m \\ 93\cdot8 \end{cases}$	$\begin{cases} 3593d \\ 3373m \end{cases}$	—
" 199 "	2·664	3671·9	93·8	3445	—
" 399 "	1·346	7265·9	41·55	3020	2916
" 510 "	1·057	9257·2	30·6	2833	2668
" 799 "	0·677	14448	17·54	2533	—
" 1500 "	0·362	27088	8·00	2163	2340
" 1599 "	0·340	28816	7·37	2124	—
" 5200 "	0·104	98490	1·085	1021	(2124)
" 8000 "	0·068	143778	0·403	58	—

(d) From "dissolution" experiments.

(m) From "mixing" experiments.

If the composition of the acid as given by the freezing point determinations be taken, the above values will be somewhat too high; that for D_4^{100} for 100 per cent. will be 50 cal. too high, that for a 50 per cent. solution, 18 cal. too high, and the others in like proportion.

TABLE D.—*Heat Evolved on Addition of Various Proportions of Water to Sulphuric Acid Solutions at 17·91°.*

<i>m.</i>	<i>n.</i>	Pickering.	Pfaundler.	Thomsen.	Cal. per mol. H ₂ O added. (Pickering.)
0	1	6667	6833	6379	6667
1	1	3239	—	3039	3239
2	1	1792	—	1719	1792
3	1	1204	1263	—	1204
4	1	840	888	—	840
5	1	665	715	—	665
5	4	1933	—	1844	484
9	10	1286	—	1304	129
19	5	175	—	—	35·0
49	50	196 d	—	174	3·9
99	100	— 14 m	—	207	— 0·14
199	200	425	—	248	2·13
399	400	487	—	328	1·22
799	800	409	—	216	0·51
0	$\frac{1}{10}$	1306	—	—	7836
$\frac{1}{8}$	$\frac{1}{8}$	1221	—	—	6326
$\frac{1}{6}$	$\frac{1}{6}$	2272	—	—	6716
$\frac{2}{5}$	$\frac{2}{5}$	1867	—	—	5601
1	$\frac{1}{2}$	1956	—	—	3912
$\frac{3}{2}$	$\frac{3}{2}$	1283	—	—	2566
510	990	670	—	—	0·677
1500	3700	1142	—	—	·0·308
0	$\frac{1}{2}$	2706	2770	—	5540
0	1	6667	6833	6379	6667
0	2	9906	—	9418	4953
0	3	11698	11647	11137	3899
0	4	12902	12910	—	3225
0	5	13742	13798	13108	2748
0	6	14407	14513	14952	2401
0	9	15675	—	—	1742
0	19	16916	—	16256	890
0	49	17361	—	16684	248
0	99	{ 17557 d 17662 m	—	16858	174
0	199	17648	—	17065	89·7
0	399	18073	—	17313	45·5
0	799	18560	—	17641	23·2
0	1599	18967	—	17857	11·8

Jahresb., 1869, 122). Table D gives the values for the heat evolved on adding various proportions, and also successive proportions, of water to the strong acid. Where there might be a doubt as to

whether the values were deduced from the mixing or dissolution experiment, the letters *m* and *d* have been inserted.

The error in these absolute values is, of course, very different from that of the relative values of successive determinations, which has heretofore been alone considered. A difference of 0.001° or 0.2 cal. in the determination of the value for a 0.4 per cent. solution would make a difference of 50 cal. in the heat of dissolution of H_2SO_4 itself;* yet the concordance of the mixing and dissolution experiments showed that the actual error accumulated as far as 18 per cent. could not have amounted to more than one-seventh of this, so that the value for H_2SO_4 , is, in all probability, right considerably within 50 cal. To compare my values with Thomsen's and Pfaundler's, these latter must all be increased by 2124 and 3411 cal. respectively, the heats of dissolution of the weakest solutions (0.34 and 4.377 per cent.) which these two physicists obtained in their final experiments. Pfaundler's values, it will be seen, agree very satisfactorily with my own, there being but one instance in which the difference between our results exceeds 100 cal., whereas Thomsen's results are all considerably lower, the difference amounting to as much as 1112 cal. in the case of the pure acid. This difference, I imagine, may be caused by errors due to Thomsen's mixing calorimeter, or to the acid which he used not being as strong as H_2SO_4 .†

It will be seen by the footnote at the bottom of Table C (p. 111) that my values are probably somewhat high, but the excess would be almost exactly counterbalanced by taking 98 instead of 97.82 , as I have done, for the molecular weight of H_2SO_4 : Pfaundler and Thomsen took the former of these values.

The manner in which the results are stated in Table D does not show the discrepancy between Thomsen's results and those of Pfaundler and myself so forcibly. A considerable difference will be noticed, however, in the case of $\text{H}_2\text{SO}_4.799\text{H}_2\text{O}$, $800\text{H}_2\text{O}$ —Thomsen's last determination. There is certainly, I think, an error here, and it will affect all his values for D_∞^m (see Trans., 1889, 325).

It will be seen from the upper portion of the last column of Table D that the heat evolved for H_2O , on the addition of successive portions of water, diminishes till $199\text{H}_2\text{O}$ have been added, that it then increases, and again diminishes. From the last portion of this column it will also be seen that the heat evolved on adding the first

* If it were determined by mixing the acid with consecutively *equal* volumes of water, as in the "mixing" experiments, the error of 0.2 cal. at 0.4 per cent. would make an error of 500 cal. in the value for H_2SO_4 .

† He says nothing about the preparation or analysis of it, and his values are such as would be obtained with a commercially "pure" acid of 97 — 98 per cent. Pfaundler took pains to prepare his acid by crystallisation.

$\frac{1}{2}$ mol. of water to H_2SO_4 is considerably less, instead of greater, than that evolved on the addition of the second $\frac{1}{2}\text{H}_2\text{O}$, as it should be if the curve were regular throughout. Thus there are at least two portions of the curve which, even on a cursory inspection, show that it does not possess that general regularity which the supporters of the physical theory of solution are so anxious to attribute to it.

PART VI.—EXPANSION BY HEAT.

A. *As a Function of Percentage Composition.*

The density determinations made, supply the means of calculating the expansion of the solutions by heat. In doing so we depend on the comparison of two series of results at *different* temperatures, and, hence, the conclusions drawn may be regarded as almost independent of those already drawn from the densities themselves, where we depended on the results of one series at the *same* temperature.

If s_1 and s_2 be the densities at t_1 and t_2 , the expansion, or increase in volume, will be $\frac{s_1}{s_2} - 1$, the volume at the lower temperature t_1 being taken as unity. In this way I have calculated the expansion in several cases, but have preferred to take, for the purposes of analysis, the complementary property of the decrease of density, $s_1 - s_2$ *: the figures in the two cases are of a similar nature, but the latter present the advantages of (1) an error in the densities causing an error of the same magnitude throughout; (2) an error in the density determinations having generally a smaller effect (actual and relative) on the results; (3) of necessitating fewer calculations, and possibilities of mistakes.

The solutions used at 17.925° had not the same composition as those used at the other temperatures, so that, if we take the actual experimental values, we can only get the expansion for about 10° , from 28.064° to 38.203° ; for about 20° , from 7.978° to 28.064° ; and for about 30° , from 7.978° to 38.203° . These values are given in Table XX.

To utilise the results at 17.925° , the values, as reduced to round percentages (and also to whole degrees of temperature), given in Tables VII and VIIA, must be taken. From these we get three series for a rise of 10° , two for a rise of 20° , and one for a rise of 30° ; they are given in Table XXI, and will probably yield more uniform results than those derived from the unreduced densities, since, in the reduction, a few obvious errors were corrected (see p. 70).

In the case of the numerous results with strong solutions, and for

* This divided by the density at the higher temperature gives the expansion.

results below 20 per cent., the reduced densities at 8° and 18° are alone sufficiently trustworthy for the present purposes. Table XXI also contains the values for the expansion proper for the three 10° intervals.

Fig. 13 gives a representation of some of the results obtained, the signs of the values for the decrease in density having been changed to +, so that the figures may be more easily compared with those for the expansion proper. A, C, and D give the decrease in density for

FIG. 13.—Decrease of Density, and Expansion of Sulphuric Acid Solutions on being heated 30° , 20° , and 10° .

intervals of 30° , 20° , and 10° , deduced from the reduced values; E and F (which should be raised $\frac{1}{2}$ and 1 division of the paper respectively), the values for the other intervals of 10° ; G (which should be raised $1\frac{1}{2}$ div. of the paper) shows the expansion proper for 10° ; and B (which should be raised $\frac{1}{2}$ div.) gives the decrease in density for the 30° interval as deduced from the unreduced density values.

All the figures resemble the first differential of the densities in being continuous throughout,* and yet necessitating their being

* Except in some parts of B, where the discontinuity is probably the result of errors.

drawn in sections, when a bent ruler is used for that purpose. The separate sections are indicated in the present illustration in the cases of A, B, and the end portions of D only.*

The agreement of the experimental points with these drawings is somewhat better than in the case of the first differential of the densities (Plates 1 and 2, p. 184) when the same scales are used.

Both as regards the position of the changes and the nature of the constituent curves, the various figures resemble each other so closely, that I have analysed by differentiation that only which refers to the 30° interval, supplementing it in the case of very strong and weak solutions by a similar examination of Fig. D.

The direct differentiation (Table XXI, and Fig. 14, A) gives a figure composed of three straight and two slightly curved lines, there being three parts of it in which the results are too doubtful to permit of

FIG. 14.—Expansion of Sulphuric Acid Solutions.

First and Second Differentials.

any drawing being made. Indeed, it could hardly be expected that the decrease in densities would stand a direct differentiation, for the original values here are merely the differences between two experimental results and, even in the case of the 30° interval, they are only comparable in accuracy with the first differential of the densities.

A differentiation of the smoothed curve (Fig. 13, A, p. 115) led to better results (Table XXII and Fig. 14, B), and supplied sufficient data

* In plotting out the results from the unreduced densities, considerable assistance may be derived from a study of Plates 1 and 2, which will indicate which determinations probably contain exceptionally large errors.

for the drawing of those parts where the direct differentiation had failed. The whole of the figure from 50 to 88 per cent. is rectilinear, the other portions of it being made up of gentle curves. A second differentiation (Table XXII) reduces all these curves to straight lines, and gives the figure illustrated by C, Fig. 14. There are, of course, non-comformable points between most of the lines constituting this figure.

The first differential of the curve for the 10° interval for weak and strong solutions will be seen from Fig. 14, D, to be made up of sundry straight lines: the portion III does not appear to apply quite as far as 0 per cent., the last few points in the diagram exhibiting an irregularity, which indicates the occurrence of some change at 0.3 to 0.4 per cent.; but this is simply a suggestion.

Table E (p. 118) summarises the information as to the position of the changes derived from a study of the various results. The numbers given at the bottom of the columns refer to the weight which has been assigned to the figures in that column in deducing the mean: the weighting has been made in proportion to the interval of temperature to which the expansion applies: the results drawn from a direct differentiation, the differentiation of the smoothed curve, and also from the inspection of the original curve, count as independent observations, so that the value attached to the results from that curve in which the changes have been established by differentiation may amount to two-thirds of that attributed to the evidence derived from a mere inspection of all the other curves together. This is the only instance in which I have attributed any weight at all to conclusions drawn from an experimental diagram, without confirming the changes shown in it by differentiation. Such changes as are specially doubtful are enclosed in brackets, and to these only half the value of the other points has been attributed.

The general concordance of the results is certainly satisfactory. Very little weight can be (and is) attached to the indications between 89 and 50 per cent. for the 10° intervals. Nearly all the results suggest a change somewhere about 62 per cent., where none of the other properties studied have shown one; this is very probably due to the results in this neighbourhood being affected by some error in the composition of one or two of the solutions (p. 76). Due, probably, to the same cause, we have the fact that a change at 57 per cent. is unmarked in most of these results, although it has been established by nearly all the other properties investigated. It is to be noticed that a change at 89 per cent. is well established by all these results, although of the density results, that at the lowest temperature was the only series which indicated it.

There are several points of interest besides the position of the changes.

TABLE E.—Position of the Changes shown by the Curves for the Expansion of Solutions by Heat.

From the unreduced values.			From the reduced values.									
8—38° curve.	8—28° curve.	28—38° curve.	8—38°.			8—28° curve.	18—38° curve.	8—18°.		18—28° curve.	28—38° curve.	Mean.
			Curve.	Direct 1st diff.	1st diff. from curve.			Curve.	1st diff. from curve.			
(98)	—	(98)	97	(97)	—	97	(98·5)	97·5	97·5	—	—	97·38
94	94	94	94	94	93·3	94	94	—	—	94	94	93·91
89	89	88·6	88·8	88·5	89	87·6	88	(89)	—	(89)	89	88·71
84·5	84·5	—	83	—	83	83·1	84·5	(82·9)	—	—	84	83·43
(80·5)	79	(80·5)	78	—	78	78·2	78·9	(77)	—	79	(73)	78·63
73	72	73	72·6	73	73	72·6	72·6	73	—	(74)	(73)	72·79
(62)	(61)	(62)	62	(61)	62	(63)	(63)	(59)	—	(63·6)	62	(61·92)
—	—	—	—	—	—	57	56·4	—	—	—	(57)	(56·73)
49	—	—	48	(50)	50	48·4	—	49	—	50	—	49·09
39	41	(41)	39·4	38	38	39	40·5	38·5	—	(40)	39·5	39·18
28·6	28·4	(28·8	29	28	29	28·5	29	29	—	30	28·5	28·83
—	—	—	—	—	—	—	—	20	19	—	—	19·50
—	—	—	—	—	—	—	—	11	10	—	—	10·50
—	—	—	—	—	—	—	—	4	4	—	—	4·00
—	—	—	—	—	—	—	—	(·35)	—	—	—	(0·35)
6	4	2	6	6	6	4	4	2	2	2	2	—

The values in this Table refer to percentages expressed according to the results of the freezing point of the acid, and are 7/10,000ths higher than in any preceding Table.

The three 10° curves, when compared together, show that the effect of temperature on this property is largely dependent on the composition of the solution taken. At about 57 per cent. the expansion from 8° to 18° (Fig. 13, D, p. 115) shows a depression, whereas that from 18° to 28° (E) shows an elevation, and that from 28° — 38° (F) shows a uniform increase, so that from 8° to 38° the rate of expansion of this solution will increase with the temperature.* With a solution of about 70 per cent. strength, the reverse will be the case. All the peculiarities exhibited by these three curves are equally shown by the corresponding curves representing the expansion proper, one of which is illustrated by Fig. 13, G.

There is a well-marked maximum of expansion, which in all cases appears to be situated at 86.3 per cent.; a percentage, be it specially noted, which corresponds with no definite hydrate, and with no sudden change in the curve.

The comparatively high points shown by the difference of density at about 33 per cent. become points of maxima in the expansion proper. The position of this second maximum is not so clearly defined as that of the first, and appears to vary somewhat with the actual temperature. From 8° to 18° it is situated at about 33 per cent., from 18° to 28° at 34 per cent., from 28° to 38° at 32%; but these variations are very doubtful. In any case it is not situated at a point corresponding to any abrupt change in curvature. With the expansion from 18° to 28° , there is, further, a slightly marked maximum at about 57 per cent. It may also be noticed that the change at the monohydrate (84.5 per cent.) is very feebly marked in the original curve, and becomes pronounced only when we come to the first differential.

That the constituent curves of the figure representing the expansion require two differentiations in some cases is, I think, fairly certain, especially when it is remembered that the small magnitude of the original quantities dealt with would favour their differentiation into practically straight lines, and that, in spite of this, six out of the eleven portions constituting the first differential (Fig. 14, B) exhibit a decided curvature. These constituent curves do not appear to meet tangentially, and, consequently, the straight lines forming the second differential do not meet at the points of change.

B. *As a Function of the Temperature.*

The above results have shown that the expansion is sometimes greater and sometimes less as the temperature is higher, according

* These features are barely visible in the rough sketch given in Fig. 13.

to the strength of the solution. A few determinations were made with a view of gaining further information on this point.

Three solutions, containing 84, 81.1, and 41.8 per cent. of acid respectively, were taken, and their densities determined at every 2° between 6° and 38°. The first of these solutions has a composition nearly corresponding with that of the monohydrate, the composition of the second coincides with no particular hydrate, and the third solution was taken simply at random, as an instance of a weaker solution. Table XXIII embodies the results.

The weights of the contents of the bottle, when differentiated, give the figures in Fig. 15.* The scale is somewhat too open for the experimental error (which here depends on the correctness of the

FIG. 15.—Weights of Water and Acid contained in a 25 c.c. bottle at t° .

actual temperatures as well as on the weighings), and the points for the 81.1 per cent. solution have not been inserted: the crosses represent the mean points given in the table. The three lines are all continuous and straight within the errors of the experiments, from which it would follow that the change of the density with temperature is represented in each case by a single parabola of the second order† as far as the determinations extended.

* Differentiation of the densities or volumes would give lines differing only in position and inclination (not in form) from those derived from the weights; but they would contain the errors due to the determination of the capacity of the bottle at each temperature.

† Mendeléeff drew the same conclusions from his determinations with alcohol solutions between 0° and 30°. The points determined with each solution, however, never exceeded five.

That this, however, is not the case with all solutions, there are theoretical considerations (given below), as well as direct evidence, to show. In constructing the table of densities of solutions of the acid, the four results with each solution were plotted against temperature, and it was found that, whilst with all solutions of 100 to 63, and from 43 to 20 per cent., the results lay in an apparently uniform curve, from 63 to 43 per cent. they could only be depicted by two different curves bending in opposite directions, or by two different straight lines* (the latter with solutions from 53 to 43 per cent.). This indicates the existence of more or less abrupt changes at certain temperatures with some solutions, and the instances found were too numerous and consistent, and the differences too great (sometimes 0·0006 of the density, or 0·76°) to admit of their being explained away by experimental error. The differential obtained in one of these cases (for a 60 per cent. solution) is given in Fig. 15, E; the three points, of which A is one, cannot be represented by the same straight line, the error here being but one-fifth of what it is with the lines for 84, 81, and 42 per cent. solutions: an instance is also given in the figure of the differential obtained from a case (20 per cent.) where the four experimental points lay on one curve, and here we get an uniform straight line.†

It was certainly unfortunate that the solutions selected for the fuller examination of the effect of temperature on density should not have included any in that region where the effect was subsequently found to be irregular.

The different inclinations of the various lines in Fig. 15 confirm the previous conclusion that the rate of expansion is sometimes greater, and sometimes less, at the higher temperature, according to the strength of the solution examined.

* Or a curve and a straight line.

† The actual values in these two cases are:—

60 per cent.				20 per cent.			
t° .	s .	w .	$\frac{dw}{dt}$.	s .	w .	$\frac{dw}{dt}$.	t° .
7·978	1·506415	37·7079	·0201 ·0204 ·0193	1·146050	28·6874	·0141 ·0142 ·0144	12·95
17·925	1·498077	37·5078		1·140179	28·5469		22·99
28·064	1·489582	37·3010		1·134250	28·4031		33·13
38·203	1·481526	37·1055		1·128243	28·2575		

PART VII.—DISCUSSION OF THE RESULTS.

The persistency with which the methods here adopted for examining curves has been misunderstood,* renders it necessary for me to say a few words on the subject, even at the risk of repeating myself.

The method does *not* consist in fitting sundry equations on to the curves, and, on the strength of the concordance observed, to conclude that these latter are continuous or otherwise. It is quite true that if a curve differentiates into a straight line after a certain number of differentiations, an equation of a certain form must represent that curve, and, if it yield several straight lines, there must be as many different equations applicable to different parts of it; but it is one thing to find equations empirically, and prove (?) their truth by a display of those, often, most fallacious of arguments known as tables of "found" and "calculated" values, and another thing to apply an ordinary process of mathematical analysis to them, letting them speak for themselves, and tell us whether they are continuous or not. On the former of these methods I would place absolutely no reliance, and so far have I been from making use of it, that I have not found the equation for any single curve here depicted.

The mathematical argument on which the method depends is that a curve, if it be continuous, will, on differentiation, give either a straight line or another continuous curve; whereas, if it be not continuous, but be made up of different curves, it will yield a series of straight lines or curves. This, I think, is an incontestable fact.

Of the dangers attending differentiation, and the consequent uncertainty of any conclusions depending entirely on this process, I have already said enough, and it is only necessary to remind my readers here that the recognition of the changes of curvature rarely depends on differentiation only, but that these are generally noticeable in the experimental curves themselves. On the other hand, it must be admitted that conclusions drawn solely from the experimental curves would be equally unsatisfactory; they would be dependent on the taste of the draughtsman, and on the drawing of a particular portion of a figure in one section—which, without the subsequent evidence supplied by differentiation, would be no proof that the section drawn is a single curve—but in no case have such unsupported conclusions been drawn.

In some instances, of course, the experimental curves might show changes of such abruptness that a mere cursory inspection would be sufficient to prove their existence, but it would be highly improbable that any of the properties here studied would do so; these properties

* See *Nature*, 40, 343.

must be continuous functions of the percentage composition, and, whatever changes they show, will be of a somewhat uncertain nature, since they must be due to changes in the unstable and dissociating liquid hydrates present.

The main point of my opponent's attack will, I imagine, be directed against the closeness with which my drawings follow the experimental values. That I have ever gone within the limits of known or probable errors, I must deny, and I have often left a considerable margin beyond these limits: that there may be other unknown sources of error, is, of course, quite possible; but ought we to conjure up unknown possibilities in order to reduce our results to regularity, in an investigation, the sole purpose of which is to settle whether they are regular or not? Surely, the only rational and scientific method of procedure is to draw the curves in the first place so as to allow not much more error in the points than we know must exist, and then ascertain the results; if such a drawing leads us to obviously incorrect conclusions, or to conclusions which are not concordant in the various cases investigated, then, and then only, shall we be justified in assuming the existence of unknown errors.

That a second differentiation deals with quantities which are, in most cases, within the limits of the error of the experimental points, is quite true (and this is the reason why the second differentiation can hardly ever be performed on the experimental values themselves), but a curve which is drawn to represent a series of points smooths out the errors of each individual point, and diminishes this error in proportion to the number of points available for the drawing, just as the mean of many repeated determinations gives a result which is more accurate than each separate determination.

Near the point at which two curves meet the differences in their readings will, of course, be very small, and at the point of junction, nil: but the existence of the two curves does not depend on the differences between the points at or near their junction, but on the position of the many points (generally 6 or 7) on either side of the junction. The question so often asked—on what differences do these changes depend?—is one to which it is impossible to give a satisfactory answer: a small difference would often obliterate certain particular changes (as with some of those in the heat of dissolution, results, which were obliterated by differentiating the values in two series); a greater amount of smoothing will obliterate others (the ultra-smoothed curve); but, smooth over and mutilate the results as much as we can, we still have left *some* changes, which gain but greater prominence as the minor ones become effaced. Such a conclusion is drawn from a study of the most (seemingly) regular portion of the most regular curve dealt with—the heat of dissolution

curve—a similar examination of those representing the other properties would but enforce this conclusion more strongly.

The multiplicity of the changes will,* no doubt, prove a stumbling block to the acceptance of my conclusions in some minds. The objection may be raised on either mathematical or chemical grounds. Every one is aware, of course, that a curvilinear figure may be regarded as being made up of a number of straight lines, of segments of circles, or of parabolas, provided we split it up sufficiently. But this is no argument that some particular figure may not in reality be made up of independent parabolas. We can, as a matter of fact, string a series of true parabolic curves together so as to make a continuous and apparently regular figure, but no one could say that such a figure was not made up of parabolas, because any curvilinear figure can be regarded, for certain purposes, and within certain limits, as being made up of such. The question must be settled by inspecting the curves, and deciding whether the number of parabolas into which they split up according to my interpretation at all approaches that theoretically infinite number into which any curvilinear figure, whatever its real nature might be, would split up; whether it is at all possible that a mere mechanical and chance distintegration of curvilinear figures of such very different magnitude and such totally different forms as those representing the densities, dilatation, heat of dissolution, and heat capacity, could result in the production of the same number of parabolas in every case, and all locating the changes at the same points. The impossibility of such a chance result will be apparent, I think, to anyone who gives the matter a fair consideration.

