"as several have the same initial letter, I shall distinguish them in the "following manner: 1. In the class which I call *metalloids*, I shall employ "the initial letter only, even when the letter is common to the metalloid "and some metal. 2. In the class of metals, I shall distinguish those that "have the same initial with another metal or a metalloid, by writing the "first two letters of the word. 3. If the first two letters be common to two "metals, I shall, in that case, add to the initial letter the first consonant "which they have not in common; for example, S = sulphur, Si = silicium, "St = stibium (antimony), Sn = stannum (tin), C = carbonicum, Co = "cobaltum (cobalt), Cu = cuprum (copper), O = oxygen, Os = osmium, etc