The chemical grounds on which the objection may be raised are still weaker. What reason have we for asserting the improbability of sulphuric acid forming seventeen different hydrates in solution? At present we know nothing whatever of the nature or number of hydrates which may exist in the liquid condition, but we do know that there are cases in which some four or five solid hydrates of the same salt have been isolated† (and that within comparatively narrow limits of composition), and, if so many compounds can exist in the solid form, where they are in a definite and stable condition, the probability is, I think, in favour of the existence of a still larger number in solution, where they are, no doubt, in a partially dissociated condition.

* And has done so. Arrhenius, *Phil. Mag.*, **28**, 37.

† With sodium carbonate we have eight; with basic ferric sulphate there is evidence of as many as fourteen (*Trans.*, 1883, 182). The isolation of different hydrates has nearly always been the result of chance experiments; a systematic attempt to obtain fresh ones would, no doubt, enlarge the number known very considerably.

It is necessary to draw special attention to the definite and specific evidence of change in a reaction, or property, deducible from changes of curvature such as the present work reveals, as opposed to the loose and insufficient evidence which, it is sometimes argued, is shown by an alteration in the general inclination of a figure. If we start with a curvilinear figure, and prove that on differentiation it ultimately yields, say, two different lines which are straight within the limits of experimental error, we prove that, within these same limits, it consists of two different parabolas—two regular and definite figures, which, we may legitimately conclude, represent two regular conditions or actions of the solutions. But a mere change in the general direction of the figure, such as occur at points of maximum or minimum elevation, can prove no specific changes at all, for it is perfectly obvious that such maxima and minima may occur in the middle of the most regular portions of the whole figure. The position of these specific changes is unaltered by the manner in which the results are expressed, and also by the conditions (such as temperature) under which the determinations are made,* and this permanency is one of the strongest arguments in favour of their reality; whereas, with mere general changes of direction, we find the reverse to be the case; the position of a maximum alters according to the mode of expression adopted—as with the densities, the contraction, the first differential, and second differential of the densities,† and we may almost add, the expansion by heat, where the maxima occur at 97·5, 68, 73, 49, and 86 (also 33) per cent. respectively—and its position varies also with the temperature, as it must in the case of the densities,‡ and has been proved (Mendeléeff, *Ber.*, 1886, 387) to do in the case of the contractions.

Agreement of the Results obtained from Different Sources.

The establishment of the particular changes of curvature which I consider exist must depend mainly on the concordance of the results obtained from the different properties studied. These are

* Unless, of course, we alter the temperature so much that a hydrate is entirely destroyed, or a fresh one makes its appearance.

† The maximum in the case of the rectilinear second differential *must* correspond to a specific change; from the examples at our disposal, I should imagine that it also does so in the case of the first differential. Its doing so with the sulphuric acid densities, explains how Mendeléeff, by the inordinate smoothing of this curved figure, was led accidentally to name some of the hydrates which actually do exist.

‡ My results show that the variation is inappreciable from 8° to 38°, but if the temperature were to be raised sufficiently high to destroy all compounds in solution, the maximum would be altered to 100 per cent. : consequently, its position must be variable.

collected in Table F (next page); the changes which are doubtful are enclosed in circular brackets, and are allowed but half value in deducing the mean; the specially doubtful ones are enclosed in square brackets, and are not included at all in the mean, nor in the following discussion. N.D. signifies that there were insufficient data to show whether a particular change existed or not.

Of the 17 changes shown, there is one (that at 0.1 per cent.) which could have been indicated by the heat of dissolution results only; of the remaining 16, we have—

1 shown in two cases.

1	„	three	„
4	„	four	„
1	„	five	„
7	„	six	„
2	„	seven	„

each “case” meaning either the study of a different property, or of the same property at a different temperature.*

There is not a single instance, I think, where the absence of evidence for any change may not fairly be attributed to the lack of sufficient data, and there can be but little doubt but that all the eight sets of results would have shown all the changes, had they been investigated sufficiently.

The average divergence of the individual results from the mean, as deduced from the 82 cases available, is only 0.388 per cent., there being but nine cases in which it reaches or exceeds 1 per cent.

When we consider the extreme difficulty in determining the exact point at which a change occurs within 1 or even 2 per cent., even where the change itself is undoubted, we must admit that this degree of concordance is quite as good as could possibly have been expected: that it could be accidental is out of the question, and we must remember that, not only were the properties investigated different, but that the greater part, and sometimes all of the solutions used in investigating one property were distinct from those used in the others, the only exceptions to this being the densities of sulphuric acid at 8°, 28°, and 38°.

There can therefore be but little doubt that, though there may be several points where uncertainty still prevails, and where future work

* I have counted the expansion results as but one case: they should, perhaps, be counted as two, since the four series of density determination yield two independent series of expansion values.

The density results at 18° are further confirmed by their treatment in the form of contractions (p.83).

TABLE F.—Position (in Percentage Values) of the Changes of Curvature shown by the various Properties of Solutions of Sulphuric Acid examined.

Densities.				Expansion by heat.	Electric conductivity.	Heat capacity.	Heat of dissolution.	Mean	Molecular composition shown.	Composition of definite hydrates.
At 38°-203	At 28°-064.	At 17°-925.	At 7°-978.							
N.D.	N.D.	N.D.	N.D.	N.D. (α)	(99·5)	N.D.	99·35	99·47†	36 H ₂ SO ₄	H ₂ O = 99·493
"	"	97·2	97·7	97·31	(96·8)	"	97·3	97·38	"	" = 99·476
93·5	94·0	93·6	94·0	93·84	94·0	"	93·83	93·89	"	" = 97·444
84·4	84·5	84·5	(88·0)	88·65	—	"	88·95	88·70	"	" = 97·030
78·2	77·5	78·0	84·5	83·37	84·0	"	84·0	84·24	2	" = 94·233*
72·8	73·3	72·8	79·0	78·57	—	"	79·0	78·43	1	" = 89·095*
59·0	57·0	58·0	72·74	(61·38)§	[73]‡	"	73·0	73·04	1	" = 84·488*
49·0	50·0	51·0	(58·0)	56·69	[63]‡	"	—	(61·88)§	2	" = 78·407*
			51·0	49·05	—	"	59·15	58·14	1	" = 73·142*
			(40·0)	39·15	—	"	49·25	49·92	(1	" = 57·656*
22·0	29·0	29·5	30·0	28·81	(37·5)	"	37·75	38·58	1	" = 49·756*
N.D.	N.D.	18·5	18·5	19·43	N.D.	"	29·55	29·59	(1	" = 52·137
"	"	8·8	10·5	10·49	9·5	"	19·15	18·92	1	" = 37·701
"	"	4·0	4·3	4·00	3·5	9·35	9·0	9·69	13	" = 29·626
"	"	1·05	1·05	—	N.D.	"	4·07	3·99	1	" = 24
"	"	0·25	0·35	(0·35)	"	N.D.	1·13	1·06	24	" = 18·492
"	"	N.D.	N.D.	N.D.	"	"	0·40	0·34	58	" = 8·585
"	"	N.D.	N.D.	N.D.	"	"	0·105	0·105	(1	" = 9·821
"	"	N.D.	N.D.	N.D.	"	"	0·105	0·105	1	" = 4·021
"	"	N.D.	N.D.	N.D.	"	"	0·105	0·105	1	" = 1·057
"	"	N.D.	N.D.	N.D.	"	"	0·105	0·105	(1	" = 1·080
"	"	N.D.	N.D.	N.D.	"	"	0·105	0·105	1	" = 0·362
"	"	N.D.	N.D.	N.D.	"	"	0·105	0·105	(1	" = 0·339
"	"	N.D.	N.D.	N.D.	"	"	0·105	0·105	1	" = 0·109
"	"	N.D.	N.D.	N.D.	"	"	0·105	0·105	1	" = 0·104

(α) The values in this column are 7/1000ths lower than those in Table E (p. 118), where the later determinations of the strength of the acid were taken.
† The values for the means are 7/1000ths higher than they should be according to the numbers in the first eight columns, the alteration having been made in accordance with the later determinations of the strength of the acid.
‡ 73 or 63 per cent., but very uncertain.
§ This change is too doubtful to be counted.
|| The position of this change is defined so much more clearly by the experimental curve of the heat of dissolution (8·7 per cent.) than by any other curve that I have taken the composition indicated by this to be the more probable one.

may introduce some modifications, the great majority of the changes which I have mentioned as existing are established beyond all reasonable question.

Composition of the Hydrates Indicated.

Strong presumptive evidence in favour of the changes here indicated will be afforded if it be found that they occur at percentages corresponding to simple molecular proportions.

Unfortunately, however, there are but seven cases from which any conclusion on this head may be drawn, cases, that is, in which the addition of another molecule of water would alter the composition by from 11 to 2 per cent. (marked by an asterisk in the table, p. 127).^{*} From these it is seen that the average difference between the mean position found and that calculated for an exact number of water molecules or half molecules (the latter in three cases) is only 0.226 per cent., or about 0.057 H₂O on the average, the greatest percentage difference (in the case of H₂SO₄.4H₂O) amounting to only 0.48, or 1/11th H₂O.[†] Such differences are well within the limits of the experimental error.[‡]

That this concordance of position of the changes in curvature with the composition of definite hydrates has not been in any way influenced by a knowledge on my part of the latter, I may confidently affirm, for, throughout nearly the whole of the work, I purposely avoided ascertaining the percentage composition of any hydrates, the only exception to this being the case of the monohydrate, and in spite of my knowledge of its composition, and the probability of its causing some marked change, I noticed no change at all corresponding to it either in the case of the experimental curves for the heat of dissolution or expansion.

The changes in the highest portion of the curves are of interest, inasmuch as their discovery was the outcome of theoretical considerations, as well as of a reliance on the correctness of the results obtained in the other portions of the curve. The former were, that, just as a weak solution of acid in water contains compounds of the acid molecule with many water molecules, so should a weak solution of water in acid contain compounds of a water molecule with many acid

^{*} The last column contains a few percentages which do not refer to the hydrates indicated by the determinations; they will be of use in showing the alteration in percentage with molecular composition.

[†] The greatest difference in molecular composition is with 3H₂SO₄.H₂O, where it amounts to one-sixth H₂SO₄, but only 0.3 per cent.

[‡] The addition of the results arrived at in the case of the calcium salts would double the force of this conclusion.

molecules, for in all very weak solutions the solvent acts as a polymer of its fundamental molecule, comparable, if not identical, with the polymers which constitute a mass of the pure liquid* (Trans., 1888, 872, and 1889, 23). The practical considerations were, that, if the second differential were really rectilinear, as the bulk of the figure showed it to be, an apparent curvature in any part of it could only be due to the lack of sufficient points to resolve it into straight lines; this had been proved to be the case with the curved portion of the second differential near the zero end, and, it was argued, it would probably be the case also with the curved portion at the 100 per cent. end.

Looking at the constitution of the various hydrates, there are some signs, in the extreme cases, of the higher ones bearing a simple relation to the lower ones: thus, the water molecules contained in the three highest hydrates are about 500, 1,500, and 5,000, whilst the four compounds richest in acid contain about 36, 6, 3, and $3/2$ H_2SO_4 to every H_2O . But such indications must be accepted with great reservation, owing to the impossibility of determining the exact molecular composition in the cases in point. Between the less complex hydrates there would seem to be no simple numerical relation at all.

The great complexity of the hydrates in very weak solutions is one of the most remarkable facts brought to light by the present work, and is such that many chemists will, no doubt, find difficulty in accepting it.† That there should be such things as chemical compounds containing several hundred, and even several thousands of molecules of one of their constituents, all bound together and united (however loosely) with 1 mol. of the other constituent, is indeed a most remarkable fact, and one which must necessitate no unimportant extension of our views as to chemical action. Yet these changes are amongst the best established in the whole work, and they are, moreover, precisely similar in character to those changes in the region of stronger solutions, which certainly do coincide with definite hydrates. If the liquid and gaseous conditions be really continuous, it follows, I think, that the *average composition* of the aggregates composing a mass of water must be about 1800 H_2O , and, if these

* The highest compounds recognised would be less complicated in the case of very strong than in that of very weak solutions; a body consisting of 5000 $\text{H}_2\text{SO}_4\text{H}_2\text{O}$ would contain only 0.004 per cent. of water, and its recognition here would have been practically impossible.

† Our opinions are naturally biased by the fact that our experience is inevitably confined, in the majority of cases, to stable compounds. Their stability is but a consequence of the simplicity of their structure; we are here dealing with unstable compounds.

aggregates combine as such with any dissolved substance (as, from the heat of neutralisation, I argue they must), the hydrates formed will have a corresponding complexity of composition. We should not therefore be surprised at a hydrate containing even $5000 \text{ H}_2\text{O}$.

The existence of such compounds gives, I think, an explanation of how "traces" of foreign matter may influence the properties of a body in a manner altogether disproportionate to the amount present, and how the effect produced may be modified or reversed by altering the proportions of the foreign substance, as, for instance, in the case of bismuth in gold, antimony in copper, silicon and carbon in iron, &c.

The comparative magnitude and frequency of the changes at the extreme ends of the curves is but a consequence of the method used for depicting the results. Percentage composition has no scientific meaning, and is but a convenient mode of expressing results: matter must be regarded as consisting of molecules, and the real nature of a mixture or compound is indicated by the relative number of the different molecules present: a small difference of, say, 0.7 per cent., such as that from 1 to 0.3 per cent., really means a trebling of the relative proportions of water and acid present, and the curve representing any action between the two points should extend over three times the distance of the whole of the rest of the diagram from 1 per cent. upwards.

In Fig. 16 I have given a sketch of one set of my results (the second differential of the densities of sulphuric acid at 8°) plotted out against molecular composition. The relative number of molecules are given at the top of the plate. The proportions of 1 : 1 would occupy the centre of the diagram, if the investigations had been pushed to the same limits with strong solutions as with weak ones. It has not been practicable to represent any changes beyond the one at 3.9 per cent., and many of them are seen with such difficulty that their position has had to be specially marked.* The relative magnitude of the changes at the simpler and more complex hydrates, as well as the relative magnitude of the different hydrates amongst the simpler ones, is very striking. The most conspicuous are those at 30, 50, 84, and 94 per cent. corresponding with hydrates with 13, 5.5, 1, and $1/3 \text{ H}_2\text{O}$.

It is very evident that this method of plotting out the results would, in most cases, be very unsuitable for working purposes.

Indication of the Monohydrate in Solution.

That the monohydrate exists in solution is, in my opinion, proved by the fact that we can crystallise it out from solutions. The

* The constituent lines are numbered so as to correspond with those in Pl. 3.

FIG. 16.—Densities of Sulphuric Acid Solutions.
Second differential plotted against molecular composition.

existence of a body in the crystalline form is not, however, entirely dependent on the stability of its molecules in the liquid condition, but on the ease with which these molecules coalesce to form the aggregates of which it is composed in the solid condition; it does not follow, therefore, that the monohydrate must necessarily be conspicuously stable when liquid, or that the change in curvature indicating its presence should be more marked than those indicating other hydrates in solution. At first sight it appears that such is not the case: the experimental curve for the heat of dissolution shows no discernible change at this point (84.5 per cent.); in the expansion curve it is but feebly marked, and in the first differential of the densities it is by no means prominent. But in all these cases it is found that a repeated application of differentiation (wherever the data are sufficient) alters this, and shows that the change at the monohydrate is really a prominent one (see especially Fig. 2, B, p. 80). Its being partially masked in the experimental curves may, I believe, be due to the fact that this hydrate is really exceptionally stable while liquid, and that, just like the other stable liquids, water and the pure acid, forms compounds containing several fundamental molecules of itself with a single water molecule on the one hand, and

a single sulphuric acid molecule on the other; the proximity of the minor changes due to such compounds would, in the absence of a very large number of experimental points, result in the rounding off of the change which shows the monohydrate itself.*

Nature of the Various Curves.

For the chief conclusions drawn from the present work—the existence of more or less sudden changes of curvature at certain points—it is important to show that the various constituent curves differentiate eventually into lines which are straight within the limits of experimental error; for their doing so shows that they are each of them single and simple curves within these same limits. But, apart from these practical considerations, the nature of the constituent curves raises several important questions of theoretical interest: whether the second differential lines are absolutely straight, whether the first differential lines are sometimes so, and whether the constituent curves of the original figure meet tangentially or otherwise. These questions can be answered only with great hesitation.

That a single differentiation is insufficient to reduce the densities (and contractions) and electric conductivities to straight lines, is beyond doubt; with the heat of dissolution, the heat capacity, and the expansion, the case is more doubtful; but the fact that a considerable portion of the first differential figure of all these properties is curved, renders it most probable that it should be curved throughout, and that the straightness observed in parts is but a consequence of comparative magnitude of the error of the determinations and the small scale on which these have to be plotted in consequence.

Whether the straightness of the lines composing the second differentials is merely the result of repeated differentiation, or whether they are straight owing to the nature of the experimental curves from which they are derived (that is, owing to these curves being parabolas of the third order), is a difficult question to settle.

It is true that the majority of (but by no means all) curves of a gentle nature, such as are here dealt with, would yield straight lines on repeated differentiation;† but, for the following reasons, I am

* Since writing the above, two changes in the vicinity of the monohydrate have been revealed by a study of the freezing points of solutions of the acid.

† As instructive instances of curves which do not do so, I may cite the end portions of the first differential of the densities, and various other gentle curves, each drawn as a single curve, but really made up of two or more independent curves, and which, on repeated differentiation, show their complex nature (instances in the densities and heat of dissolution have been quoted above); and, again, curves representing the molecular heat of dissolution plotted against percentage composition, which are not parabolic at all.

inclined to think that the straightness of second differential is really a consequence of the parabolic nature of the experimental curves.

(1.) The curvature of the first differential is often greater than that of the experimental curve, and the straight lines which it yields on further differentiation cannot, therefore, be of a result of a gradual straightening process.*

(2.) The second differential lines are straight in nearly every instance, in spite of the great variations in the curvature of the various first differentials which yield them.

(3.) The first differential of the densities differentiates into straight lines, whereas the experimental curve of the expansions—a curve comparable in its nature and curvature with the density first differential—differentiates, in most parts, into a series of curves.

(4.) Wherever a curved second differential has been obtained, its curvature has been found to be the result of insufficient data.

The question has been raised as to what limit we should put to the process of differentiation (Morley, *Proc.*, 1888, 127), and Crompton's answer—that “a limit to the differentiation would necessarily have to be made according to the nature of the case under investigation, and the discretion exercised by the investigator”—has, I think, been somewhat misunderstood (see Arrhenius, *Phil. Mag.*, 28, 37). For the purposes of the present work, the limit to be put to the process of differentiation is that at which we get a rectilineal figure, for a straight line is the only form of line which, on mere inspection, is evidently regular, and which must prove regularity in the curve which yields it. A further differentiation would not add to our knowledge (unless we wished to determine diagrammatically the constants in the equations for the curves), for our series of straight lines would simply yield thereby a series of horizontal lines at different levels, and a still further differentiation would yield nothing at all.

A practical limit to the differentiation will also be determined in each individual case by the error of the original experiments. Even when we reduce these errors by taking the curve which represents them, instead of the actual experimental values, there are few cases in which we could proceed beyond a second differentiation so as to obtain results of any value.

* A comparison of the curvature of the experimental and differential curves is a difficult matter, for the scales used must bear a fixed relationship to each other in the three cases, and the various curves thus produced generally have a different inclination to the axis. Should we determine the curvature in the same *lengths*, or between the same *percentages*? If the former, the curvature of the first differential would nearly always be greater than that of the experimental curve. The expansions and the mixing experiments are the simplest instances to take for such an investigation.

A difference of considerable importance may be noticed between the heat results and the density results. The former are represented throughout by a series of curves, which, on production, cut each other, and from which second differentials will be obtained, which, consequently, do not meet at the points where the change occurs, if indeed they meet at all; whereas the first differentials derived from the densities, and consequently the densities themselves, form a series of curves, which, for the most part, meet tangentially or very nearly so, and the second differentials from these will meet *at* the points of change. This is certainly not always so, but the general tendency is unmistakable. This difference is, no doubt, connected with the difference in the nature of the two properties, the former being a condition of the solutions, the latter a measure of potential energy possessed by them.

The curves for the electric conductivity seem for the most part to be of the same nature as those for the density: the change at 9.5 per cent., however, is a marked exception. The contraction on mixing, the expansion, and the heat capacity, on the other hand, appear to resemble the heat of dissolution more closely; the constituent curves certainly do not meet tangentially, and indeed, in the case of the last, do not appear to meet at all, though, as I have shown above, there must be some connecting link between them (p. 93).

•
Influence of Temperature on the Hydrates in Solution.

The influence of temperature on the first differential of the densities is of considerable interest. Each figure in Plates 1 and 2* (p. 184) should, if they were all identical, occupy positions five small divisions of the paper below or above its neighbour; but the actual distance between them varies considerably, and shows that all the changes of curvature become more marked as the temperature is lower. The upward curvature at the zero end, and the whole of the constituent curves up to 73 per cent., show this progressive increase very clearly. The portion between 84 and 94 per cent. is also of special interest: it has a decided downwards curvature at 8°, which becomes so slight at 18° and 28°, that it is here practically a straight line, whilst at 38° the curvature is decidedly upwards, and, if we could extend the determinations to still higher temperatures, it would, no doubt, increase, this portion of the diagram becoming less and less distinguishable from the neighbouring curves. The result of this would be that changes in its vicinity would become less marked, and would eventually disappear altogether; the rest of the figure would, no doubt, become simplified in the same way, and would exhibit less

* Including that representing the results collected by Mendeléeff.

and less curvature, till finally reduced to a horizontal line at a temperature sufficiently high to prevent any hydrates at all being formed. The possibility of making determinations would, however, cease long before such a temperature was reached.

But the different hydrates, being of different degrees of stability, will not all disappear at the same temperature, and, consequently, some solutions will show a more or less sudden alteration in the rate at which their density is affected by temperature, under conditions where others, consisting of stabler hydrates, will show no such change. The experimental evidence already discussed tends to confirm this conclusion, and we may reasonably argue that the evidence of sudden changes in the rate of increase of the density with temperature would have been of a more certain character had the method adopted permitted of the examination of very weak solutions, the hydrates in such cases being more complex, and, presumably, less stable, than in the case of strong solutions.

Further evidence as to the existence of such sudden changes has been afforded by my work on the effect of temperature on the heat of dissolution of salts (Trans., 1887, 223), which showed that this property, and, consequently, the heat capacity of the weak solutions obtained in the determinations, exhibited sudden alterations in its rate of increase at certain temperatures.

The highest line in Fig. 15 (p. 120) is also of considerable interest in connection with this point: it represents the rate of increase in the density of water with temperature, and, according to my interpretation of it (details of which cannot be given here), it exhibits abrupt changes at certain points, such as I have concluded would be exhibited by the densities of weak solution, and such as the analogy between the constitution of the weak solutions and of the pure solvent (both being mixtures of molecular aggregates of different degrees of complexity) would lead us to expect.

A consideration of the effects of temperature on the densities must make us recognise the possibility of there being yet other hydrates than those at present discovered, hydrates which would only be revealed by experiments at lower temperatures; it is probable, however, that these would be confined mainly to very weak or very strong solutions. That the densities at 8° should have indicated (though feebly) two changes which were not found at higher temperatures, supports such a conjecture.

Summary and Conclusion.

The curves representing the first differential coefficient of the densities of sulphuric acid solutions form a curvilinear figure, and not a rectilinear figure, as Mendeléeff imagined. This figure, though

continuous, is made up of a series of separate curves, which, on further differentiation, yield a series of straight lines.

When we plot out the contractions occurring on mixing sulphuric acid and water, instead of the densities of the solutions obtained, we get a figure totally unlike that formed by the densities: on a first differentiation it gives another curvilinear figure, also totally unlike the first differential of the densities; but, on a second differentiation, a rectilinear figure is obtained, closely resembling the second differential of the densities, and indicating the existence of changes at the same points as the latter does.

The electric conductivities resemble the densities in giving straight lines on a second differentiation only, as shown by Crompton, and they indicate changes at certain points, though the position of these changes are, according to the author, not all identical with those mentioned by Crompton.

The heat capacity is represented by a series of gentle curves, which probably require two differentiations to reduce them to a series of straight lines.

A critical examination of Thomsen's results on the heat evolved by diluting solutions with successive quantities of water leads to the conclusion that the actions are eminently irregular, instead of being regular as he concluded.

The author's present determinations lead to the same results. The heat of dissolution (or dilution) of solutions of different strengths are represented by a series of intersecting curves, each of which requires (in most cases) two differentiations to reduce it to a straight line.

The expansion of sulphuric acid solutions through various ranges of temperature between 8° and 38° gave results which formed irregular curved figures, and these figures split up on two differentiations into a series of straight lines, showing changes at the same points as the other properties did.

An examination of three solutions of sulphuric acid at every 2° showed that the effect of temperature on the densities of these solutions was represented by a single parabola of the second order; but the less numerous density determinations with other solutions indicated that, in some cases, the results cannot be represented by less than two different curves, more or less sudden changes occurring at certain temperatures.

The points at which the changes occur are the same whichever of the above properties be taken for their determination, this concordance placing the existence of the majority of them beyond doubt.

The points at which they occur, moreover, correspond to definite and simple hydrates, considerably within such limits of error as might reasonably be expected.

The hydrates thus recognised amount to as many as 17, the monohydrate being one of them.

The highest hydrates contain a very large amount of water; in the extreme case, as much as $5000\text{H}_2\text{O}$.

There may be some simple numerical relationship between the constitution of the various hydrates, but only in very weak and in very strong solutions.

As a consequence of the results obtained on analysing the experimental values and the curves representing them, it follows that these latter are represented by a series of parabolas of the third order, such as $s = A + Bp + Cp^2 + Dp^3$, this probably being true in the case of all the properties, though sometimes the last constant is so small in comparison with the experimental error that it may be neglected, and the results be expressed by a parabola of the second order.

In the case of the densities and the electric conductivities, the various curves constituting the first differential appear to meet tangentially, and, consequently, the straight lines constituting the second differential meet *at* the points of change.

This is not the case with the contraction on mixing, the heat of dissolution, or the expansion by heat, the first differential curves (and consequently the experimental curves also), in these cases, intersecting each other on prolongation.

In the case of the heat capacity, the constituent curves representing the experimental values do not appear to meet at all.

The main facts elucidated by this work afford absolute proof that the properties of solutions do not vary regularly with their composition, and that the nature of the solution is, therefore, not merely physical. There can be no doubt but that solutions consist of hydrates of a definite composition, though these may always be in a state of partial dissociation.

It may be urged that, although this may be the case where the solvent is water, in other cases similar compounds would not exist. It is extremely improbable, however, that actions seemingly so analogous as the dissolution of a substance in water and its dissolution in another liquid, should belong to totally different classes of phenomena, the one being chemical, the other physical. It is, however, a question which calls for an answer based on experiment, and, as it would be difficult, if not impossible, to find a solvent other than water with which solutions might be obtained possessing sufficient differences in density, &c., to render them suitable subjects for investigation, some other means of investigation must be adopted. I hope that the freezing points of solutions of different strengths may afford

the requisite information, and the results which I have already obtained, since writing the above, from a study of this property in the case of sulphuric acid, justify the expectation that such may be the case.

I am fully aware that the present work supplies material for far more discussion than I have ventured to raise. The precise nature of the changes which occur when solutions are diluted has scarcely been discussed at all. What is the meaning of these various properties being representable by a series of parabolic curves of certain orders? Why should the component curves of the density, the heat of dissolution, and the heat capacity diagrams, show such differences as that of meeting tangentially in one case, cutting each other in the second, and (apparently) not meeting at all in the third case? How can the fact that the changes occur so sharply at the exact composition of certain hydrates be reconciled with the extent to which we must, I think, necessarily imagine that these hydrates are dissociated, even when the water and salt is present in the exact proportions required for their formation (see *Trans.*, 1889, 22)? These, and other questions, I leave for the discussion of abler mathematicians than myself: the present work has no pretensions beyond being an experimental investigation.

But one word remains to be said: a word of thanks to a little girl who has devoted all her spare time to the laborious calculations involved in the present work: to the patience and accuracy of Miss Ethel Willmott all who are interested in the question of the nature of solutions owe much.

TABLE I.—*Densities of Sulphuric Acid Solutions at 17·925°, and First Differentiation.*

p .	s .	$\frac{ds}{dp}$.	p .	Alternate series A and B.			
				$\frac{ds'}{dp'}$.	p' .	$\frac{ds''}{dp''}$.	p'' .
Full series, with differences not less than about 1 <i>per cent.</i>							
99·85700*	1·834221						
99·85000	1·834281						
99·85350	1·834251 A & B	—·00310	99·34	—·00310 A	99·34		
		—·00307	99·32			—·00307 B	99·32
98·82200	1·837452 A						
98·77812*	1·837550 B	—·00116	98·32	—·00116 A	98·32	—·00043 B	97·76
		—·00111	98·30				
97·82685	1·838610 A	+·00017	97·29	+·00057 A	96·92	—·00152 B	95·88
96·74952*	1·838428 B	·00116	96·39	·00224 A	95·06		
96·02135	1·837587 A	·00179	95·52			·00299 B	94·00
95·01355*	1·835781 B	·00268	94·51	·00378 A	92·81	·00431 B	92·01
93·99780	1·833055 A	·00330	93·50			·00561 B	90·03
92·99056*	1·829734 B	·00413	92·31	·00504 A	90·83	·00689 B	88·03
91·62209	1·824078 A	·00472	91·32	·00628 A	89·00	·00836 B	86·01
91·02467*	1·821258 B	·00524	90·53			·00953 B	83·98
90·04606	1·816130 A	·00597	89·53	·01021 A	82·76	·01052 B	82·04
89·03102*	1·810075 B	·00657	88·49	·01094 A	80·98	·01125 B	80·04
87·95802	1·803025 A	·00727	87·49				
87·03615*	1·796325 B	·00791	86·50	·01141 A	79·12		
85·95828	1·787795 A	·00884	85·47				
84·97907*	1·779138 B	·00933	84·27				
83·56640	1·765953 A	·01000	83·27				
82·98206*	1·760117 B	·01034	82·48				
81·98460	1·749799 A	·01071	81·54				
81·09315*	1·740248 B	·01112	80·54				
79·98477	1·727926 A	·01140	79·48				
78·98995*	{1·716598} B						
	{1·716570} B						
78·25462	1·708182 A	·01143	78·62				
75·95699	1·681361	·01167	77·11				
74·00440	1·658412	·01175	74·98				
72·02272	1·635093	·01177	73·01				
70·09785	1·612557	·01171	71·06				
68·10148	1·589410	·01159	69·10				
66·13310	1·566839 A	·01147	67·12				
64·89103	1·552790	·01131	65·51	·01132 A	65·12		
64·11204	1·543960 A	·01133	64·50				
62·04053	1·520910	·01113	63·08				
59·98903	1·498474 A	·01094	61·01				
57·88930	1·475942	·01073	58·94	·01060 A	57·94		
55·87689	1·454879 A	·01047	56·89				
53·89570	1·434523	·01027	54·89				
51·91839	1·414643	·01005	52·91				
49·90183	1·394858	·00982	50·91				
47·92908	1·375924	·00960	48·91				
45·95806	1·357386	·00938	46·94				
44·02251	1·339628	·00920	44·99				

TABLE I—*continued*.

p .	s .	$\frac{ds}{dp}$.	p .	Alternate series A and B.			
				$\frac{ds'}{dp'}$.	p' .	$\frac{ds''}{dp''}$.	p'' .
44·02251	1·339628						
41·97705	1·321255	·00898	43·00				
39·99233	1·303711	·00884	40·98				
38·03978	1·286773	·00868	39·01				
35·99121	1·269262	·00854	37·01				
34·03459	1·252802	·00842	35·01				
31·99420	1·235836	·00831	33·01				
30·03628	1·219752	·00822	31·00				
28·06891	1·203804	·00811	29·05				
26·21825	1·188953	·00803	27·14				
24·01732	1·171509	·00793	25·12				
22·06137	1·156221	·00782	23·04				
20·04282	1·140640	·00772	21·05				
18·00597	1·125186	·00759	19·02				
15·99627	1·110138	·00749	17·00				
13·99655	1·095416	·00736	15·00				
12·13767	1·081045 C	·00725	13·07				
9·804053	1·065349 A	·00710	10·97				
8·970256*	1·059554 B	·00695	9·387				
7·955370	1·052408 A & C	·00704	8·463	·00706 C	10·05		
6·962185*	1·045656 B	·00680	7·459	·00700 A	8·85		
6·025176	1·039192 A	·00690	6·494			·00692 B	7·966
4·915919*	1·031704 B	·00675	5·471	·00685 A	6·99		
4 003331	1·025572 A	·00672	4·460			·00682 B	5·939
3 042904	1·019150	·00669	3·523	·00674 A	5 01		
1·796562	1·010864	·00665	2·420				
0·997007	1·005348	·06665	1·397				
0	0·998695	·00687	0·499				

Strong solutions.

99·85350	1·834251 A						
99·69763*	1·834912 B	— ·00424	99·776	— ·00391 A	99·686		
99·51810*	1·835563 A	— ·00363	99·608			— ·00338 B	99·505
		— ·00317	99·415			— ·00347 B	99·501
		— ·00335	99·412				
99·31215*	1·836214 B			— ·00308 A	99·363		
99·30558*	1·836274 B	— ·00293	99·260			— ·00293 B	99·203
		— ·00251	99·256			— ·00273 B	99·199
99·20729*	1·836521 A	— ·00292	99·108	— ·00272 A	99·096		
99·09372*	1·836853 B	— ·00252	99·039				
98·98452*	1·837128 A	— ·00199	98·903			— ·00273 B	98·958
		— ·00204	98·881			— ·00229 B	98·936
93·82200	1·837542 B			— ·00195 A	98·827		
93·77812*	1·837550 B	— ·00191	98·745			— ·00173 B	98·670
		— ·00178	98·723			— ·00163 B	98·648
98·66856*	1·837745 A	— ·00153	98·594	— ·00126 A	98·402		
98·51877*	1·837974 B	— ·00115	98·328				
98·13654*	1·838414 A	— ·00063	97·981				
97·82685	1·838610						

TABLE I—*continued.*Strong solutions—*continued.*

$p.$	$s.$	$\frac{ds}{dp}.$	$p.$	Alternate series A and B.			
				$\frac{ds'}{dp'}.$	$p'.$	$\frac{ds''}{dp''}.$	$p''.$
97·82685	1·838610	-·00022 +·00012	97·677				
97·52668*	1·838693		97·332				
97·13589*	1·838647	·00057	96·943				
96·74952*	1·838428	·00089	96·559				
		·00100	96·542				
96·36863*	1·838087						
96·33480	1·838011	·00144	96·195				
96·02135*	1·837587	·00135	96·178				

Weak solutions.

4·915919*	1·031704	·00674	4·635				
4·355266*	1·027924	·00668	4·179				
4·003331	1·025572	·00680	3·905				
3·806007	1·024231	·00668	3·610				
3·413022	1·021607	·00664	3·228				
3·042904	1·019150	·00667	2·819				
2·594819	1·016163	·00660	2·409				
2·222768	1·013706	·00667	2·010				
1·796562	1·010864	·00662	1·602				
1·407762	1·008291	·00668	1·202				
0·997077	1·005548	·00661	0·902				
0·807416	1·004294	·00674	0·703				
0·599067	1·002889	·00·83	0·499				
0·399816	1·001528	·00692	0·301				
0·202068	1·000159	·00706	0·152				
0·101357	0·999448	·00743	0·056				
0	0·998695						
0·296800*	1·000831	·00688	0·222				
0·147963*	0·999807	·00714	0·099				
0·049453*	0·999104	·00827	0·025				
0	0·998695						

TABLE II.—*Densities of Sulphuric Acid Solutions at 7·978°, 28·064°, and 38·205°, and First Differentiation.*

<i>p.</i>	7·978°.		28·064°.		38·205°.		<i>p.</i>
	<i>s.</i>	<i>ds/dp.</i>	<i>s.</i>	<i>ds/dp.</i>	<i>s.</i>	<i>ds/dp.</i>	
99·85700	1·844560	—·00299	1·824246	—·00301	1·814298	—·00327	99·32
98·77812	1·847784		1·827492		1·817828	—·00096	98·28
		—·00089		—·00092	1·818780	—·00081	98·15
97·78818	1·848901		1·828646		1·818836	+·00026	97·27
96·74952	1·848646	+·00033	1·828308	+·00043	1·818515	·00042	97·14
95·87631	1·847660	·00113	1·827296	·00116	1·817403	·00127	96·31
95·01355	1·846066	·00185	1·825592	·00198	1·815640	·00204	95·45
93·90505	1·843306	·00249	1·822561	·00273	1·812510	·00283	94·46
92·99056	1·840179	·00342	1·819375	·00348	1·809215	·00360	93·45
91·86622	1·835750	·00394	1·814691	·00417	1·804407	·00428	92·43
91·02467	1·831899	·00458	1·810652	·00480	1·800268	·00492	91·45
89·85667	1·825796	·00523	1·804277	·00546	1·793788	·00555	90·44
89·03102	1·821006	·00580	1·799251	·00608	1·788694	·00616	89·44
87·83725	1·813232	·00652	1·791296	·00664	1·780606	·00678	88·44
87·03615	1·807388	·00729	1·785271	·00752	1·774564	·00754	87·44
85·85956	1·798115	·00788	1·776002	·00788	1·765265	·00790	86·45
84·97907	1·790292	·00889	1·768252	·00880	1·757576	·00873	85·42
84·01970	1·781343	·00932	1·759444	·00918	1·748805	·00914	84·56
82·98206	1·771021	·00995	1·749241	·00983	1·738808	·00963	83·51
81·85008	1·759072	·01056	1·737792	·01011	1·727413	·01007	82·42
81·09315	1·750673	·01110	1·729727	·01066	1·719593	·01033	81·47
79·96809	1·738076	·01122	1·717424	·01093	1·707359	·01087	80·53
78·98995	1·726694	·01164	1·706389	·01129	1·696495	·01111	79·48
77·94749	1·714570	·01163	1·694596	·01131	1·684849	·01117	78·47
75·90717	1·690580	·01176	1·671094	·01152	1·661610	·01139	76·92
73·98643	1·667782	·01187	1·648712	·01165	1·639397	·01157	74·95
72·02232	1·644541	·01183	1·625844	·01164	1·616740	·01154	73·01
69·93139	1·619860	·01181	1·601468	·01166	1·592543	·01157	70·98
68·00851	1·597410	·01168	1·579326	·01152	1·570547	·01144	68·97
66·02517	1·574588	·01151	1·556737	·01139	1·548091	·01132	67·02
64·04535	1·552015	·01140	1·534480	·01124	1·525956	·01118	65·03
61·91205	1·528012	·01125	1·510701	·01115	1·502586	·01096	62·98
59·97052	1·506801	·01092	1·489842	·01074	1·481687	·01076	60·95
57·85589	1·483720	·01092	1·467133	·01074	1·459055	·01070	58·91
56·00914	1·464315	·01051	1·447899	·01042	1·439903	·01037	56·93
54·00142	1·443536	·01035	1·427382	·01022	1·419514	·01016	55·00
52·02681	1·423653	·01007	1·407699	·00997	1·399899	·00993	52·71
50·06998	1·404296	·00990	1·388553	·00978	1·380826	·00975	51·05
48·02648	1·384578	·00965	1·369025	·00957	1·361383	·00951	49·05
45·71655	1·362804	·00943	1·347438	·00935	1·343308	·00931	46·65
43·58981	1·343309	·00917	1·328068	·00911	1·320568	·00908	44·65
41·76736	1·326892	·00901	1·311779	·00894	1·304308	·00892	42·58
39·64778	1·308168	·00883	1·293169	·00878	1·285793	·00874	40·71
37·73112	1·291527	·00868	1·276647	·00862	1·269316	·00859	38·69
35·71882	1·274323	·00855	1·259589	·00848	1·252326	·00844	36·72
33·85203	1·258517	·00847	1·243964	·00837	1·236792	·00832	34·78
31·80782	1·241463	·00834	1·227117	·00824	1·220101	·00817	32·83

TABLE II—*continued*.

p .	7° 978°.		28° 064°.		38° 205°.		p .
	s .	ds/dp .	s .	ds/dp .	s .	ds/dp .	
31·80782	1·241463	·00827	1·227117	·00811	1·220101	·00811	30·79
29·78239	1·224724	·00818	1·210687	·00803	1·203677	·00794	28·77
27·75282	1·208121	·00812	1·194382	·00790	1·187565	·00783	26·96
26·16642	1·195236	·00804	1·181842	·00781	1·175151	·00772	25·00
23·83699	1·176502	·00795	1·163649	·00768	1·157168	·00758	22·87
21·92292	1·161292	·00787	1·148945	·00760	1·142654	·00750	20·88
19·84133	1·144905	·00775	1·133122	·00740	1·127048	—	19·01
18·18353	1·132053		1·112085				

Alternate Determinations.

97·52668	—	—	1·828646	·00082	—	—	96·70
95·87631	—	—	1·827296	—	—	—	—
95·01355	1·846066	·00291	1·825592	—	—	—	94·00
92·99056	1·840179	—	1·819375	—	—	—	—
89·03102	—	—	1·799251	·00701	1·788694	·00708	88·03
87·03615	1·807388	·00831	1·785271	·00827	1·774564	·00826	86·01
84·97907	1·790292	—	1·768252	·00952	1·757576	—	83·98
82·98206	1·771021	·01077	1·749241	·01033	—	—	82·04
81·09315	1·750673	·01140	1·729727	—	—	—	80·04
78·98995	1·726694	—	—	—	—	—	—
81·85008	1·759072	·01116	—	—	1·727413	·01066	80·91
79·96809	1·738076	·01163	1·717428	·01130	1·707359	·01114	78·96
77·94749	1·714570	—	1·694596	—	1·684849	·01147	75·97
73·98643	1·667782	·01182	1·648712	·01165	1·639307	·01156	71·96
69·93139	1·619860	—	1·601468	—	1·592543	—	—
66·02517	—	—	—	—	1·548091	·01106	63·97
61·91205	1·528012	·01092	—	—	1·502586	·01073	59·88
57·85589	1·483720	·01043	—	—	1·459055	—	56·93
54·00142	1·443536	—	—	—	—	—	—
64·04535	—	—	1·534480	·01088	—	—	60·95
57·85589	—	—	1·467133	—	—	—	—
33·85203	—	—	—	—	1·236792	·00814	31·82
29·78239	—	—	—	—	1·203677	—	—

TABLE II—*continued*.*Other Determinations at 7.978°.*

<i>p.</i>	<i>s.</i>	<i>ds/dp.</i>	<i>p.</i>	<i>p.</i>	<i>s.</i>	<i>ds/dp.</i>	<i>p.</i>
1 per cent. series.				Strong solutions— (continued).			
18.18353	1.132053	} .00767 .00755 .00747 .00734 .00725 .00719 .00716 .00711 .00706 .00702 .00698 .00692 .00691 .00695 .00723	16.96	98.13654	1.848651	} — .00063 97.69 — .00016 97.66 — .00001 97.46 + .00009 97.33 .00057 96.94 .00094 96.54 .00131 96.10	
15.73349	1.113271		14.83	97.78818	1.848861		
13.92476	1.099626		12.91	97.52668	1.848901		
11.90393	1.084542		10.96	97.13689	1.848865		
10.01131	1.070660		9.49	96.74952	1.848646		
8.97026	1.063110		8.46	96.33480	1.848257		
7.94729	1.055752		7.45	95.87631	1.847660		
6.96219	1.048704		6.93	Weak solutions, full series.			
5.92138	1.041353		6.44				
4.91592	1.034300		5.42				
3.76125	1.026234		4.34	4.91592	1.034300	} .00704 .00698 .00694 .00690 .00694 .00692 .00691 .00690 .00696 .00695	4.635
2.97588	1.020800		3.37	4.35527	1.030357		4.338
1.77511	1.012505		2.38	3.76125	1.026234		4.058
0.99888	1.007108		1.39	3.33425	1.023286		3.548
0	0.999890		0.50	2.97588	1.020800		3.154
			2.58432	1.018089	2.780		
			2.20353	1.015459	2.394		
			1.77511	1.012505	1.989		
Strong solutions, full series.			1.37881	1.009748	1.577		
			0.99888	1.007108	1.188		
Alternate dets.							
99.85700	1.844560 A	— .00386 A 99.687 — .00343 B 99.497 — .00300 A 99.363 — .00271 B 99.202 — .00251 A 92.097 — .00212 B 98.941 — .00186 A 98.827 — .00151 B 98.648 — .00132 A 98.402	99.687	0.79381	1.005680 A	Alternate dets. .00708 A 0.593 .00708 B 0.447 .00723 A 0.295 .00743 B 0.222 .00761 A 0.149 .00764 B 0.099 .00792 A 0.049	
99.69763	1.845196 B		99.497	0.59736	1.004289 B		
99.51810	1.845867 A		99.363	0.39182	1.002831 A		
99.30558	1.846542 B		99.202	0.29680	1.002160 B		
99.20729	1.846800 A		99.097	0.19901	1.001435 A		
99.09372	1.847115 B		98.941	0.14796	1.001055 B		
98.98453	1.847359 A		98.827	0.09852	1.000670 A		
98.77812	1.847784 B		98.648	0.04945	1.000302 B		
98.66856	1.847948 A		98.402	0	0.999890 A		
98.51877	1.848176 B						
98.13654	1.848651 A						

TABLE III.—*Densities of Sulphuric Acid Solutions at 38·203°, 28·064°, 17·925°, and 7·978°.**Second Differentiation from the Smoothed First Differential Curves.*

p.	At 38°20'3".		At 28°06'4".		At 17°9'25".		At 7°9'78".		p.
	$\frac{ds}{dp}$ 10 ⁶ .	$\frac{d^2s}{dp^2}$ 10 ⁶ .	$\frac{ds}{dp}$ 10 ⁶ .	$\frac{d^2s}{dp^2}$ 10 ⁶ .	$\frac{ds}{dp}$ 10 ⁶ .	$\frac{d^2s}{dp^2}$ 10 ⁶ .	$\frac{ds}{dp}$ 10 ⁶ .	$\frac{d^2s}{dp^2}$ 10 ⁶ .	
1 per cent. series.									
99	—	2450	—	2320	—	2420	—	2280	98.5
98	—	630	—	670	—	780	—	720	97.5
97	+	580	+	540	+	480	+	430	96.5
96	—	1580	—	1520	—	1480	—	1400	95.5
95	—	2410	—	2330	—	2290	—	2190	94.5
94	—	3140	—	3070	—	3000	—	2920	93.5
93	—	3900	—	3760	—	3670	—	3570	92.5
92	—	4570	—	4420	—	4300	—	4230	91.5
91	—	5230	—	5080	—	4960	—	4870	90.5
90	—	5860	—	5730	—	5620	—	5530	89.5
89	—	6490	—	6400	—	6280	—	6180	88.5
88	—	7090	—	7030	—	6920	—	6840	87.5
87	—	7690	—	7670	—	7580	—	7500	86.5
86	—	8260	—	8300	—	8260	—	8260	85.5
85	—	8820	—	8930	—	8930	—	8960	84.5
84	—	9380	—	9490	—	9550	—	9650	83.5
83	—	9870	—	9970	—	10100	—	10230	82.5
82	—	10290	—	10400	—	10570	—	10720	81.5
81	—	10630	—	10770	—	10940	—	11110	80.5
80	—	10900	—	11060	—	11230	—	11420	79.5
79	—	11120	—	11280	—	11440	—	11620	78.5
78	—	11260	—	11420	—	11580	—	11700	77.5
77	—	11370	—	11540	—	11640	—	11770	76.5
76	—	11460	—	11610	—	11720	—	11800	75.5
75	—	11530	—	11660	—	11770	—	11840	74.5
74	—	11570	—	11690	—	11780	—	11850	73.5
73	—	11600	+	11690	+	11770	+	11850	72.5
72	—	11570	—	11647	—	11750	—	11813	71.0
70	—	11487	—	11564	—	11645	—	11727	69.0
68	—	11378	—	11455	—	11523	—	11618	67.0
66	—	11247	—	11322	—	11380	—	11483	65.0
64	—	11088	—	11162	—	11220	—	11325	63.0
62	—	10898	—	10980	—	11033	—	11142	61.0
60	—	10691	—	10776	—	10830	—	10933	59.5
59	—	—	108*	—	124*	—	10703	10785	58.5
58	—	10475	—	10528	—	10602	—	10683	57.5
57	—	10373	—	10426	—	10497	—	10577	56.5
56	—	10270	—	10323	—	10399	—	10473	55.5
55	—	10162	—	10218	—	10285	—	10360	54.5
54	—	10058	—	10107	—	10177	—	10245	53.5
53	—	9952	—	9980	—	10065	—	10123	52.5
52	—	9840	—	9885	—	9955	—	9995	51.5
51	—	9725	—	9770	—	9863	—	9863	50.5
50	—	9629	—	9655	—	9724	—	9755	49.0
48	—	9418	—	9455	—	9503	—	9514	47.0
46	—	9212	—	9255	—	9293	—	9298	45.0
44	—	9023	—	9060	—	9098	—	9100	43.0
42	—	8950	—	8885	—	8923	—	8924	41.0
40	—	8868	—	8724	—	8760	—	8769	39.0
38	—	8032	—	8572	—	8610	—	8630	37.0
36	—	8393	—	8438	—	8484	—	8512	35.0
34	—	8262	—	8305	—	8262	—	8407	33.0
32	—	8142	—	8285	—	8257	—	8320	31.0
30	—	8020	—	8075	—	8165	—	8240	29.0
28	—	7893	—	7970	—	8074	—	8162	27.0
26	—	7774	—	7837	—	7976	—	8082	25.0
24	—	7657	—	7755	—	7874	—	8000	23.0
22	—	7545	—	7648	—	7763	—	7907	21.0
20	—	7435	—	7543	—	7648	—	7808	19.5
19	—	—	—	—	—	7592	—	7749	—

* At 59.

† At 51.

TABLE III—continued.

p .	At 17° 9' 25".		At 7° 9' 78".		p .
	$\frac{ds}{dp}$.	$\frac{d^2s}{dp^2}$.	$\frac{ds}{dp}$.	$\frac{d^2s}{dp^2}$.	
1 per cent. series.					
19	·007592	·000052	·007749	·000039	18·5
18	·007540	·000056	·007710	·000040	17·5
17	·007484	·000057	·007670	·000047	16·5
16	·007427	·000055	·007623	·000047	15·5
15	·007372	·000062	·007576	·000052	14·5
14	·007310	·000057	·007524	·000057	13·5
13	·007253	·000061	·007467	·000059	12·5
12	·007192	·000066	·007408	·000060	11·5
11	·007126	·000064	·007348	·000066	10·5
10	·007062	·000072	·007282	·000062	9·5
9	·006990	·000067	·007220	·000063	8·5
8	·006923	·000060	·007157	·000059	7·5
7	·006863	·000056	·007100	·000050	6·5
6	·006807	·000052	·007050	·000050	5·5
5	·006755	·000048	·007000	·000047	4·5
4	·006707	·000042	·006953	+ ·000043	3·5
3	·006665	+ ·000035	·006910	— ·000010	2·5
2	·006630	— ·000070	·006920	— ·000105	1·5
1	·006700	— 000340	·007025	— ·000410	0·75
0·5	·006870		·007230		
Strong solutions.					
99·8	— ·00418	— ·00250	— ·00420	— ·00263	99·6
99·4	— ·00318	— ·00213	— ·00315	— ·00228	99·2
99·0	— ·00233	— ·00188	— ·00224	— ·00195	98·8
98·6	— ·00158	— ·00160	— ·00146	— ·00150	98·4
98·2	— ·00094	— ·00135	— ·00086	— ·00128	98·0
97·8	— ·00040	— ·00115	— ·00035	— ·00108	97·6
97·4	+ ·00006	— ·00110	+ ·00008	— ·00103	97·2
97·0	·000050	— ·00108	·000049	— ·00093	96·8
96·6	·00093	— ·00098	·00086	— ·00093	96·4
96·2	·00132	— ·00090	·00123	— ·00090	96·0
95·8	·00168	— ·00085	·00159	— ·00080	95·6
95·4	·00202	— ·00075	·00191	— ·00075	95·2
95·0	·00232	— ·00073	·00221	— ·00073	94·8
94·6	·00261	— ·00068	·00250	— ·00070	94·4
94·2	·00288		·00278		
Weak solutions.					
3·8	·006690	·000067	—	—	3·65
3·5	·006670	·000050	·006915	+ ·000010	3·25
3·0	·006645	·000020	·006910	— ·000010	2·75
2·5	·006635	0	·006915	— ·000030	2·25
2·0	·006635	— ·000030	·006930	— ·000030	1·75
1·5	·006650	— ·000050	·006945	— ·000050	1·25
1·0	{ ·006675 }		·006970		
	·006560	— ·000600		+ ·000200	0·95
0·9	·006620	— ·000550	·006950	— ·000700	0·85
0·8	·006685	— ·000550	·007020	— ·000500	0·75
0·7	·006740	— ·000550	·007070	+ ·000250	0·65
0·6	·006795	— ·000450	·007095	0	0·55
0·5	·00840	— ·000500	·007095	+ ·000200	0·45
0·4	·006890	— ·000400	·007075	—	0·35
0·3	·006930	+ ·000250	—	—	0·27
0·24	·006915	— ·001130	—	—	0·22
0·20	·006960	— ·001500	—	—	0·18
0·16	·007020	— ·001750	—	—	0·14
0·12	·007090	— ·005000	—	—	0·10
0·08	·007290	— ·009250	—	—	0·06
0·04	·007660		—		

TABLE III—*continued*.

p .	At 17·925°.		At 7·978°.		p .
	$\frac{ds}{dp}$.	$\frac{d^2s}{dp^2}$.	$\frac{ds}{dp}$.	$\frac{d^2s}{dp^2}$.	
0·4	—	—	·007075	—·001700	0·375
0·35	—	—	·007160	—·001500	0·325
0·30	—	—	·007235	—·0018·0	0·275
0·25	—	—	·007325	—·002100	0·225
0·20	—	—	·007430	—·002800	0·175
0·15	—	—	·007570	—·003000	0·125
0·10	—	—	·007720	—·003300	0·075
0·05	—	—	·007885	—·004100	0·025
0	—	—	·008090		

TABLE IV.—*First Differential of the Densities of Sulphuric Acid at 0°, according to Mendeléeff, with Values altered for comparison with Pickering's results.*

p .	$\frac{ds}{dp}$.	$\frac{ds}{dp}$ altered.
95·86	·00110	·00090
87·94	·00693	·00684
83·50	·00995	·00992
80·99	·01110	·01093
76·49	·01177	·01198
71·00	·01177	·01203
64·96	·01138	·01155
56·97	·01056	·01079
43·87	·00916	·00911
32·75	·00836	·00844
24·98	·00799	·00815
14·15	·00751	·00770
7·46	·00714	·00737
3·75	·00695	·00716
1·98	·00692	·00709
0·70	·00715	·00770

TABLE V.—*Contraction in c.c. on the Formation of 1 gram of Sulphuric Acid Solutions at 17·925°.*

Volume of 1 gram of water = 1·001307 c.c.
 „ „ „ sulphuric acid = 0·545379 c.c.

<i>p.</i>	Sum of volumes.	Volume of mixture.	Contraction C.	$\frac{dC}{dp}$	<i>p.</i>
99·85350	·546047	·545184	·000863	— ·005482	99·34
98·82200	·550749	·544232	·006518	— ·005478	99·32
98·77812	·550957	·544203	·006754	— ·004904	98·32
97·82685	·555287	·543889	·011398	— ·004882	98·30
96·74952	·560199	·543943	·016256	— ·004509	97·29
96·02135	·563519	·544192	·019327	— ·004215	96·39
95·01355	·568113	·544727	·023386	— ·004028	95·52
93·99780	·572745	·545539	·027206	— ·003761	94·51
92·99056	·577384	·546527	·030856	— ·003624	93·50
91·62209	·583576	·548222	·035354	— ·003287	92·31
91·02467	·586300	·549071	·037229	— ·003139	91·32
90·04606	·590762	·550621	·040140	— ·002975	90·53
89·03102	·595390	·552463	·042926	— ·002745	89·53
87·95802	·600284	·554627	·045657	— ·002545	88·49
87·03615	·604485	·556692	·047793	— ·002317	87·49
85·95828	·609507	·559348	·050159	— ·002195	86·50
84·97907	·613864	·562169	·051695	— ·001569	85·47
83·56640	·620294	·566266	·054028	— ·001652	84·27
82·98206	·622968	·558131	·054837	— ·001385	83·27
81·98460	·627516	·571494	·056022	— ·001188	82·48
81·09315	·631581	·574631	·056950	— ·001041	81·54
79·98477	·636634	·578729	·057905	— ·000862	80·54
78·98995	·641170	·582552	·058618	— ·000717	79·48
78·25462	·644523	·585418	·059105	— ·000662	78·62
75·95699	·654998	·594754	·060344	— ·00539	77·11
74·00440	·663900	·602987	·060914	— ·000287	74·98
72·02272	·672935	·611586	·061349	— ·000220	73·01
70·09785	·681710	·620133	·061577	— ·000118	71·06
68·10148	·690813	·629165	·061648	— ·000036	69·10
66·13310	·699787	·638228	·061559	+ ·000045	67·12
64·89103	·745451	·643999	·061452	·000086	65·51
64·11204	·709000	·647683	·061347	·000135	64·50
62·04053	·718447	·665701	·060946	·000194	63·08
59·98903	·727716	·667345	·060371	·000280	61·01
57·88930	·737373	·677534	·059839	·000253	58·94
55·87689	·746549	·687342	·059207	·000314	56·89
53·89570	·755581	·697096	·058485	·000364	54·89
51·91839	·764597	·706892	·057705	·000394	52·91
49·90183	·773791	·716919	·056872	·000413	50·91
47·92908	·773791	·716919	·056000	·000442	48·91
45·95306	·782784	·726784	·054984	·000514	46·94
44·02251	·791694	·736710	·054107	·000454	44·99
41·97705	·809921	·756856	·053065	·000509	43·00
39·99233	·819070	·767041	·051929	·000572	40·98
38·03978	·827873	·777138	·050785	·000612	39·01
35·99021	·837217	·787859	·049358	·000672	37·01
34·03459	·846134	·798211	·047923	·000734	35·01

TABLE V—*continued*.

p .	Sum of volumes.	Volume of mixture.	Contraction C.	$\frac{dC}{dp}$.	p .
34·03459	·846134	·798211	·047923	·000790	33·01
31·99420	·855440	·809129	·046311	·000913	31·00
30·03628	·864363	·819839	·044524	·000961	29·05
28·06891	·873333	·830700	·042633	·001048	27·14
26·21825	·881770	·841076	·040694	·001131	25·12
24·01732	·891805	·853600	·038205	·001211	23·04
22·06137	·900723	·864886	·035837	·001292	21·05
20·04282	·909926	·876696	·033230	·001355	19·02
18·00597	·919213	·888742	·030471	·001436	17·00
15·99627	·928375	·900789	·027586	·001495	15·00
13·99655	·937493	·912896	·024597	·001556	13·07
12·13767	·945968	·924263	·021705	·001613	10·97
9·80405	·956599	·938659	·017940	·001680	8·85
7·955370	·965036	·950202	·014834	·001701	6·99
6·025176	·973836	·962285	·011551	·001762	5·01
4·003331	·983054	·975065	·007989	·001838	3·52
3·042904	·987433	·981209	·006224	·001894	2·42
1·796562	·993116	·989253	·003863	·001980	1·40
0·997007	·996762	·994482	·002280	·002281	0·49
0		1·001307	0		
8·970256	·960409	·943793	·016616	·001688	7·97
6·162185	·969564	·965337	·013227	·001762	5·94
4·915919	·978894	·969272	·009622		
Strong solutions.					
100·00000		·545379	0	— ·005891	99·927
99·85350	·546047	·545184	·000863	— ·005593	99·505
99·69763	·546758	·544986	·001772	— ·005617	99·510
99·31215	·548517	·544599	·003918	— ·005407	99·26
99·30558	·548545	·544581	·003964	— ·005301	99·26
99·20729	·548993	·544508	·004485	— ·005433	99·11
99·09372	·549511	·544409	·005102	— ·005302	99·04
98·98452	·550009	·544328	·005681	— ·005150	98·90
98·82200	·550749	·544322	·006518	— ·005199	98·88
98·77812	·550957	·544203	·006754	— ·005129	98·75
98·66856	·551450	·544145	·007305	— ·005007	98·72
98·51877	·552132	·544077	·008055	— ·004900	98·59
98·13654	·553875	·543947	·009928	— ·004747	97·98
97·82685	·555287	·543889	·011398	— ·004641	97·68
97·52668	·556655	·543864	·012791	— ·004551	97·33
97·13589	·558443	·543878	·014565	— ·004363	96·94
96·74953	·560199	·543943	·016256	— ·004293	96·56
96·36863	·561934	·544043	·017891	— ·004256	96·54
96·33480	·562088	·544067	·018021	— ·004147	96·20
96·02135	·563519	·544192	·019327	— ·004167	96·18

TABLE V—*continued*.

p .	Sum of volumes.	Volume of mixture.	Contraction C.	$\frac{dC}{dp}$.	p .
Weak solutions.					
4·915919	·978894	·969272	·009622	— ·001787	4·655
4·355266	·981450	·972830	·008620	— ·001793	4·179
4·003331	·983054	·975065	·007989	— ·001875	3·905
3·806007	·983954	·976335	·007619	— ·001853	3·610
3·413022	·985746	·978855	·006891	— ·001802	3·228
3·042904	·987433	·981209	·006224	— ·001870	2·819
2·594819	·989480	·984094	·005386	— ·001863	2·409
2·222768	·991172	·986479	004693	— ·001947	2·010
1·796562	·993116	·989253	·003863	— ·001929	1·602
1·407762	·994889	·991776	·003113	— ·002028	1·202
0·997077	·996762	·994482	·002280	— ·001972	— ·902
0·807416	·997626	·995720	·001906	— ·002160	— ·703
0·599067	·998576	·997120	·001456	— ·002238	— ·409
0·399816	·999484	·998474	·001010	— ·002357	— ·301
0·202068	1·000385	·999841	·000544	— ·002473	— ·152
0·101357	1·000845	1·000550	·000295	— ·002911	— ·056
0		1·001377	0		
0·296800	·999954	·999163	·000791	— ·002352	— ·222
0·147963	1·000634	1·000193	·000441	— ·002445	— ·099
0·049453	1·001097	1·000897	·000200	— ·004048	— ·025
0		1·001307	0		

TABLE VI.—*Contraction on the formation of Sulphuric Acid Solutions at 17·925°.**Second Differentiation from the Smoothed First Differential Curve.*

$p.$	$\frac{dC}{dp} 10^6.$	$\frac{d^2C}{dp^2} 10^6.$	$p.$	$\frac{d^2C}{dp^2} 10^6.$ or 1 c.c.	$p.$	$\frac{dC}{dp} 10^6.$	$\frac{d^2C}{dp^2} 10^6.$	$p.$	$\frac{d^2C}{dp^2} 10^6.$ for 1 c.c.
100	—5970	—700	99·5	—1280	66	90	—34	65	—53
99	—5270	—520	98·5	—960	64	157	—33	63	—50
98	—4750	—370	97·5	—680	62	223	—2	61	—3
97	—4380	—280	96·5	—510	60	220	—30	59	—44
96	—4100	—220	95·5	—460	58	280	—28	57	—41
95	—3880	—170	94·5	—310	56	335	—20	55	—29
94	—3710	—230	93·5	—420	54	375	—15	53	—21
93	—3480	—230	92·5	—420	52	405	—13	51	—18
92	—3250	—200	91·5	—360	50	430	—7	49	—10
91	—3050	—210	90·5	—380	48	443	—	—	—
90	—2840	—200	89·5	—360	44	480	—27	43	—36
89	—2640	—190	88·5	—340	42	533	—30	41	—39
88	—2450	—180	87·5	—320	40	592	—27	39	—35
87	—2270	—150	86·5	—270	38	645	—30	37	—38
86	—2120	—	—	—	36	705	—28	35	—35
84	—1580	—280	83·75	—960	34	760	—32	33	—40
83·5	—1440	—240	83·25	—420	32	824	—	—	—
83	—1320	—240	82·75	—420	30	910	—48	29	—58
82·5	—1200	—220	82·25	—390	28	1005	—44	27	—53
82	—1090	—200	81·75	—350	26	1092	—42	25	—50
81·5	—990	—140	81·25	—240	24	1175	—39	23	—45
81	—920	—140	80·75	—240	22	1252	—38	21	—44
80·5	—850	—140	80·25	—240	20	1327	—33	19	—37
80	—780	—100	79·5	—170	18	1393	—35	17	—39
79	—680	—80	78·5	—140	16	1462	—33	15	—36
78	—500	—80	77·5	—140	14	1527	—28	13	—30
77	—520	—120	76·5	—290	12	1583	—26	11	—28
76	—400	—120	75·5	—200	10	1635	—25	9	—27
75	—280	—120	74·5	—200	8	1685	—20	7	—21
74	—160	—	—	—	6	1725	—38	5	—39
					4	1800	—64	3	—65
					2	1928	—122	1·5	—124
					1	2050	—330	0·5	—331
					0	2380			
74	—273	—50	73	—83					
72	—173	—49	71	—79					
70	—75	—42	69	—67					
68	+8	—41	67	—65					
66	90								

TABLE VII.—*Densities of Sulphuric Acid Solutions at Temperatures between 40° and 0°.*
 p = per cent. by weight of H_2SO_4 .

p .	40°.	38°.	36°.	34°.	32°.	30°.	28°.	26°.	24°.	22°.	20°.	p .
100·0	1·81217	1·81404 9	1·81603	1·81801	1·81998	1·82195	1·82393 2	1·82590	1·82785	1·82982	1·83180	100·0
99·5	1·81393	1·81590 2	1·81787	1·81984	1·82183	1·82384	1·82584 2	1·82784	1·82982	1·83181	1·83381	99·5
99·0	1·81541	1·81737 1	1·81933	1·82131	1·82327	1·82525	1·82725 2	1·82923	1·83121	1·83319	1·83518	99·0
98·5	1·81644	1·81835 5	1·82028	1·82222	1·82417	1·82612	1·82806 4	1·83004	1·83203	1·83403	1·83604	98·5
98·0	1·81699	1·81886 9	1·82077	1·82269	1·82462	1·82657	1·82852 7	1·83050	1·83250	1·83450	1·83650	98·0
97·5	1·81713	1·81903 0	1·82095	1·82288	1·82483	1·82680	1·82878 5	1·83075	1·83270	1·83465	1·83664	97·5
97·0	1·81695	1·81885 3	1·82076	1·82268	1·82462	1·82658	1·82855 7	1·83052	1·83249	1·83448	1·83650	97·0
96	1·81580	1·81769 6	1·81961	1·82153	1·82349	1·82546	1·82744 8	1·82943	1·83141	1·83342	1·83543	96
95	1·81370	1·81564 3	1·81758	1·81951	1·82146	1·82345	1·82546 3	1·82743	1·82939	1·83142	1·83347	95
94	1·81084	1·81280 0	1·81476	1·81672	1·81870	1·82070	1·82271 1	1·82472	1·82672	1·82873	1·83077	94
92	1·80299	1·80496 0	1·80693	1·80891	1·81092	1·81298	1·81406 2	1·81714	1·81920	1·82125	1·82330	92
90	1·79245	1·79445 7	1·79646	1·79847	1·80054	1·80265	1·80479 8	1·80692	1·80904	1·81116	1·81330	90
88	1·77937	1·78143 9	1·78352	1·78562	1·78772	1·78983	1·79196 4	1·79413	1·79630	1·79844	1·80062	88
86	1·76393	1·76600 4	1·76810	1·77018	1·77229	1·77442	1·77659 2	1·77878	1·78097	1·78317	1·78537	86
*84·5	1·75083	1·75282	1·75485	1·75692	1·75901	1·76114	1·76330	1·76547	1·76763	1·76980	1·77199	*84·5
84	1·74624	1·74826 2	1·75029	1·75238	1·75448	1·75658	1·75869 6	1·76083	1·76297	1·76514	1·76732	84
82	1·72657	1·72856 1	1·73056	1·73258	1·73462	1·73668	1·73874 3	1·74079	1·74288	1·74501	1·74715	82
80	1·70537	1·70728 0	1·70923	1·71120	1·71319	1·71519	1·71721 2	1·71923	1·72125	1·72329	1·72535	80
78	1·68314	1·68500 8	1·68691	1·68883	1·69077	1·69273	1·69465 5	1·69658	1·69853	1·70050	1·70250	78
76	1·66042	1·66224 7	1·66409	1·66597	1·66781	1·66971	1·67160 5	1·67348	1·67538	1·67730	1·67924	76
74	1·63732	1·63912 5	1·64095	1·64277	1·64460	1·64645	1·64831 2	1·65012	1·65197	1·65387	1·65579	74
72	1·61423	1·61597 8	1·61774	1·61952	1·62131	1·62312	1·62496 2	1·62680	1·62862	1·63045	1·63230	72
70	1·59121	1·59293 5	1·59470	1·59645	1·59819	1·59995	1·60174 2	1·60356	1·60536	1·60716	1·60897	70
68	1·56835	1·57006 4	1·57177	1·57350	1·57524	1·57698	1·57873 0	1·58050	1·58225	1·58400	1·58579	68
66	1·54579	1·54745 3	1·54911	1·55079	1·55249	1·55422	1·55597 6	1·55772	1·55946	1·56121	1·56297	66
64	1·52354	1·52517 2	1·52681	1·52846	1·53013	1·53181	1·53351 3	1·53522	1·53694	1·53866	1·54040	64

* 84·5, more accurately 84·4878, the composition of the monohydrate.

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TABLE VII—continued.

p .	40°.	38'.	36°.	34°.	32°.	30°.	28°.	26°.	24°.	22°.	20°.	p .
62	1·50159	1·50818	4	1·50638	1·50801	1·50866	1·51133	7	1·51800	1·51645	1·51819	62
60	1·47998	1·48152	6	1·48307	1·48625	1·48789	1·48958	2	1·49126	1·49466	1·49636	60
58	1·45876	1·46029	8	1·46186	1·46502	1·46665	1·46826	9	1·46993	1·47331	1·47500	58
56	1·43804	1·43956	5	1·44110	1·44264	1·44428	1·44584	6	1·44809	1·45074	1·45241	56
54	1·41776	1·41926	7	1·42079	1·42233	1·42388	1·42544	1	1·42865	1·43029	1·43194	54
52	1·39792	1·39942	3	1·40094	1·40245	1·40398	1·40553	1	1·40869	1·41027	1·41186	52
50	1·37845	1·37996	1	1·38148	1·38299	1·38451	1·38603	3	1·38914	1·39072	1·39229	50
48	1·35949	1·36096	6	1·36245	1·36396	1·36548	1·36700	1	1·37003	1·37157	1·37313	48
46	1·34089	1·34234	5	1·34381	1·34529	1·34678	1·34829	1	1·35133	1·35286	1·35440	46
44	1·32267	1·32412	7	1·32560	1·32708	1·32857	1·33005	1	1·33304	1·33454	1·33604	44
42	1·30482	1·30626	3	1·30770	1·30916	1·31063	1·31214	1	1·31513	1·31663	1·31812	42
40	1·28732	1·28873	7	1·29019	1·29165	1·29309	1·29456	1	1·29752	1·29901	1·30048	40
38	1·27011	1·27152	2	1·27296	1·27440	1·27685	1·27831	5	1·28023	1·28170	1·28318	38
36	1·25321	1·25462	8	1·25604	1·25746	1·25889	1·26033	1	1·26324	1·26468	1·26612	36
34	1·23655	1·23795	3	1·23937	1·24078	1·24220	1·24362	1	1·24650	1·24794	1·24938	34
32	1·22017	1·22155	4	1·22295	1·22436	1·22576	1·22716	1	1·22995	1·23137	1·23279	32
30	1·20478	1·20539	5	1·20677	1·20815	1·20953	1·21091	1	1·21370	1·21508	1·21646	30
28	1·18816	1·18948	8	1·19085	1·19221	1·19355	1·19489	3	1·19758	1·19894	1·20032	28
26	1·17252	1·17384	4	1·17516	1·17648	1·17780	1·17912	1	1·18175	1·18306	1·18438	26
24	1·15716	1·15843	0	1·15972	1·16100	1·16228	1·16356	1	1·16612	1·16738	1·16866	24
22	1·14197	1·14323	1	1·14449	1·14573	1·14699	1·14824	4	1·15068	1·15191	1·15314	22
20	1·12705	1·12824	3	1·12945	1·13065	1·13185	1·13305	1	1·13545	1·13663	1·13780	20
18	1·11254	1·11368		1·11482	1·11597	1·11711	1·11825	1	1·12053	1·12167	1·12279	18
16	1·09815	1·09923		1·10033	1·10141	1·10250	1·10360	1	1·10579	1·10684	1·10791	16
14	1·08405	1·08511		1·08617	1·08723	1·08827	1·08930	1	1·09133	1·09234	1·09334	14
12	1·07025	1·07125		1·07225	1·07325	1·07425	1·07524	1	1·07717	1·07811	1·07905	12
10	1·05662	1·05760		1·05856	1·05952	1·06047	1·06139	1	1·06319	1·06407	1·06493	10
8	1·04339	1·04429		1·04518	1·04608	1·04696	1·04783	1	1·04951	1·05032	1·05112	8
6	1·03048	1·03133		1·03218	1·03301	1·03382	1·03462	1	1·03617	1·03690	1·03760	6
5	1·02409	1·02492		1·02576	1·02659	1·02738	1·02814	1	1·02959	1·03032	1·03159	5

TABLE VII—continued.

p .	40°.	38°.	36°.	34°.	32°.	30°.	28°.	26°.	24°.	22°.	20°.	p .
4	1·01776	1·01856	1·01938	1·02018	1·02093	1·02165	1·02235	1·02304	1·02369	1·02431	1·02493	4
3·5	1·01455	1·01534	1·01612	1·01689	1·01765	1·01838	1·01909	1·01978	1·02043	1·02104	1·02162	3·5
3	1·01135	1·01213	1·01190	1·01365	1·01438	1·01510	1·01580	1·01648	1·01712	1·01772	1·01830	3
0·5	1·00824	1·00901	1·00977	1·01052	1·01122	1·01192	1·01261	1·01326	1·01387	1·01446	1·01502	0·5
2·0	1·00508	1·00586	1·00661	1·00735	1·00804	1·00872	1·00939	1·01002	1·01063	1·01119	1·01174	2·0
1·5	1·00211	1·00283	1·00353	1·00422	1·00490	1·00553	1·00616	1·00676	1·00735	1·00791	1·00844	1·5
1·0	0·99878	0·99950	1·00024	1·00095	1·00164	1·00228	1·00292	1·00352	1·00411	1·00465	1·00515	1·0
0·5	0·99567	0·99640	0·99712	0·99783	0·99849	0·99911	0·99971	1·00035	1·00083	1·00132	1·00179	1·5
0	0·99240	0·99314	0·99386	0·99453	0·99518	0·99579	0·99636	0·99691	0·99742	0·99797	0·99831	0

p .	18°.	16°.	15°.	14°.	12°.	10°.	8°.	6°.	4°.	2°.	0°.	p .
100·0	1·83378	2	1·83585	1·83793	1·84003	1·84212	1·84421	5	1·84634	1·84849	1·85066	100·0
99·5	1·83580	8	1·83754	1·83988	1·84195	1·84404	1·84612	8	1·84825	1·85038	1·85249	99·5
99·0	1·83717	6	1·83921	1·84123	1·84328	1·84536	1·84745	5	1·84959	1·85172	1·85382	99·0
98·5	1·83805	5	1·84007	1·84211	1·84418	1·84625	1·84831	1	1·85039	1·85249	1·85460	98·5
98·0	1·83851	2	1·84053	1·84256	1·84462	1·84671	1·84879	6	1·85088	1·85300	1·85508	98·0
97·5	1·83864	9	1·84068	1·84272	1·84476	1·84681	1·84889	6	1·85101	1·85310	1·85516	97·5
97·0	1·83850	7	1·84053	1·84256	1·84460	1·84665	1·84874	4	1·85092	1·85301	1·85509	97·0
96	1·83747	4	1·83950	1·84153	1·84364	1·84564	1·84771	9	1·84984	1·85195	1·85406	96
95	1·83554	3	1·83760	1·83963	1·84165	1·84370	1·84582	9	1·84800	1·85016	1·85230	95
94	1·83281	3	1·83486	1·83690	1·83898	1·84109	1·84320	0	1·84534	1·84750	1·84968	94
92	1·82539	8	1·82751	1·82964	1·83176	1·83388	1·83602	1	1·83818	1·84034	1·84250	92
90	1·81545	9	1·81760	1·81973	1·82186	1·82402	1·82621	1	1·82841	1·83061	1·83281	90
88	1·80282	7	1·80505	1·80724	1·80946	1·81172	1·81387	0	1·81615	1·81841	1·82067	88
86	1·78758	1	1·78982	1·79194	1·79414	1·79637	1·79862	2	1·80088	1·80315	1·80542	86

TABLE VII—continued.

<i>p.</i>	18°.	16°.	15°.	14°.	12°.	10°.	8°.	6°.	4°.	2°.	0°.	<i>p.</i>
*84·5	1·77419	1·77639	1·77749	1·77859	1·78079	1·78300	1·78520	1·78740	1·78960	1·89180	1·79402	*84·5
84	1·76951 9	1·77171	1·77280	1·77389	1·77608	1·77829	1·78055 4	1·78283	1·78510	1·78737	1·78964	84
82	1·74929 3	1·75143	1·75250	1·75357	1·75573	1·75788	1·76003 3	1·76219	1·76437	1·76657	1·76877	82
80	1·72740 6	1·72949	1·73052	1·73155	1·73362	1·73570	1·73776 6	1·73986	1·74198	1·74410	1·74622	80
78	1·70448 9	1·70645	1·70744	1·70844	1·71044	1·71247	1·71451 1	1·71655	1·71858	1·72062	1·72266	78
76	1·68118 7	1·68318	1·68416	1·68513	1·68707	1·68904	1·69101 4	1·69293	1·69485	1·69677	1·69871	76
74	1·65769 7	1·65962	1·66058	1·66154	1·66348	1·66541	1·66729 7	1·66915	1·67101	1·67285	1·67471	74
72	1·63418 3	1·63606	1·63699	1·63791	1·63978	1·64167	1·64356 7	1·64551	1·64744	1·64938	1·65132	72
70	1·61080 1	1·61265	1·61357	1·61450	1·61636	1·61822	1·62006 0	1·62195	1·62385	1·62574	1·62764	70
68	1·58762 3	1·58947	1·59038	1·59128	1·59309	1·59492	1·59673 8	1·59863	1·60046	1·60234	1·60422	68
66	1·56475 0	1·56654	1·56744	1·56833	1·57011	1·57189	1·57369 0	1·57551	1·57735	1·57921	1·58105	66
64	1·54215 4	1·54391	1·54478	1·54566	1·54741	1·54915	1·55091 7	1·55272	1·55452	1·55633	1·55815	64
62	1·51993 9	1·52167	1·52252	1·52337	1·52507	1·52678	1·52848 1	1·53024	1·53200	1·53376	1·53553	62
60	1·49807 7	1·49978	1·50061	1·50143	1·50307	1·50473	1·50641 5	1·50812	1·50984	1·51156	1·51330	60
58	1·47664 1	1·47828	1·47910	1·47991	1·48153	1·48316	1·48480 2	1·48646	1·48813	1·48981	1·49150	58
56	1·45570 7	1·45732	1·45813	1·45894	1·46056	1·46218	1·46378 4	1·46536	1·46696	1·46856	1·47013	56
54	1·43515 8	1·43676	1·43756	1·43836	1·43996	1·44154	1·44311 1	1·44467	1·44621	1·44775	1·44929	54
52	1·41505 9	1·41667	1·41747	1·41828	1·41988	1·42145	1·42300 3	1·42454	1·42607	1·42760	1·42914	52
50	1·39543 3	1·39690	1·39778	1·39856	1·40012	1·40169	1·40324 9	1·40480	1·40634	1·40788	1·40942	50
48	1·37623 9	1·37780	1·37857	1·37935	1·38089	1·38244	1·38398 3	1·38553	1·38708	1·38862	1·39017	48
46	1·35748 3	1·35900	1·35976	1·36052	1·36206	1·36360	1·36513 8	1·36669	1·36824	1·36980	1·37136	46
44	1·33910 4	1·34062	1·34138	1·34214	1·34366	1·34520	1·34673 6	1·34828	1·34982	1·35137	1·35293	44
42	1·32115 9	1·32266	1·32342	1·32418	1·32569	1·32719	1·32868 5	1·33021	1·33175	1·33329	1·33485	42
40	1·30349 2	1·30499	1·30575	1·30649	1·30799	1·30949	1·31098 7	1·31251	1·31403	1·31555	1·31709	40
38	1·28616 3	1·28763	1·28837	1·28911	1·29061	1·29211	1·29359 7	1·29508	1·29657	1·29807	1·29957	38
36	1·26909 4	1·27057	1·27131	1·27205	1·27353	1·27501	1·27647 8	1·27794	1·27941	1·28087	1·28233	36
34	1·25227 6	1·25374	1·25446	1·25518	1·25662	1·25808	1·25954 0	1·26100	1·26247	1·26395	1·26542	34

* 84·5, more accurately 84·4878, the composition of the monohydrate.

TABLE VII—continued.

p .	18°.	16°.	15°.	14°.	12°.	10°.	8°.	6°.	4°.	2°.	0°.	p .
32	1·23566	1	1·23708	1·23852	1·23998	1·24142	1·24285	1·24431	1·24576	1·24721	1·24867	32
30	1·21925	2	1·22067	1·22207	1·22348	1·22490	1·22632	1·22774	1·22917	1·23061	1·23205	30
28	1·20306	7	1·20445	1·20583	1·20721	1·20858	1·20996	1·21136	1·21274	1·21414	1·21554	28
26	1·18703	4	1·18837	1·18971	1·19105	1·19239	1·19372	1·19508	1·19644	1·19782	1·19921	26
24	1·17121	0	1·17250	1·17380	1·17510	1·17638	1·17765	1·17898	1·18029	1·18161	1·18291	24
22	1·15559	6	1·15682	1·15805	1·15929	1·16053	1·16176	1·16301	1·16425	1·16549	1·16673	22
20	1·14017	9	1·14135	1·14253	1·14370	1·14488	1·14605	1·14721	1·14838	1·14955	1·15074	20
18	1·12502	3	1·12612	1·12722	1·12832	1·12943	1·13052	1·13161	1·13269	1·13377	1·13487	18
16	1·11006	2	1·11110	1·11212	1·11314	1·11418	1·11521	1·11620	1·11720	1·11821	1·11921	16
14	1·09534	1	1·09633	1·09729	1·09824	1·09918	1·10009	1·10100	1·10188	1·10276	1·10364	14
12	1·08088	4	1·08178	1·08266	1·08352	1·08436	1·08518	1·08598	1·08675	1·08749	1·08821	12
10	1·06664	0	1·06746	1·06826	1·06904	1·06979	1·07051	1·07121	1·07186	1·07247	1·07304	10
8	1·05266	9	1·05341	1·05413	1·05482	1·05547	1·05608	1·05665	1·05720	1·05771	1·05819	8
6	1·03898	5	1·03961	1·04021	1·04080	1·04135	1·04187	1·04236	1·04281	1·04320	1·04357	6
5	1·03225	1	1·03285	1·03340	1·03391	1·03439	1·03485	1·03531	1·03570	1·03602	1·03631	5
4	1·02553	0	1·02607	1·02656	1·02702	1·02746	1·02786	1·02828	1·02860	1·02886	1·02909	4
3·5	1·02218	1	1·02269	1·02316	1·02360	1·02402	1·02441	1·02478	1·02510	1·02537	1·02561	3·5
3	1·01885	1	1·01935	1·01979	1·02020	1·02060	1·02094	1·02126	1·02153	1·02176	1·02197	3
0·5	1·01553	1	1·01598	1·01641	1·01680	1·01717	1·01749	1·01780	1·01805	1·01824	1·01841	0·5
2·0	1·01222	2	1·01266	1·01305	1·01341	1·01375	1·01405	1·01432	1·01454	1·01473	1·01479	2·0
1·5	1·00890	3	1·00931	1·00969	1·01003	1·01032	1·01057	1·01082	1·01102	1·01115	1·01116	1·5
1·0	1·00556	9	1·00594	1·00629	1·00659	1·00686	1·00710	1·00729	1·00743	1·00760	1·00756	1·0
0·5	1·00221	7	1·00258	1·00287	1·00313	1·00337	1·00359	1·00383	1·00403	1·00408	1·00400	0·5
0	0·99869	5	0·99903	0·99932	0·99956	0·99975	0·99989	0·99997	1·00000	0·99997	0·99988	0

TABLE VIIA.—*Densities of Sulphuric Acid Solutions at 38°, 28°, 18°, and 8°.*

<i>p.</i>	38°.	28°.	18°.	8°.
99·8	1·814845	1·824760	1·834743	1·845070
99·6	1·815555	1·825497	1·835479	1·845806
99·4	1·816250	1·826186	1·836137	1·846450
99·2	1·816850	1·826766	1·836713	1·847004
98·8	1·817830	1·827626	1·837578	1·847845
98·6	1·818194	1·827936	1·837912	1·848168
98·4	1·818505	1·828191	1·838198	1·848454
98·2	1·818760	1·828396	1·838373	1·848634
96·5	1·818470	1·828151	1·838111	1·848338
93	1·809210	1·819228	1·829431	1·839952
91	1·800024	1·810262	1·820765	1·831459
89	1·718279	1·798706	1·809429	1·820398
87	1·774018	1·984586	1·795526	1·806623
85	1·757434	1·767969	1·778898	1·789912
83	1·738604	1·748901	1·759648	1·770573
81	1·718071	1·728137	1·738544	1·749074
79	1·696232	1·706022	1·716010	1·726197
77	1·673645	1·683189	1·692867	1·702749
75	1·650756	1·659976	1·669457	1·679193
73	1·627562	1·636621	1·645942	1·655397
71	1·604441	1·613325	1·622454	1·631802
69	1·581463	1·590203	1·599193	1·608368
67	1·558715	1·567313	1·576146	1·585178
65	1·536280	1·5447 6	1·553409	1·562266
63	1·514138	1·522393	1·531006	1·539653
61	1·492282	1·500387	1·508963	1·517389
59	1·470823	1·478857	1·487286	1·495538
57	1·449876	1·457806	1·466143	1·474294
55	1·429368	1·427182	1·435384	1·443401
53	1·409313	1·417038	1·425057	1·433042
51	1·389620	1·397281	1·405197	1·413067
49	1·370414	1·379982	1·385774	1·393553
47	1·351623	1·359111	1·366818	1·374521
45	1·333197	1·340614	1·348235	1·355890
43	1·315164	1·322544	1·330112	1·337677
41	1·297453	1·314800	1·312289	1·319801
39	1·280100	1·287358	1·294805	1·302260
37	1·263035	1·270239	1·277611	1·285003
35	1·246256	1·253394	1·260660	1·267979
33	1·229724	1·236768	1·243936	1·251164
31	1·213454	1·220397	1·227424	1·234568
29	1·197410	1·204254	1·211140	1·218116
27	1·181645	1·188302	1·195024	1·201830
25	1·166112	1·172602	1·179104	1·185673
23	1·150802	1·157121	1·163388	1·169687
21	1·135703	1·141819	1·147841	1·153867
19	—	—	1·132576	1·138268
17	—	—	1·117505	1·122834
15	—	—	1·102675	1·107612
13	—	—	1·088 71	1·092620
11	—	—	1·073725	1·077813
9	—	—	1·059634	1·063270
7	—	—	1·045788	1·048940
4·5	—	—	1·028890	1·031357

TABLE VIIA—continued.

p .	38°.	28°.	18°.	8°.
2·8	—	—	1·017516	1·019565
2·6	—	—	1·016187	1·018185
2·4	—	—	1·014875	1·016803
2·2	—	—	1·013550	1·015420
1·8	—	—	1·010892	1·012665
1·6	—	—	1·009567	1·011271
1·4	—	—	1·008238	1·009884
1·2	—	—	1·006899	1·008498
·8	—	—	1·004247	1·005716
·6	—	—	1·002899	1·004302
·4	—	—	1·001534	1·002884
·3	—	—	1·000844	1·002179
·2	—	—	1·000152	1·001438
·1	—	—	0·999446	1·000678

TABLE VIII.—*Electric Conductivity of Sulphuric Acid Solutions. Direct First and Second Differentiation.*

First differentiation.				Second differentiation.	
p .	$k_{180} 10^8$.	$\frac{dk}{dp} 10^8$.	p .	$\frac{d^2k}{dp^2} 10^8$.	p .
100·00	0				
*99·44	199	—355·4	99·72	+ 62·2	99·49
*99·08	337·4	—384·4	99·26	—113·1	99·00
*98·42	553	—326·7	98·75	—157·3	98·20
*96·87	790	—152·9	97·645	—36·2	96·84
95·20	948	—94·6	96·035	—30·8	95·04
92·90	1025	—33·5	94·05	—16·2	92·87
90·50	1014	+ 4·6	91·7	—5·0	90·35
87·52	954	20·1	89·01	+ 0·5	87·91
86·10	927	19·0	86·81	6·1	86·05
84·49	914	+ 8·1	85·295	10·3	84·28
82·06	945	—12·8	83·275	12·5	81·83
78·70	1109	—48·8	80·38	10·1	78·61
75·00	1421	—84·3	76·85	8·1	75·04
71·46	1823	—113·6	73·23	5·5	71·02
66·16	2554	—137·9	68·81	2·3	65·93
59·95	3494	—151·4	63·055	+ 0·6	58·92
49·61	5112	—156·5	54·78	—2·7	49·74
39·79	6383	—129·4	44·70	—7·3	41·02
34·87	6784	—75·9	37·33	—10·2	34·86
29·92	6911	—25·6	32·395	—13·5	29·90
24·89	6701	+ 41·7	27·405	—16·0	24·91
19·95	6100	121·6	22·42	—16·8	20·03
15·33	5168	201·7	17·64	—16·2	15·16
10·05	3679	282·0	12·69	—12·2	10·11
5·02	1944	344·9	7·535	—5·5	5·65
2·51	1026	365·7	3·765	—14·5	2·77
1·03	443	394·6	1·77	—28·3	1·14
0	0	430·1	0·515		

TABLE IX.—*Second Differentiation of Part of the Curve representing the Conductivity of Sulphuric Acid Solutions.*

$p.$	$\frac{dk}{dp} 10^8.$	$\frac{d^2k}{dp^2} 10^8.$	$p.$
0	448·5		
1	415·5	− 33·0	0·5
2	391·5	− 24·0	1·5
3	375·5	− 16·0	2·5
4	363·0	− 12·5	3·5
5	354·8	− 8·2	4·5
6	349·0	− 5·8	5·5
7	345·5	− 3·2	6·5
8	344·3	− 1·2	7·5
9	345·5	+ 1·2	8·5
10	349·0	+ 3·5	9·5

TABLE X.—*Determination of the Heat Capacity of Weak Solutions of Sulphuric Acid by dissolving w grams of a 57.85540 per cent. solution at $t^\circ = 14.957^\circ$, and at $t^\circ = 21.051^\circ$, in 599.98 grams of Water.*

$t' - t = 6.092$. Heat capacity of Water = $c = 1.005$, $Wc = 602.983$, Water Equivalent of Apparatus = $w'c_1 = 8.8$ grams, Heat capacity of Strong Acid = $c' = 5.487$.

Also the first differentiation of the Results.

w .	r at t° .	w .	r' at t' .	w .	r .	$\bar{r}$ (mean value).	r' (mean value).	$r' - r$.	Per cent. H_2SO_4 in the final solution.	c'' .	$\frac{dc''}{d\bar{r}}$.	p .
2.218	.1412	2.200	.1424	2.0	.1300	.12958	.13188	.00230	0	1.0050	-.00989	0.10
2.182	.1396	2.181	.1425						.19212	1.0031	-.01078	0.29
4.097	.2385	3.985	.2349	4.0	.2335	.23300	.23865	.00565	.38317	1.00104	-.00928	0.57
4.068	.2365	4.310	.2553	8.0	.4275	.42797	.43664	.00867	.76180	.99753	-.01501	0.88
7.684	.4124	7.925	.4231	10.5	.5425	.54336	.55565	.01229	.99152	.99511	-.00769	1.41
10.767	.5555	8.302	.4405	13.0	.6585	.65783	.6695	.01219	1.22702	.99330	-.00994	1.80
12.811	.6458	10.284	.5467	17.0	.8350	.83477	.85160	.01683	1.59417	.98965	-.00813	2.11
15.894	.8291	12.787	.6809	21.5	1.3338	1.03288	1.0305	.01751	2.00155	.98634	-.00867	2.45
17.315	.8766	17.319	.8637	24.0	1.3390	1.13902	1.1575	.01856	2.22534	.98440	-.00790	2.92
21.400	1.0516	21.452	1.0366	29.0	1.3518	1.35136	1.3706	.01907	2.66758	.98084	-.00664	3.31
23.700	1.1271	23.731	1.1462	35.0	1.6043	1.60380	1.6215	.01704	3.18906	.97672	-.00727	3.66
29.240	1.3609	29.414	1.3882	38.5	1.7475	1.74790	1.7635	.01572	3.48875	.97473	-.01049	3.97
29.231	1.3629	29.387	1.3850	42.5	1.9145	1.91350	1.9285	.02044	3.82724	.97227	-.00950	4.28
34.954	1.6007	34.734	1.6108	46.0	2.0537	2.05311	2.0725	.02390	4.11907	.96920	-.00703	4.59
34.952	1.6010	34.677	1.6200	50.0	2.2137	2.21255	2.2360	.02553	4.45067	.96606	-.00863	4.90
35.293	1.6202	35.010	1.6300	53.5	2.3526	2.35245	2.3735	.02393	4.73672	.96405		
38.721	1.7576	38.294	1.7565	57.5	2.5120	2.51152	2.5345		5.03989	.96125		
42.067	1.8982	42.636	1.9345									
45.725	2.0433	46.174	2.0790									
49.756	2.2082	50.473	2.2556									
53.704	2.3619	53.596	2.3777									
57.242	2.5609	57.761	2.5459									

Also the First Differentiation of the Results.

w .	r at t^0 .	w .	r' at t^0 .	r (from $\frac{r}{w}$).	r' (from $\frac{r'}{w}$).	$r' - r$.	Per cent. H_2SO_4 in the final solution.	c' .	$\frac{dc'}{dp}$.	p .
3.266	1541	3.088	1477							
2.957	1421	3.053	1460							
2.871	1417	2.961	1425							
8.541	4041	8.493	4077	144584 (.141600)	143751	-000903 (+ -002200)	4.96917	96278 (.96224)	-00603	4.79
8.944	4067	8.506	4076							
8.472	4220									
11.766	5654	11.744	5591	403801	404260 (.407146)	+00459 (+ .003944)	5.48427	95860 (.95802)	-00812	5.23
11.770	5662	11.493	5822							
14.807	6061	14.183	6084							
14.872	6069	13.344	7223	566216	567900	+01584	5.80687	95593	-00828	5.64
22.746	10882	22.439	10743							
22.609	10584	22.381	10582	704745	706905	+02160	6.08024	95374	-00801	5.94
32.953	15141	32.593	15095							
31.949	14695	33.463	15346	1070420	107198	+001564	6.79539	94833	-00757	6.44
42.610	19318	41.844	18890	151496	151417	-000490	7.66205	94200	-00730	7.28
41.960	19041	40.756	18668							
—	—	41.302	18724	151496	151417					
—	—	41.908	19050	190596	190470	-00126	8.41728	93631	-00753	8.04
56.677	25247	55.428	24794							
56.564	25272	55.239	24701	249833	250275	+00442	9.54797	92668	-00862	8.98
73.128	31859	70.454	30673							
72.195	31511	71.225	31173	314244	314604	+00360	10.77853	91733	-00769	10.16
—	—	72.296	31522							
—	—	70.269	31622	388388	388343	-00045	12.16084	90731	-00725	11.47
91.665	39071	89.611	38689							
91.714	39133		38264							

TABLE XII.—*Heat Capacities of Sulphuric Acid Solutions. Second Differentiation from the Smoothed First Differential Curve.*

p .	$\frac{dc''}{dp}$.	$\frac{d^2c''}{dp^2}$.	p .
9.0	— .00845		
8.5	— .00805	— .00080	8.75
8.0	— .00770	— .00070	8.25
7.5	— .00750	— .00040	7.75
7.0	— .00750	0	7.25
6.5	— .00760	+ .00020	6.75
6.0	— .00793	.00066	6.25
5.5	— .00818	.00050	5.75
5.0	— .00870	.00104	5.25
4.5	— .00915	.00090	4.75
4.0	— .00995	+ .00160	4.25
3.5	— .00685	— .00620	3.75
3.0	— .00760	+ .00150	3.25
2.5	— .00807	.00094	2.75
2.0	— .00852	.00090	2.25
1.5	— .00880	.00056	1.75
1.0	— .00887	.00014	1.25
0.8	— .00975	.00440	0.9
0.6	— .00990	.00075	0.7
0.4	— .01010	.00100	0.5
0.2	— .01035	.00125	0.3
0	— .01063	.00140	0.1

TABLE XIII.—*First Differentiation of the Heat Capacity of Solutions of Sulphuric Acid from the Smoothed Curve representing the Determinations.*

p .	c'' .	$\frac{dc''}{dp}$.	p .
12·5	·90480	— ·00764	12·25
12·0	·90862	— ·00734	11·75
11·5	·91229	— ·00720	11·25
11·0	·91589	— ·00732	10·75
10·5	·91955	— ·00736	10·25
10·0	·92323	— ·00744	9·75
9·5	·92695	— ·00882	9·25
9·0	·93137	— ·00782	8·75
8·5	·93528	— ·00774	8·25
8·0	·93915	— ·00776	7·75
7·5	·94303	— ·00764	7·25
7·0	·94685	— ·00770	6·75
6·5	·95070	— ·00764	6·25
6·0	·95452	— ·00750	5·75
5·5	·95827	— ·00736	5·25
5·0	·96195	— ·00776	4·75
4·5	·96583	— ·00982	4·25
4·0	·97075	— ·00700	3·9
3·8	·97215	— ·00690	3·7
3·6	·97359	— ·00735	3·5
3·4	·97506	— ·00755	3·3
3·2	·97659	— ·00775	3·1
3·0	·97812	— ·00785	2·9
2·8	·97969	— ·00800	2·7
2·6	·98129	— ·00815	2·5
2·4	·98292	— ·00835	2·3
2·2	·98459	— ·00850	2·1
2·0	·98629	— ·00870	1·9
1·8	·98803	— ·00870	1·7
1·6	·98977	— ·00890	1·5
1·4	·99155	— ·00895	1·3
1·2	·99334	— ·00910	1·1
1·0	·99516	— ·00995	0·9
·8	·99715	— ·00930	0·7
·6	·99901	— ·00960	0·5
·4	1·00093	— ·01000	0·3
·2	1·00293	— ·01035	0·1
0	1·00500		

TABLE XIV.—*Heat evolved on Mixing Solutions of Sulphuric Acid with Water at $17.91^{\circ} \pm .01$.
Water used (W) = 419.47 grams, $w'' = W + w$; $w'_c = 21.74$ grams.*

p .	w .	$(t' - t)^{\circ}$.	p' .	c' .	$w'c'$.	$w''c'' + w'_c t_1$.	D ¹⁰⁰ obs.	Correction for infinit.	D ¹⁰⁰ approx.	Correction due to p' .	D ¹⁰⁰ corr.	$\frac{D^{100}}{p}$.
First Series.												
17.88046	472.16	$\left\{ \begin{array}{l} 0.2628 \\ 0.2644 \end{array} \right\}$	9.44212	0.92783	827.28	850.36	$\left\{ \begin{array}{l} 47.321 \\ 47.623 \end{array} \right\}$	655.866	703.388	-0.315	703.023	80.428
17.88046	471.41	$\left\{ \begin{array}{l} 0.2495 \\ 0.2496 \end{array} \right\}$	9.43500	0.92780	826.56	849.64	$\left\{ \begin{array}{l} 44.976 \\ 45.007 \end{array} \right\}$	656.357	701.348	-0.826	700.522	80.288
9.44272	446.10	$\left\{ \begin{array}{l} 0.0874 \\ 0.0872 \end{array} \right\}$	4.86661	0.90300	833.54	856.62	$\left\{ \begin{array}{l} 16.781 \\ 16.747 \end{array} \right\}$	330.548	349.312	-0.136	347.176	86.767
4.86949	482.60	$\left\{ \begin{array}{l} 0.0548 \\ 0.0581 \end{array} \right\}$	2.47226	0.98233	837.01	860.09	$\left\{ \begin{array}{l} 10.907 \\ 10.565 \end{array} \right\}$	159.623	170.359	+0.044	170.403	84.994
2.47354	426.85	$\left\{ \begin{array}{l} 0.0341 \\ 0.0346 \end{array} \right\}$	1.24755	0.99293	840.34	863.42	$\left\{ \begin{array}{l} 6.8939 \\ 7.0092 \end{array} \right\}$	6.9515	81.0415	+0.022	81.0635	82.789
1.24755	422.19	$\left\{ \begin{array}{l} 0.0247 \\ 0.0255 \end{array} \right\}$	0.62563	0.99878	840.63	863.71	$\left\{ \begin{array}{l} 5.0455 \\ 5.2335 \end{array} \right\}$	32.2285	—	—	37.368	29.957
0.62563	420.66	$\left\{ \begin{array}{l} 0.0143 \\ 0.0146 \end{array} \right\}$	0.31326	1.00183	841.67	864.75	$\left\{ \begin{array}{l} 2.9842 \\ 3.0119 \end{array} \right\}$	13.189	—	—	16.162	25.833
0.31326	420.47	$\left\{ \begin{array}{l} 0.0091 \\ 0.0092 \end{array} \right\}$	0.15681	1.00338	842.78	865.86	$\left\{ \begin{array}{l} 1.8795 \\ 1.8917 \end{array} \right\}$	4.7182	—	—	6.6038	21.08
0.15681	419.79	$\left\{ \begin{array}{l} 0.0065 \\ 0.0060 \end{array} \right\}$	0.07844	1.00418	842.77	865.85	$\left\{ \begin{array}{l} 1.2417 \\ 1.3431 \end{array} \right\}$	1.0695	—	—	2.3619	15.06
0.07844	420.00	$\left\{ \begin{array}{l} 0.0010 \\ 0.0016 \end{array} \right\}$	0.03924	1.04555 for	877.96	901.04	$\left\{ \begin{array}{l} 0.0831 \\ 3.4925 \end{array} \right\}$ for	0.25615	—	—	0.5349	6.82
0.03924	—	—	0	1.004585	—	—	0.26806	0.12816	—	—	0.12816	3.26
Second Series.												
6.78103	438.38	$\left\{ \begin{array}{l} 0.0592 \\ 0.0590 \end{array} \right\}$	3.46571	0.97463	836.09	859.17	$\left\{ \begin{array}{l} 11.608 \\ 11.554 \end{array} \right\}$	229.828	241.409	+0.142	241.551	35.617
3.46437	429.03	$\left\{ \begin{array}{l} 0.0456 \\ 0.0451 \end{array} \right\}$	1.75180	0.98849	838.73	861.81	$\left\{ \begin{array}{l} 9.1672 \\ 9.0628 \end{array} \right\}$	108.332	117.447	+0.006	117.453	33.901
1.75170	424.19	$\left\{ \begin{array}{l} 0.0341 \\ 0.0311 \end{array} \right\}$	0.86075	0.99633	842.56	865.64	$\left\{ \begin{array}{l} 6.9224 \\ 6.3060 \end{array} \right\}$	48.162	54.776	-0.001	54.775	33.270
0.86077	421.06	$\left\{ \begin{array}{l} 0.0172 \\ 0.0181 \end{array} \right\}$	0.44122	1.00053	840.98	864.06	$\left\{ \begin{array}{l} 3.5268 \\ 3.7225 \end{array} \right\}$	20.591	—	—	24.216	27.494
0.44122	420.24	$\left\{ \begin{array}{l} 0.0101 \\ 0.0106 \end{array} \right\}$	0.22081	1.00273	842.00	865.08	$\left\{ \begin{array}{l} 2.0787 \\ 2.1782 \end{array} \right\}$	8.1865	—	—	10.315	23.378
0.22081	420.30	$\left\{ \begin{array}{l} 0.0087 \\ 0.0073 \end{array} \right\}$	0.11031	1.00388	843.03	866.11	$\left\{ \begin{array}{l} 1.8008 \\ 1.5096 \end{array} \right\}$	2.4418	—	—	4.0970	18.556
0.11031	419.51	$\left\{ \begin{array}{l} 0.0028 \\ 0.0037 \end{array} \right\}$	0.05526	1.0441 for	875.98	899.06	$\left\{ \begin{array}{l} 0.6035 \\ 0.7975 \end{array} \right\}$ for	0.5217	—	—	1.2221	11.06
0.05526	—	—	0	1.0041	—	—	0.67452	0.26083	—	—	0.26083	4.72

TABLE XV.—Heat of Dissolution of Sulphuric Acid Solutions at 17.91° ± 0.01. Water used = 599.983 grams, $w'c_1 = 8.83$ to 8.66 grams, $w'' = 599.983 + w$.

p .	w .	$(t' - t)^\circ$.	p' .	c'' .	$w'c''$.	$w''c'' + w'c_1$.	D^{100} obs.	Correction for infinity.	D^{100} .	$\frac{dD}{dp}$.	p .
99.8500	6.0445	1.8358	0.9959	.99532	603.19	611.85	18583	2847	21430	Alternate detts.	
"	6.6502	2.0115	1.0946	.99437	603.21	611.87	18507	2914	21422		
"	6.7513	2.0413	1.1111	.99420	603.21	611.87	18500	2922	21422		A
99.7838	5.2643	1.6019	0.86789	.99651	603.14	611.80	18617	2757	21374		
"	5.7570	1.7430	0.94834	.99576	603.17	611.83	18545	2810	21355		B
"	5.8940	1.7876	0.97070	.99554	603.18	611.84	18557	2827	21384		547 A 99.63
99.5181 (2)	4.3486	1.3236	0.7161	.99793	603.08	611.74	18619	2618	21237		
"	4.2060	1.2826	0.6927	.99814	603.07	611.73	18654	2596	21250		619 B 99.44
99.0637 (2)	6.0585	1.7950	0.93055	.99536	603.23	611.89	18129	2821	20950		
"	6.7199	1.9815	1.0375	.99434	603.26	611.92	18044	2893	20937		707 A 99.15
98.7781 (2)	6.6204	1.9317	1.0780	.99452	603.28	611.94	17936	2775	20711		
"	6.6142	1.9302	1.0770	.99453	603.28	611.88	17857	2873	20730		651 B 98.44
97.7882 (2)	4.8754	1.3909	0.7882	.99728	603.22	611.88	17457	2632	20089		
"	4.4702	1.2800	0.7231	.99787	603.16	611.82	17518	2573	20097		632 A 97.99
97.1924	6.2830	1.7374	1.0072	.99520	603.36	612.02	16924	2780	19704		
"	6.5407	1.8082	1.0481	.99481	603.37	612.03	16919	2815	19734		628 B 96.93
"	6.8606	1.8919	1.0988	.99432	603.39	612.05	16878	2840	19718		
95.8763 (2)	6.3577	1.6779	1.0052	.99479	603.18	611.84	16147	2742	18889		627 A 96.04
"	6.3727	1.6819	1.0076	.99520	603.46	612.12	16155	2742	18897		
94.8949	6.4129	1.6312	1.0035	.99523	603.51	612.17	15571	2712	18283		
"	6.2086	1.5798	0.9719	.99554	603.49	612.15	15576	2687	18263		604 B 94.89
"	6.4400	1.6383	1.0077	.99520	603.51	612.17	15573	2716	18289		
93.9051 (2)	7.1524	1.7448	1.1063	.99426	603.05	613.71	14970	2744	17714		17702.5 B 93.72
"	6.4171	1.5707	0.9937	.99533	604.96	613.62	15016	2675	17691		607 A
92.5471	6.7066	1.5548	1.0231	.99504	603.68	612.34	14146	2662	16858		
"	7.2825	1.6814	1.1098	.99423	603.77	612.43	14140	2708	16848		618 B 92.88

TABLE XV—continued.

p .	w .	$(t' - t)^\circ$.	p' .	c'' .	$w''c''$.	$w''c'' + w'a_1$.	D^{100} obs.	Correction for infinity.	D_x^{100} .	$\frac{dD}{dp}$.	p .
91·8662 (2)	7·6554	1·7156	1·1573	·99378	603·86	612·52	13727	2708	16435	606	91·78
"	7·4176	1·6659	1·1218	·99410	603·82	612·48	13756	2692	16448	A	
91·0247 (2)	8·8394	1·9009	1·3215	·99228	604·12	612·78	13178	2739	15917	596	91·12
"	7·9070	1·7104	1·1839	·99354	603·96	612·62	13253	2693	15945	B	
90·3750	8·2540	1·7333	1·2265	·99815	604·07	612·73	12867	2690	15557	A	
"	7·7055	1·6211	1·1460	·99388	603·97	612·63	12889	2659	15548	568	90·03
89·0310 (2)	8·1677	1·6211	1·1956	·99342	604·15	612·83	12163	2638	14801	A	
"	6·9338	1·3860	1·0174	·99510	603·95	612·63	12242	2555	14797	B	89·34
88·2980	7·1391	1·3824	1·0383	·99490	604·02	612·70	11864	2550	14414	A	
"	6·9305	1·3118	1·0083	·99520	604·00	612·68	11862	2528	14390	B	88·03
87·0362 (2)	7·2725	1·3300	1·0423	·99487	604·15	612·83	11207	2518	13725	A	
"	7·0664	1·2973	1·0313	·99515	604·11	612·79	11215	2495	13710	B	87·24
86·1863	9·0260	1·5701	1·2773	·99266	604·54	613·22	10892	2582	13274	A	
"	8·4737	1·4312	1·2003	·99337	604·41	613·09	10717	2537	13274	B	86·00
84·9791 (2)	7·5783	1·2661	1·0599	·99470	604·34	613·02	10241	2467	12·08	A	
"	6·7827	1·1393	0·9499	·99574	604·19	612·87	10294	2395	12698·5	B	85·09
84·0197 (2)	8·6524	1·3748	1·1949	·99340	604·61	613·26	9744	2491	12235	A	83·99
"	10·8926	1·7111	1·4988	·99066	605·16	613·84	9643	2582	12225	B	83·98
83·0117 (2)	8·4082	1·2855	1·1472	·99386	604·65	613·33	9377	2442	11819	A	
"	6·3466	0·9856	0·8689	·99652	604·22	612·90	9517	2294	11811	A	
82·9927	9·9196	1·4976	1·3498	·99202	605·03	613·80	9267	2507	11774	B	82·94
"	9·3407	1·4155	1·2723	·99270	604·87	613·64	9299	2484	11784	A	
81·8501 (2)	7·4067	1·0843	0·9980	·99526	604·51	613·19	8977	2334	11311	B	82·00
"	9·0729	1·3123	1·2192	·99320	604·91	613·59	8875	2434	11309	A	81·99
80·9875	8·8076	1·2290	1·1717	·99366	604·93	613·61	8562	2391	10953	B	
"	8·9415	1·2406	1·1892	·99347	604·94	613·62	8555	2398	10953	A	80·91

Alternate data.

TABLE XV—continued.

p .	w .	$(t' - t)^\circ$.	p' .	c'' .	$w''e''$.	$w'e'' + w'e_r$.	D^{100} obs.	Correction for infinity.	D_g^{100} .	$\frac{dD}{dp}$.	p .
79·9681 (2)	9·3886	1·2530	1·2320	·99310	605·17	613·87	8192	2381	10573	379 A	79·98
"	12·9973	1·7036	1·6955	·98894	606·20	614·90	8000	2502	10562	349 A'	79·87
78·9900 (2)	9·7204	1·2407	1·2592	·99282	605·32	614·02	7836	2360	10567·5 B	351 B	78·57
78·7547	11·7938	1·4882	1·5182	·99048	605·96	614·66	7756	2424	10196 A		
"	11·4747	1·4476	1·4779	·99084	605·86	614·56	7753	2416	10174·5 A'		
77·1791	11·9868	1·4069	1·5117	·99055	606·19	614·89	7217	2373	9590 B	323 A	77·44
"	11·1388	1·3126	1·4067	·99150	605·93	614·63	7243	2346	9589	342 A'	77·33
75·9072 (2)	10·7821	1·2119	1·3399	·99213	605·96	614·69	6909	2289	9198	318 B	76·09
"	9·4882	1·0744	1·1816	·99355	605·54	614·24	6956	2246	9201	318 A	74·97
75·0013	12·4940	1·3380	1·5300	·99039	606·59	615·29	6389	2311	8897 B	301 A'	74·94
"	12·0207	1·2900	1·4732	·99087	606·41	615·11	6395	2299	8894	288 B	73·51
74·0417	14·9857	1·5240	1·8043	·98800	607·57	616·29	6267	2336	8603		
"	12·8268	1·3177	1·5498	·99020	606·80	615·50	6323	2286	8609		
73·9864 (2)	9·6883	1·0147	1·1756	·99360	605·77	614·47	6435	2187	8622 A'		
72·0223 (2)	7·4586	0·7342	0·8844	·99637	605·24	613·94	6043	1996	8039	278 A	72·58
"	10·8939	1·0422	1·2845	·99260	606·36	615·06	5883	2159	8042	289 A'	72·55
71·1257	15·7316	1·4141	1·8172	·98786	608·23	616·93	5546	2245	7791	258 B	70·02
"	14·1996	1·2861	1·6444	·98938	607·66	616·36	5583	2216	7799		
68·0085 (2)	11·7437	0·9463	1·3055	·99244	607·11	615·83	4963	2042	7005	7006 B	68·54
"	10·8696	0·8809	1·2101	·99320	606·75	615·47	4987	2020	7007		
65·9711	21·378	1·5034	2·2699	·98404	611·44	620·16	4367	2142	6509	6504 A	66·03
"	22·742	1·5931	2·4093	·98285	612·04	620·76	4349	2158	6507		
"	29·568	2·0275	3·0984	·97734	615·28	624·00	4279	4216	6495		
64·0454 (2)	11·2840	0·7724	1·1822	·99355	607·33	616·07	4217	1894	6111	6105·5 B	63·63
"	12·6730	0·8575	1·3247	·99226	607·92	616·64	4172	1928	6100		
61·2986	25·472	1·4346	2·4965	·98211	614·26	622·98	3509	2015	5524		
"	26·287	1·4722	2·5729	·98150	614·68	623·40	3491	2023	5514	5518 A	62·01
"	23·954	1·3540	2·3533	·98332	613·53	622·25	3517	2000	5517		

Alternate detts.

379 A

349 A'

351 B

323 A

342 A'

318 B

318 A

301 A'

288 B

278 A

289 A'

258 B

250 A

227 B

211 A

203 B

TABLE XV—continued.

p .	w .	$(t'-t)^\circ$.	p' .	c'' .	$w''c''$.	$w''c'' + w'e_1$.	D^{100} obs.	Correction for infinity.	D^{100} .	$\frac{dD}{dp}$.	p .
59·9705 (2)	15·7950	0·8755	1·5382	·99033	609·83	618·57	3429	1850	5279	189	59·57
"	18·4438	1·0085	1·7843	·98818	611·12	619·86	3389	1885	5274	A	
57·8568	25·010	1·1374	2·3153	·98364	614·77	623·51	2985	1884	4869	B	57·99
"	26·490	1·2596	2·4461	·98257	615·55	624·29	2968	1898	4866		
56·0091 (2)	17·466	0·7942	1·5842	·98992	611·23	619·97	2819	1736	4555	B	55·68
"	19·280	0·8669	1·7437	·98853	612·16	620·90	2792	1759	4551	A	
53·5069	24·903	0·9574	2·1324	·98520	615·63	624·37	2400	1725	4125	B	54·02
"	28·370	1·0748	2·4158	·98280	617·54	626·28	2373	1751	4124		
52·0268 (2)	16·932	0·6351	1·4278	·99132	611·73	620·30	2327	1586	3913	B	51·55
"	17·232	0·6454	1·4524	·99110	611·56	620·47	2323	1590	3913	A'	51·38
49·59205	29·256	0·8937	2·3055	·98374	619·00	627·76	1918	1613	3531		
"	25·689	0·7993	2·0362	·98603	616·93	625·63	1947	1589	3536	B	50·03
49·2519	38·181	1·1027	2·9468	·97007	622·57	633·93	1829	1647	3476		
"	34·756	1·0170	2·6970	·98052	622·38	631·14	1847	1632	3479	5 A'	
48·0265 (2)	18·594	0·5551	1·4435	·99116	613·11	621·87	1857	1466	3323	A	47·65
"	16·623	0·5037	1·2946	·99250	611·98	620·74	1881	1441	3322	A'	47·49
45·7167 (2)	24·865	0·6204	1·8191	·98786	617·26	626·05	1562	1463	3006	B	45·80
"	27·563	0·6793	2·0078	·98624	618·92	627·68	1543	1443	3005	A	
43·5898 (2)	15·339	0·3658	1·0865	·99446	611·91	620·67	1480	1269	2749	B	43·74
"	17·259	0·4053	1·2256	·99316	613·12	621·88	1452	1297	2749		
41·7674 (2)	19·923	0·4061	1·3422	·99207	614·99	623·75	1271	1261	2532	A	41·62
"	21·855	0·4367	1·4678	·99096	616·22	624·98	1249	1278	2527	B	
39·6478 (2)	18·674	0·3366	1·1967	·99341	614·58	623·35	1124	1174	2298	A	39·75
"	21·396	0·3737	1·3651	·99188	616·33	625·10	1092	1199	2291	B	37·68
37·7311 (2)	22·112	0·3395	1·3410	·99210	617·19	625·96	961	1138	2099	A	
"	22·760	0·3439	1·3789	·99174	617·60	626·37	947	1143	2090	B'	37·61

Alternate detls.

TABLE XV—continued.

$p.$	$w.$	$(\ell-t)^{\circ}.$	$p'.$	$c''.$	$w''c''.$	$w''c''+w'c_1.$	D^{100} obs.	Correction for infinity.	D_{∞}^{100}	$\frac{dD}{dp}.$	$p.$
35-7188 (2)	25-458	0-3269	1-4538	-99107	619-86	628-63	807	1092	1899	B	Alternate data.
35-5663	29-627	0-3604	1-6736	-98914	622-77	631-54	772	1112	1884	B'	
40-834	0-4588	2-2681	2-2681	-98406	631-57	640-34	720	1144	1864		
33-8520 (2)	23-637	0-2739	1-2880	-99260	619-01	627-78	728	1015	1743	A	
"	23-052	0-2692	1-2524	-99289	618-60	627-37	732	1011	1743		
32-0398	33-722	0-3100	1-7049	-98887	626-67	635-44	584	1004	1588		
"	36-918	0-3301	1-8572	-98874	628-93	637-70	570	1015	1585	B	
"	27-591	0-2669	1-4090	-99148	622-22	630-99	609	975	1584		
29-2423	36-961	0-2755	1-6969	-98890	629-88	638-66	476	915	1391		
"	35-469	0-2598	1-6322	-98951	628-79	637-57	467	910	1377	A	
"	30-704	0-2348	1-4236	-99137	625-25	634-03	485	891	1376		
27-7528 (2)	26-234	0-1877	1-1625	-99372	622-29	631-07	454	819	1273		
"	31-000	0-2112	1-3634	-99188	625-86	634-64	432	840	1272		
25-5694	38-988	0-2082	1-5620	-99011	632-65	641-43	343	790	1133		
"	31-195	0-1835	1-2637	-99278	626-62	635-40	374	765	1139	A	
23-8370 (2)	24-454	0-1389	0-9834	-99588	621-87	630-65	358	669	1027		
"	22-337	0-1340	0-8577	-99060	620-26	629-04	377	657	1034		
27-862	27-862	1-3468	0-9847	-99540	624-96	633-74	306	631	937		
22-1891	37-547	1-6041	1-3068	-99242	632-70	641-48	274	667	941	A	
21-9229 (2)	26-061	0-1259	0-9112	-99610	624-49	633-27	306	611	917	A'	
"	25-727	0-1259	0-9013	-99617	623-31	632-09	310	609	919		
19-8413 (2)	21-632	0-1004	0-6304	-99816	620-48	629-28	292	517	809		
"	20-729	0-0985	0-6326	-99841	619-72	628-52	298	512	810		
18-1835 (2)	27-504	0-1043	0-7370	-99716	625-70	634-50	240	491	731		
"	27-896	0-1070	0-8078	-99709	626-05	634-85	243	463	736		
16-1315 (2)	23-305	0-0839	0-6032	-99898	622-66	631-46	237	405	632		
"	24-271	0-0861	0-6272	-99874	623-46	632-26	224	410	634	B	

TABLE XV—continued.

p .	w .	$(\ell' - t)^\circ$.	p' .	e'' .	$w''e''$.	$w''e'' + w'e_r$.	D^{100} obs.	Correction for infinity.	D_{α}^{100} .	$\frac{dD}{dp}$.	p .
14·0271 (2)	24·707	0·0778	0·5548	·99943	624·34	633·14	199	346	545 } 543 } 544 A	42·4 B	14·07
"	24·972	0·0772	0·5605	·99936	624·55	633·35	196	347	543 }	40·5 A	12·03
12·0073 (2)	26·982	0·0706	0·5167	·99979	626·83	635·63	167	290	457 } 459 } 458 B	40·3 A'	12·02
"	27·973	0·0727	0·5349	·99960	627·70	636·50	165	294	459 }	38·6 B	10·47
10·0378	30·016	0·0662	0·4782	1·00015	630·09	638·89	141·4	238·4	279·4 }		
"	29·622	0·0686	0·4723	1·00024	629·76	638·56	148·0	237·8	285·8 }		
10·0113 (2)	27·395	0·0642	0·4371	1·00057	627·74	636·54	149·2	232·3	381·5 A'		
8·9703 (2)	22·925	0·0551	0·3301	1·00166	623·94	632·74	151·0	192·6	344·6 }	36·6 A	9·15
"	22·441	0·0552	0·3234	1·00170	623·48	632·28	155·7	191·8	347·5 }	37·0 A'	9·14
8·2660	27·541	0·0570	0·3628	1·00134	628·36	637·16	131·0	183·0	314·9 }	36·5 B	7·97
"	28·522	0·0605	0·3751	1·00117	629·25	638·05	135·4	184·3	319·7 }	38·7 B'	7·83
"	25·941	0·0567	0·3426	1·00153	626·88	635·68	139·0	179·6	318·6 }		
6·9622 (2)	22·400	0·0454	0·2506	1·00246	623·91	632·71	128·4	133·9	262·3 }	43·3 A	7·22
"	22·958	0·0462	0·2566	1·00240	624·44	633·24	127·5	135·7	263·2 }		
6·6981	22·204	0·0470	0·2390	1·00256	623·78	632·58	133·9	126·9	260·8 }	41·8 A'	7·09
"	23·333	0·0465	0·2507	1·00247	624·86	633·66	126·3	129·0	255·3 }	38·9 B	5·94
6·1461	26·928	0·0450	0·2640	1·00230	628·35	637·15	106·4	121·6	228·0 A		
"	29·687	0·0472	0·2898	1·00208	630·98	639·28	101·6	126·3	227·9 }		
5·9214 (2)	26·387	0·0429	0·2494	1·00248	627·92	636·72	103·5	114·2	217·7 }	42·1 B'	5·81
"	26·907	0·0450	0·2541	1·00240	628·39	637·18	106·5	115·4	221·9 }		
4·9159 (2)	31·133	0·0420	0·2425	1·00253	632·72	641·52	86·6	93·8	180·4 }		
"	31·867	0·0452	0·2479	1·00249	633·42	642·22	91·0	94·7	185·7 }		

Those solutions marked (2) belonged to the C series of preparations (p. 73); the others to the A series.

TABLE XVI.—*Heat of Dissolution of Sulphuric Acid Solutions*
Differentiation of the Smoothed Curve representing the Results.

First differentiation.			Second differentiation.				
p .	D.	$\frac{dD}{dp}$.	p .	p .	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	p .
99·5	21215	676	99·25	99·4	680	35	99·2
99·0	20877	660	98·75	99·0	666	30	98·8
98·5	20547	646	98·25	98·6	654	27·5	98·4
98·0	20224	634	97·75	98·2	643	22·5	98·0
97·5	19907	610	97·25	97·8	634	20·0	97·6
97·0	19602	630	96·75	97·4	626	—11	97·07
96·5	19287	634	96·25	96·75	634	14	96·5
96·0	18967	626	95·75	96·25	627	16	96·0
95·5	18657	614	95·25	95·75	619	18	95·5
95·0	18350	600	94·75	95·25	610	24	95·0
94·5	18050	592	94·25	94·75	600	22	94·5
94·0	17754	626	93·75	94·25	589	—144	94·13
93·5	17441	628	93·25	94·0	625	4	93·75
93·0	17127	604	92·75	93·5	623	8	93·25
92·5	16825	620	92·25	93·0	619	14	92·75
92·0	16515	600	91·75	92·5	612	14	92·25
91·5	16215	596	91·25	92·0	605	20	91·75
91·0	15917	578	90·75	91·5	595	24	91·25
90·5	15628	556	90·25	91·0	583	28	90·75
90·0	15350	566	89·75	90·5	569	30	90·25
89·5	15067	568	89·25	90·0	554	—50	89·75
89·0	14783	552	88·75	89·5	579	34	89·25
88·5	14507	544	88·25	89·0	563	30	88·75
88·0	14235	528	87·75	88·5	548	26	88·25
87·5	13971	530	87·25	88·0	535	24	87·75
87·0	13707	514	86·75	87·5	523	18	87·25
86·5	13450	500	86·25	87·0	514	18	86·75
86·0	13200	490	85·75	86·5	505	14	86·25
85·5	12955	496	85·25	86·0	498	12	85·75
85·0	12707	484	84·75	85·5	492	6	85·25
84·5	12465	466	84·25	85·0	489	2	84·75
84·0	12232	439	83·5	84·5	488	47	84·0
83	11793	428	82·5	83·5	441	15	83
82	11365	408	81·5	82·5	426	17	82
81	10957	392	80·5	81·5	409	18·5	81
80	10565	368	79·5	80·5	390·5	22	80
79	10197	332	78·5	79·5	368·5	24	79
78	9865	335	77·5	78·5	334·5	9·0	78·5 to 73·5
77	9530	310	76·5	73·5	290·5	6·5	
76	9222	312	75·5	72·5	284·0	10·0	73
75	8910	295	74·5	71·5	274·0	9·5	72
74	8615	292	73·5	70·5	264·5	9·0	71
73	8323	286	72·5	69·5	255·5	7·5	70
72	8037	272	71·5	68·5	246·5	8·0	69
71	7765	268	70·5	67·5	239·0	9·7	68
70	7497	—	69·5	66·5	231·0		67
69	7237	245	68·5	65·5	223·3		66

TABLE XVI—*continued*.

First differentiation.				Second differentiation.			
p .	D.	$\frac{dD}{dp}$.	p .	p .	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	p .
68	6992	235	67·5	65·5	223·3	6·3	65
67	6757	232	66·5	64·5	217·0	6·5	64
66	6525	282	65·5	63·5	210·5	7·0	63
65	6303	216	64·5	62·5	203·5	6·0	62
64	6087	212	63·5	61·5	197·5	5·5	61
63	5875	207	62·5	60·5	192·0	2·6	60·25
62	5668	195	61·5	60·0	190·7	4·97	{ 60 to
61	5473	193	60·5				{ 51
60	{ 5280			51·0	146·0	4·0	{ 50·25
	5271	189	59·5	49·5	140·0	3·23	{ 49·5 to
59	5082	185	58·5				{ 36·5
58	4897	179	57·5	36·5	98·0	7·2	35·75
57	4718	172	56·5				
56	4548	168	55·5	35	87·2	3·3	34·5
55	4378	165	54·5	34	83·9	3·1	33·5
54	4213	160	53·5	33	80·8	2·9	31·5
53	4053	155	52·5	32	77·9	2·5	31·5
52	3898	147	51·5	31	75·4	2·2	30·5
51	3751	166	50·5	30	73·2	1·9	29·5
50	3585	141	49·5	29	71·3	5·6	28·5
49	3444	138	48·5	28	65·7	4·13	{ 28 to
48	3306	134	47·5				{ 20
47	3172	129	46·5	20	32·7	-11·5	19·25
46	3043	126	45·5	18·5	50·0	1·5	18
45	2917	124	44·5	17·5	48·5	1·5	17
44	2793	121	43·5	16·5	47·0	1·6	16
43	2672	117	42·5	15·5	45·4	1·6	15
42	2557	114	41·5	14·5	43·8	1·6	14
41	2441	111	40·5	13·5	42·2	1·8	13
40	2330	108	39·5	12·5	40·4	1·7	12
39	2222	104	38·5	11·5	38·7	1·8	11
38	2118	101	37·5	10·5	36·9	-4·2	9·63
37	2017	99	36·5	8·75	44·2	2·6	8·5
36	1918	86·8	35·5	8·25	42·9	2·4	8·0
35	1831·5	84·5	34·5	7·75	41·7	2·0	7·5
34	1747·0	83·5	33·5	7·25	40·7	1·2	7·0
33	1663·5			6·75	40·1	1·0	6·5
				6·25	39·6	0·6	6·0
				5·75	39·3	0·2	5·5
				5·25	39·2		

TABLE XVI—*continued.*

First differentiation.				First differentiation.			
$p.$	D.	$\frac{dD}{dp}$	$p.$	$p.$	D.	$\frac{dD}{dp}$	$p.$
33	1663·5	78·3	32·5	8·5	326·0	42·4	8·25
32	1585·2	77·0	31·5	8·0	304·8	42·0	7·75
31	1508·2	73·5	30·5	7·5	283·8	40·6	7·25
30	1434·7	73·0	29·5	7·0	263·5	40·0	6·75
29	1361·7	72·2	28·5	6·5	243·5	39·0	6·25
28	1289·5	64·2	27·5	6·0	224·0	40·0	5·75
27	1225·3	63·6	26·5	5·5	204·0	39·0	5·25
26	1161·7	60·7	25·5	5·0	185·0		
25	1101·0	61·5	24·5		Another reading.		
24	1039·5	57·5	23·5	46	3042	122	45·5
23	982·0	56·0	22·5	45	2920	118	44·5
22	926·0	55·0	21·5	44	2802	121	43·5
21	871·0	53·5	20·5	43	2681	118	42·5
20	817·5	33·5	19·5	42	2563	114	41·5
19	774·0	50·0	18·5	41	2449	113	40·5
18	724·0	48·5	17·5	40	2336	109	39·5
17	675·5	46·8	16·5	39	2227	106	38·5
16	628·7	44·7	15·5	38	2121	103	37·5
15	584·0	44·0	14·5	37	2018	92	36·5
14	540·0	41·8	13·5	36	1926	92	35·5
13	498·2	41·0	12·5	35	1834	87	34·5
12	457·2	38·5	11·5	34	1747	84	33·5
11	418·7	37·7	10·5	33	1663	79	32·5
10	381·0	32·7	9·5	32	1582	76	31·5
9	348·3	44·6	8·75	31	1506	70	30·5
8·5	326·0			30	1436	70	29·5
				29	1366		

TABLE XVII.—*Heat of Dissolution of Sulphuric Acid Solutions.*
First Differentiation of the Ultra-smoothed Curve representing the Results.

<i>p.</i>	D.	$\frac{dD}{dp}$	<i>p.</i>	<i>p.</i>	D.	$\frac{dD}{dp}$	<i>p.</i>
100	24555	670	99·5	70	7505	260	69
99	20885	645	98·5	68	6995	255	67
98	20240	640	97·5	66	6527	234	65
97	19590	643	96·5	64	6088	220	63
96	18957	622	95·5	62	5671	209	61
95	18335	620	94·5	60	5274	199	59
94	17715	607	93·5	58	4902	175	57
93	17108	588	92·5	56	4553	168	55
92	16520	587	91·5	54	4217	158	53
91	15933	570	90·5	52	3902	151	51
90	15363	570	89·5	50	3600	144	49
89	14793	543	88·5	48	2313	129	47
88	14250	545	87·5	46	3055	128	45
87	13705	515	86·5	44	2800	123	43
86	13190	487	85·5	42	2555	113	41
85	12703	463	84·5	40	2330	104	39
84	12240	450	83·5	38	2123	98	37
83	11790	425	82·5	36	1927	92	35
82	11365	405	81·5	34	1743	79	33
81	10960	395	80·5	32	1585	74	31
80	10565	370	79·5	30	1438	69	29
79	10195	345	78·5	28	1300	69	27
78	9850	337	77·5	26	1163		
77	9513	313	76·5				
76	9200	293	75·5	46	3049	129	45
75	8907	292	74·5	44	2791	120	43
74	8615	302	73·5	42	2552	112	41
73	8313	278	72·5	40	2329	104	39
72	8035	270	71·5	38	2121	96	37
71	7765	260	70·5	36	1929	90·5	35
70	7505	253	69	34	1748	82·5	33
68	7000	238	67	32	1583	76	31
66	6525	220	65	30	1431	71	29
64	6085	205	63	28	1289	65	27
62	5675			26	1159	60	25
				24	1039	57	23
78	9877	328	77·5	22	926	53	21
77	9540	324	76·5	20	820	49	19
76	9225	315	75·5	18	722	47	17
75	8910	303	74·5	16	629	44	15
74	8607	287	73·5	14	541	41	13
73	8328	283	72·5	12	460	38	11
72	8037	272	71·5	10	384	35	9
71	7765	272	70·5	8	314		
70	7505						

TABLE XVIII.—*Heat of Dissolution of Sulphuric Acid Solutions.*
Second Differentiation from the Smoothed First Differential Curve.

$p.$	$\frac{dD}{dp}$	$\frac{d^2D}{dp^2}$	$p.$	$p.$	$\frac{dD}{dp}$	$\frac{d^2D}{dp^2}$	$p.$
99·6	547	− 600	99·4	55	165·5		
99·2	695	+ 48	98·6	54	161·5	+ 4·0	54·5
98	637	+ 8·56	98 to 94	53	157·5	4·0	53·5
94	602·7	− 12	93·5	52	154	3·5	52·5
93	614·7	+ 8·7	92·5	51	150	4·0	51·5
92	606	15·5	91·5	50	146	4·0	50·5
91	590·5	23·0	90·5	49	140	6·0	49·5
90	567·5	+ 30·5	89·5	39	109·5	3·05	49 to 39
89	537	− 5·7	88·5	38	101·7	7·8	38·5
88	542·7	+ 21·4	88 to 80	37	97·2	4·5	37·5
80	371·5	15·5	79·5	36	92·3	4·9	36·5
79	356	14	78·5	35	88·0	4·3	35·5
78	342	12·5	77·5	34	84·7	3·7	34·5
77	329·5	12·5	76·5	33	81·0	3·7	33·5
76	317	11·5	75·5	32	78·0	3·0	32·5
75	305·5	10·5	74·5	31	75·3	2·7	31·5
74	295	8	73·5	30	72·7	2·6	30·5
73	287	10	72·5	29	70·7	3·0	29·5
72	277	9·25	71	28	67·5	3·2	28·5
70	258·5	9	69	27	65·7	1·8	27·5
68	240·5	7·25	66	26	63·8	1·9	26·5
66	226	6·5	65	25	61·8	2·0	25·5
64	213	5·75	63	24	59·5	2·3	24·5
62	201·5	5·25	61	23	57·5	2·0	23·5
60	191	5·5	59·5	22	55·5	2·0	22·5
59	185·5	5·0	58·5	21	53·0	2·5	21·5
58	180·5	5·2	57·5	20	51·0	2·0	20·5
57	175·3	5·0	56·5	19	48·4	2·6	19·5
56	170·3	4·8	55·5	9	36·0	+ 0·84	19 to 9
55	165·5			6	41·0	− 1·67	9 to 6

TABLE XIX.—*Heat evolved on mixing Sulphuric Acid Solutions with Water. Differentiation of the Smoothed Curve representing the Results.*

First differentiation.				Second differentiation.			
p .	D.	$\frac{dD}{dp}$.	p .	p .	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	p .
9	329.7	40.4	8.5	9	40.83	.91	8.5
8	289.3	39.4	7.5	8	39.92	1.05	7.5
7	249.9	38.1	6.5	7	38.87	1.24	6.5
6	211.8	36.9	5.5	6	37.63	1.48	5.5
5	174.9	35.4	4.5	5	36.15	1.65	4.5
4	139.5	43.3	3.8	4	34.50	—	—
3.6	122.20	35.8	3.5	3.6	35.7	—2.0	3.5
3.4	115.05	36.0	3.3	3.4	36.1	—1.75	3.3
3.2	107.85	37.0	3.1	3.2	36.45	—1.25	3.1
3	100.45	36.3	2.9	3.0	36.7	— .75	2.9
2.8	93.20	37.0	2.7	2.8	36.85	— .50	2.7
2.6	85.83	36.7	2.5	2.6	36.95	+ .25	2.5
2.4	78.50	36.8	2.3	2.4	36.9	1	2.3
2.2	71.15	35.8	2.1	2.2	36.7	1.50	2.1
2	64.00	36.3	1.9	2	36.4	1.75	1.9
1.8	56.75	35.4	1.7	1.8	36.05	2	1.7
1.6	49.67	35.6	1.5	1.6	35.56	2.75	1.5
1.4	42.55	34.9	1.3	1.4	35.10	2.75	1.3
1.2	35.57	34.4	1.15	1.2	34.55	—15.50	1.15
1.1	32.13	35.8	1.05	1.1	36	+ 5.7	1.05
1	28.55	35.1	.95	1	35.43	7.3	.95
.9	25.04	34.1	.85	.9	34.7	9	.85
.8	21.63	33.1	.75	.8	33.8	10.5	.75
.7	18.32	32.3	.65	.7	32.75	12	.65
.6	15.09	30.8	.55	.6	31.55	13.5	.55
.5	12.01	29.6	.475	.5	30.2	15	.45
.45	10.53	29.0	.425	.4	28.7		
.40	9.08						
	From D/p						
	curve.						
1.2	35.72	33.5	1.15	1.2	33.10	— 8.2	1.15
1.1	32.37	34.4	1.05	1.1	33.92	— 3.5	1.05
1	28.93	34.0	.95	1	34.27	— 1.3	.95
.9	25.53	34.9	.85	.9	34.40	+ 2.7	.85
.8	22.04	34.0	.75	.8	34.13	5.6	.75
.7	18.64	33.4	.65	.7	33.57	9.5	.65
.6	15.30	31.6	.55	.6	32.62	12.7	.55
.5	12.14	31.2	.475	.5	31.35	16.3	.455
.45	10.38	33.4	.425	.4	29.72	+ 50.4	.375
.40	8.91	25.6	.375	.35	27.20	—12.6	.325
.35	7.63	28.1	.325	.3	27.83	+ 4.6	.275
.30	6.225	27.74	.275	.25	27.60	18.6	.225
.25	4.838	27.68	.225	.20	26.67	33.8	.175
.20	3.454	25.88	.175	.15	24.94	47.6	.12
.15	2.160	24.60	.125	.10	22.60		
.10	.930	18.50	.09	.08	20.40		
.08	.560				15.20	26.0	.09

TABLE XIX—continued.

First differentiation.				Second differentiation.			
p .	D.	$\frac{dD}{dp}$.	p .	p .	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	p .
·08	·560	12·79	·07	·08	15·20	22·8	·07
·06	·3042	3·65	·05	·06	10·75	198	·05
·04	·1312	5	·03	·04	6·8	178	·03
·02	·0312	1·56	·01	·02	+ 3·25	170	·01
0	0			0	- ·15		
Another reading.							
·16	2·48	32·0	·15	·016	+ 35·0	287·5	·15
·14	1·84	26·8	·13	·14	29·25	270·0	·13
·12	1·304	23·7	·11	·12	23·85	242·5	·11
·10	·89	16·7	·09	·10	19·0	217·5	·09
·08	·556	12·8	·07	·08	14·65	207·5	·07
·06	·30	8·6	·05	·06	10·55	185	·05
·05	·128	4·9	·03	·04	6·8	175	·03
·02	·030	1·5	·01	·02	3·3	160	·01
0	0			0	·1		

TABLE XX.—Decrease of Density of Sulphuric Acid Solutions by Heat. Unreduced Values.

p .	From 28·06° to 38·20°.	From 7·99° to 28·06°.	From 7·99° to 38·20°.	p .	From 28·06° to 38·20°.	From 7·99° to 28·06°.	From 7·99° to 38·20°.
99·93	·009948	·020314	·030262	69·98	·008925	·018392	·027317
98·85	·009664	·020292	·029956	68·06	·008770	·018084	·026863
97·60	·009810	·020255	·030065	66·06	·008648	·017851	·026497
96·82	·009793	·020338	·030131	64·09	·008524	·017535	·026059
95·95	·009893	·020364	·030237	61·95	·008115	·017311	·025426
95·08	·009952	·020474	·030426	60·01	·008155	·016959	·025114
93·97	·010051	·020745	·030796	57·90	·008078	·016587	·024665
93·06	·010160	·020804	·030964	56·05	·007996	·016416	·024412
91·93	·010284	·021059	·031343	54·04	·007868	·016154	·024022
91·09	·010384	·021249	·031631	52·07	·007800	·015969	·023759
89·92	·010489	·021519	·032008	50·11	·007727	·015743	·023470
89·09	·010557	·021755	·032312	48·07	·007642	·015553	·023195
87·91	·010690	·021936	·032626	45·76	·007549	·015366	·022915
87·09	·010709	·022117	·032824	43·53	·007500	·015421	·022741
85·92	·010737	·022113	·032850	41·81	·007471	·015113	·022584
85·04	·010676	·022040	·032716	39·68	·037586	·014999	·022385
84·08	·010639	·021904	·032543	37·76	·007331	·014880	·022211
83·04	·010433	·021780	·032213	35·74	·007263	·014734	·021997
81·91	·010379	·021280	·031659	33·87	·007172	·014553	·021725
81·15	·010134	·020946	·031080	31·83	·007016	·014346	·021361
80·03	·010065	·020652	·030717	29·80	·007010	·014037	·021047
79·04	·009894	·020305	·030199	27·77	·006817	·013739	·020556
78·00	·009747	·019974	·029721	26·18	·006691	·013394	·020085
75·96	·009484	·019486	·028970	23·85	·006481	·012853	·019334
74·04	·009315	·019070	·028385	21·94	·006221	·012347	·018638
72·07	·009104	·018697	·027801	19·86	·006074	·011783	·017857

TABLE XXI.—*Decrease of Density, and Expansion, of Sulphuric Acid Solutions by Heat.**Reduced Values.**All the Values, except those for p, being multiplied by 10⁶.*

p.	28—38°.		18—28°.		8—18°.		18—38°.	8—28°.	8—38°, Diff. of Dens. (E).	
	Expn.	Diff. of Dens.	Expn.	Diff. of Dens.	Expn.	Diff. of Dens.	Diff. of Dens.	Diff. of Dens.	Diff. of Dens.	p.
100	5448	9883	5450	9940	5638	10343	19823	20283	30166	—
99·8	—	—	—	—	—	10327	—	—	—	—
99·6	—	—	—	—	—	10327	—	—	—	—
99·4	—	—	—	—	—	10313	—	—	—	+82 99·5
99·2	—	—	—	—	—	10291	—	—	—	—
99	5437	9881	5431	9924	5594	10279	19805	20203	30084	—
98·8	—	—	—	—	—	10267	—	—	—	—
98·6	—	—	—	—	—	10256	—	—	—	—
98·4	—	—	—	—	—	10256	—	—	—	+157 98·5
98·2	—	—	—	—	—	10260	—	—	—	—
98	5310	9658	5460	9985	5593	10284	19643	20269	29927	—
97·5	—	—	—	—	—	10247	—	—	—	+36 97·5
97	5335	9704	5441	9950	5568	10237	19654	20187	29891	—
96·5	—	—	—	—	—	10227	—	—	—	—
96	5365	9752	5463	10026	5598	10245	19778	20271	30023	—132 96·5
95	5408	9820	5522	10080	5603	10286	19900	20366	30186	—163 95·5
94	5467	9911	5542	10102	5667	10387	20013	20489	30400	—214 94·5
93	5583	10018	5537	10203	5751	10521	20221	20724	30742	—342 93·5
92	5597	10102	5694	10336	5820	10623	20438	20959	31061	—319 92·5
91	5688	10238	5802	10503	5873	10694	20741	21197	31435	—374 91·5
90	5762	10341	5907	10661	5922	10752	21002	21413	31754	—319 90·5
89	5831	10427	5961	10723	6062	10969	21150	21692	32119	—365 89·5
88	5909	10525	6061	10863	6090	11043	21388	21906	32431	—312 88·5
87	5957	10568	6130	10940	6180	11097	21507	22037	32605	—174 87·5
86	5995	10588	6185	10989	6177	11041	21577	22030	32618	—13 86·5
85	5994	10535	6177	10929	6196	11014	21464	21943	32478	+114 85·5
84	5966	10434	6154	10823	6236	11035	21257	21858	32292	186 84·5
83	5923	10297	6145	10747	6208	10925	21044	21672	31969	323 83·5
82	5890	10182	6068	10550	6139	10740	20732	21290	31472	497 82·5
81	5859	10066	6022	10407	6057	10530	20473	20937	31003	369 81·5
80	5848	9932	5916	10194	5997	10360	20126	20554	30486	517 80·5
79	5771	9790	5854	9988	5936	10187	19778	20175	29965	521 79·5
78	5727	9647	5800	9834	5880	10022	19481	19856	29503	462 78·5
77	5702	9544	57·0	9678	5837	9882	19222	19569	29104	399 77·5
76	5630	9358	5732	9582	5846	9827	18940	19409	28767	337 76·5
75	5585	9220	5711	9481	5832	9736	18701	19217	28437	330 75·5
74	5605	9187	5693	9385	5792	9600	18572	18985	28172	265 74·5
73	5566	9059	5695	9321	5742	9455	18380	18776	27835	337 73·5
72	5559	8984	5674	9221	5742	9384	18205	18605	27589	246 72·5
71	5537	8884	5658	9129	5761	9348	18013	18477	27361	228 71·5
70	5528	8807	5655	9059	5748	9259	17866	18318	27125	236 70·5
69	5526	8740	5653	8990	5737	9175	17730	18165	26905	220 69·5
68	5520	8666	5633	8893	5741	9115	17559	18008	26674	231 68·5
67	5518	8598	5636	8833	5730	9032	17431	17865	26463	211 67·5
66	5507	8523	5639	8774	5713	8940	17297	17714	26237	226 66·5
65	5484	8426	5634	8703	5702	8857	17129	17560	25986	241 65·5
64	5469	8341	5634	8641	5682	8763	16982	17404	25745	241 64·5
63	5451	8255	5658	8613	5648	8647	16868	17260	25515	280 63·5
62	5424	8153	5691	8602	5620	8542	16755	17150	25297	218 62·5
61	5430	8105	5715	8576	5584	8426	16681	17002	25107	190 61·5
60	5437	8056	5703	8495	5566	8338	16551	16833	24889	218 60·5
59	5462	8034	5700	8429	5548	8252	16463	16681	24715	174 59·5
58	5458	7971	5702	8372	5526	8161	16343	16533	24504	211 58·5
57	5446	7930	5719	8337	5559	8151	16267	16488	24418	86 57·5
56	5474	7881	5707	8261	5548	8077	16142	16338	24219	199 56·5
55	5467	7814	5707	8202	5546	8017	16016	16219	24033	186 55·2
54	5477	7774	5688	8117	5541	7953	15891	16070	23844	189 54·5
53	5474	7715	5666	8019	5603	7985	15744	16004	23729	115 53·5
52	5492	7686	5650	7950	5611	7944	15686	15894	23580	131 52·5
51	5513	7661	5665	7916	5601	7870	15577	15786	23447	133 51·5
50	5523	7622	5657	7850	5602	7816	15472	15666	23288	159 50·5
49	5522	7568	5653	7792	5615	7779	15360	15571	23139	149 49·5

TABLE XXI—*continued.*

<i>p.</i>	28—38°.		18—28°.		8—18°.		18—38°.	8—28°.	8—38°, Diff. of Dens. (F.).		<i>dE.</i>	<i>p.</i>
	Expn.	Diff. of Dens.	Expn.	Diff. of Dens.	Expn.	Diff. of Dens.	Diff. of Dens.	Diff. of Dens.	Diff. of Dens.			
49	5522	7568	5653	7792	5615	7779	15360	15571	23139	122	48·5	
48	5536	7535	5655	7738	5626	7744	15273	15482	23017	119	47·5	
47	5540	7488	5670	7707	5635	7703	15195	15410	22898	105	46·5	
46	5558	7461	5687	7677	5639	7655	15138	15332	22793	100	45·5	
45	5566	7417	5682	7621	5670	7655	15038	15276	22693	84	44·5	
44	5596	7410	5678	7567	5699	7632	14977	15199	22609	91	43·5	
43	5611	7380	5722	7568	5687	7565	14948	15133	22513	84	41·5	
42	5640	7363	5731	7533	5695	7526	14896	15069	22422	91	42·5	
41	5662	7347	5740	7489	5726	7512	14836	15001	22348	84	41·5	
40	5663	7298	5753	7457	5750	7495	14755	14952	22250	98	40·5	
39	5670	7258	5784	7442	5757	7455	14705	14902	22160	90	39·5	
38	5696	7243	5785	7398	5777	7434	14641	14832	22075	85	38·5	
37	5704	7204	5803	7372	5786	7392	14576	14764	21968	107	37·5	
36	5709	7159	5788	7307	5818	7384	14466	14691	21850	118	36·5	
35	5727	7138	5797	7266	5805	7319	14404	14585	21723	127	35·5	
34	5729	7093	5807	7230	5804	7264	14323	14494	21587	136	34·5	
33	5728	7044	5795	7168	5810	7228	14212	14396	21440	147	33·5	
32	5725	6993	5790	7114	5813	7195	14107	14319	21302	138	32·5	
31	5721	6943	5758	7027	5820	7144	13970	14171	21114	188	31·5	
30	5730	6917	5733	6950	5800	7072	13857	14022	20929	185	30·5	
29	5716	6844	5718	6886	5760	6976	13730	13862	20706	223	29·5	
28	5670	6745	5704	6824	5738	6903	13569	13727	20472	234	28·5	
27	5633	6657	5657	6722	5695	6806	13379	13528	20185	287	27·5	
26	5610	6585	5595	6605	5639	6694	13190	13299	19884	301	26·5	
25	5565	6490	5545	6502	5571	6569	12992	13069	19561	323	25·5	
24	5537	6414	5465	6366	5503	6445	12780	12811	19225	336	24·5	
23	5490	6319	5416	6267	5414	6299	12586	12566	18885	340	23·5	
22	5445	6224	5341	6141	5339	6169	12365	12310	18534	351	22·5	
21	5385	6116	5274	6022	5249	6026	12138	12048	18164	370	21·5	
20	5324	6007	5227	5929	5149	5871	11936	11800	17807	357	20·5	

TABLE XXI—*continued.*—*Decrease of Densities of Sulphuric Acid Solutions between 8 and 18°.*

<i>p.</i>	Expn.	Diff. of Dens.	<i>p.</i>	Expn.	Diff. of Dens.	<i>p.</i>	Expn.	Diff. of Dens.
19	5025	5692	7	2777	3152	1·8	—	1773
18	4892	5504	6	2526	2885	1·6	—	1704
17	4769	5329	5	2281	2607	1·4	—	1646
16	4632	5162	4·5	—	2467	1·2	—	1599
15	4482	4937	4·0	2057	2339	1·0	1529	1538
14	4342	4756	3·5	—	2231	0·8	—	1469
13	4180	4549	3·0	1806	2096	0·6	—	1403
12	3975	4297	2·8	—	2049	0·4	—	1350
11	3807	4088	2·6	—	1998	0·3	—	1339
10	3432	3878	2·4	—	1928	0·2	—	1286
9	3240	3636	2·2	—	1870	0·1	—	1232
8	3014	3413	2·0	—	1828	0	1194	1195

TABLE XXII.—*Decrease of Densities of Sulphuric Acid Solutions by Heat. Differentiation of the Smoothed Curve representing the Results between 8° and 38°.*

First differentiation.				Second differentiation.			
p .	E 10 ⁶ .	$\frac{dE}{dp}$ 10 ⁶ .	p .	p .	$\frac{dE}{dp}$ 10 ⁶ .	$\frac{d^2E}{dp^2}$ 10 ⁶ .	p .
100	30170			100	127		
99·5	30110	120	99·75	99·5	117	20	99·75
99	30050	120	99·25	99	105	24	99·25
98·5	29990	120	98·75	98·5	93	24	98·75
98	29950	80	98·25	98	76	34	98·25
97·5	29915	70	97·75	97·5	57	38	97·75
97	29890	50	97·25	97	— 95	304	97·25
96·5	29945	—110	96·75	96·5	—117	44	96·75
96	30015	—140	96·25	96	—142	50	96·25
95·5	30085	—140	95·75	95·5	—168	52	95·75
95	30185	—200	95·25	95	—192	48	95·25
94·5	30285	—200	94·75	94·5	—222	60	94·75
94	30400	—230	94·25	94	—250	56	94·25
93·5	30535	—270	93·75	93·5	—277	54	93·75
93	30725	—380	93·25	93	—215	56	93·25
92·5	30890	—330	92·75	92·5	—345	60	92·75
92	31060	—340	92·25	92	—355	20	92·25
91·5	31235	—350	91·75	91·5	—357	4	91·75
91	31415	—360	91·25	91	—359	4	91·25
90·5	31595	—360	90·75	90·5	—360	2	90·75
90	31775	—360	90·25	90	—362	4	90·25
89·5	31960	—370	89·75	89·5	—360	— 4	89·75
89	32140	—360	89·25	89	—357	— 6	89·25
88·5	32300	—320	88·75	88	—227	— 60	88·5
88	32435	—270	88·25	84	+ 280	—127	88 to 84
87·5	32535	—200	87·75	83·5	503	—	—
87	32590	—110	87·25	78·5	492	+ 2	83·5 to 78·5
86·5	32620	— 60	86·75	77·5	365	—	—
86	32620	0	86·25	73·5	280	21	77·5 to 73·5
85·5	32585	+ 70	85·75	72·5	235	—	—
85	32530	110	85·25	63·5	230	5	72·5 to 63·5
84·5	32435	190	84·75	62·5	195	—	—
84	32315	240	84·25	50	142	4	62·5 to 50
83·5	32145	330	83·75	49	130	12	49·5
83	31975	350	83·25	48	124	6	48·5
82	31470	505	82·5	47	115	9	47·5
81	30980	490	81·5	46	103	12	46·5
80	30470	510	80·5	45	95	8	45·5
79	29970	500	79·5	44	92	3	44·5
78	29480	490	78·5	43	90	2	43·5
77	29110	370	77·5	42	87	3	42·5
76	28760	350	76·5	41	87	0	41·5
75	28435	325	75·5	40	85	2	40·5
74	28130	295	74·5	39	80	+ 5	39·5
73	27840	290	73·5	38	107	— 27	38·5
72	27600	240	72·5	37	110	— 3	37·5
71	27360	240	71·5	36	122	— 12	36·5

TABLE XXII—*continued*.

First differentiation.				Second differentiation.			
p .	$E \ 10^6$.	$\frac{dE}{dp} \ 10^6$.	p .	p .	$\frac{dE}{dp} \ 10^6$.	$\frac{d^2E}{dp^2} \ 10^6$.	p .
71	27360	225	70·5	36	122	— 11	35·5
70	27315	245	69·5	35	133	— 7	34·5
69	27890	225	68·5	34	140	— 7	33·5
68	27665	220	67·5	33	147	— 13	32·5
67	27445	235	66·5	32	160	— 13	31·5
66	27210	235	65·5	31	173	— 13	30·5
65	26975	230	64·5	30	180	— 15	29·5
64	26745	240	63·5	29	195	— 80	28·5
63	26505	215	62·5	28	275	— 18	27·5
62	26290	195	61·5	27	293	— 18	26·5
61	26095	180	60·5	26	315	— 12	25·5
60	25915	195	59·5	25	327	— 13	24·5
59	25720	160	58·5	24	340	— 8	23·5
58	25560	180	57·5	23	348	— 4	22·5
57	25380	165	56·5	22	352	— 5	21·5
56	25215	175	55·5	21	357	— 5	20·5
55	25040	165	54·5	20	362		
54	24875	155	53·5				
53	24720	150	52·5				
52	24570						

First differentiation continued.

p .	$E \ 10^6$.	$\frac{dE}{dp} \ 10^6$.	p .	p .	$E \ 10^6$.	$\frac{dE}{dp} \ 10^6$.	p .
52	24570	165	51·5	36	22850	125	35·5
51	24415	135	50·5	35	22725	135	34·5
50	24280	140	49·5	34	22590	145	33·5
49	24140	140	48·5	33	22445	160	32·5
48	24000	110	47·5	32	22285	180	31·5
47	23890	105	46·5	31	22105	180	30·5
46	23785	100	45·5	30	21925	190	29·5
45	23685	95	44·5	29	21735	265	28·5
44	23590	95	43·5	28	21470	280	27·5
43	23495	80	42·5	27	21190	310	26·5
42	23415	90	41·5	26	20880	315	25·5
41	23325	85	40·5	25	20565	320	24·5
40	23240	80	39·5	24	20245	355	23·5
39	23160	80	38·5	23	19890	355	22·5
38	23080	110	37·5	22	19535	365	21·5
37	22970	120	36·5	21	19170	365	20·5
36	22850			20	18805		

TABLE XXII—*continued*.

First differentiation, between 8° and 18°.

p .	E 10 ⁶ .	$\frac{dE}{dp}$ 10 ⁶ .	p .	p .	E 10 ⁶ .	$\frac{dE}{dp}$ 10 ⁶ .	p .
100	10350	90	99·75	20	5870	170	19·5
99·5	10305	60	99·25	19	5700	185	18·5
99·0	10275	50	98·75	18	5515	185	17·5
98·5	10250	20	98·25	17	5330	185	16·5
98·0	10240	0	97·75	16	5145	205	15·5
97·5	10240	30	97·25	15	4940	200	14·5
97·0	10225	0	96·75	14	4740	210	13·5
96·5	10225	— 16	96·25	13	4530	215	12·5
96·0	10233	— 48	95·75	12	4315	220	11·5
95·5	10257	— 6	95·25	11	4095	220	10·5
95·0	10290	— 80	94·75	10	3875	235	9·5
94·5	10330	— 120	94·25	9	3640	250	8·5
94·0	10390			8	3390	245	7·5
				7	3145	270	6·5
				6	2875	265	5·5
				5	2610	280	4·5
29	6980	80	28·5	4	2330	220	3·75
28	6900	100	27·5	3·5	2220	140	3·25
27	6800	105	26·5	3·0	2100	260	2·75
26	6695	120	25·5	2·5	1970	280	2·25
25	6575	120	24·5	2·0	1830	290	1·75
24	6455	140	23·5	1·5	1685	200	1·25
23	6315	140	22·5	1·0	1535	220	0·75
22	6175	145	21·5	0·5	1375		
21	6030	160	20·5				
20	5870						

Second differentiation, between 8° and 18°.

p .	$\frac{dE}{dp}$ 10 ⁶ .	$\frac{d^2E}{dp^2}$ 10 ⁶ .	p .	p .	$\frac{dE}{dp}$ 10 ⁶ .	$\frac{d^2E}{dp^2}$ 10 ⁶ .	p .
99·75	90	+ 43	99·75 to 97·75	19	180	— 4	19 to 10·5
97·75	5	— 22	97·5	10·5	217		
97·25	27	+ 42	97·25 to 94·25	9·5	240	— 5	25 to 4·5
94·25	— 100			4·5	277		
28	92	— 8	28 to 19	4·0	210	— 36	4 to 1
19	180			1·0	317		

TABLE XXIII.—Weights of Sulphuric Acid Solutions contained in a 25 c.c. Density Bottle at t° .

t° .	84.1370 per cent.		81.09315 per cent.		41.76736 per cent.		t° .
	w .	dw/dt .	w .	dw/dt .	w .	dw/dt .	
38.203	(43.80801)	(-0.0242)	(43.0737)	(-0.0230)	(32.6733)	(-0.0167)	37.15
36.103	43.8589	-0.0251	43.1219	-0.0242	32.7084	-0.0178	35.10
34.090	43.9095	-0.0252	43.1707	-0.0243	32.7441	-0.0177	33.08
32.075	43.9605	-0.0258	43.2199	-0.0248	32.7799	-0.0181	31.07
30.060	44.0125	(-0.0263)	43.2698	(-0.0255)	32.8163	(-0.0185)	29.06
28.064	(44.0349)	-0.0256	(43.3207)	-0.0246	(32.8533)	-0.0177	28.05
26.036	44.1155	(-0.0249)	43.3689	(-0.0238)	32.8877	(-0.0170)	27.05
23.835	44.1723	-0.0258	43.4238	-0.0249	32.9235	(-0.0163)	24.94
21.905	44.2233	-0.0264	43.4727	-0.0253	32.9601	-0.0175	23.97
19.881	44.2751	-0.0256	43.5224	-0.0246	32.9957	(-0.0189)	22.87
17.925	44.3269	-0.0264	(43.5753)	(-0.0270)	33.0305	-0.0176	20.89
15.946	44.3794	-0.0265	43.6174	(-0.0242)	33.0667	-0.0178	18.90
13.939	44.4302	-0.0253	43.6685	(-0.0213)	33.1032	-0.0183	17.91
11.956	44.4809	-0.0257	43.7198	-0.0255	33.1387	-0.0182	16.94
9.995	44.5320	-0.0261	43.7687	-0.0260	33.1749	-0.0180	14.94
7.978	(44.5877)	(-0.0276)	(43.8198)	-0.0249	33.2125	-0.0185	12.95
6.015	44.6397	(-0.0271)	43.8719	(-0.0253)	33.2479	-0.0186	10.98
		(-0.0265)		(-0.0259)		-0.0181	8.99
				(-0.0265)		-0.0181	7.00

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TABLE XXIV.—*List of the most convenient Scales used in the Working Diagrams.*

Property.	Scale.
Densities, 1st diff.,* 100 to 94 per cent. ..	·002 and 0·5 per cent. to the inch.
„ „ 100 „ 60 „ ..	·002 „ 2 „ „
„ „ 76 „ 0 „ ..	·0005 „ 4 „ „
„ „ 20 „ 0 „ ..	·0005 „ 2 „ „
„ „ 10 „ 0 „ ..	·001 „ 0·5 and „ „
	0·2
Contractions, 1st diff.	Same as for the densities.
Conductivities, 1st and 2nd diff.	·000001 and 2 per cent. to the inch.
Heat capacities and 1st diff., 12 to 0 per cent.	·01 „ ·05 „ „
„ „ 4 „ 0 „ ..	·002 „ ·02 „ „
Heat of dissolution, 100 to 94 per cent. ..	500 „ 0·5 „ „
„ „ 100 „ 59 „ ..	500 „ 1 „ „
„ „ 70 „ 29 „ ..	200 „ 1 „ „
„ „ 40 „ 5 „ ..	100 „ 1 „ „
„ „ 9 „ 0 „ ..	20 „ 1 „ „
„ „ 5 „ 0 „ ..	10 „ ·2 „ „
„ „ 2 „ 0 „ ..	5 „ ·1 „ „
„ „ 0·16 „ 0 „ ..	·2 „ ·02 „ „
„ „ 1st diff., 100 to 40 p.ct.	100 „ 2 „ „
„ „ 1st diff., 47 to 5 p.ct.	50 „ 2 „ „
Expansion, main curves	·001 „ 2 „ „
„ „ curves for very weak and very strong solutions	·001 „ ·5 „ „

* All the differentials here mentioned are those obtained directly from the experimental values: the scales used for those obtained from readings of curves have been sufficiently indicated in the text, p. 68.

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PLATE 3. SECOND DIFFERENTIAL OF THE FIGURES REPRESENTING THE DENSITIES AND CONTRACTIONS OF SULPHURIC ACID SOLUTIONS AT 18°.

Per Cent H₂SO₄. Figs. B D and F.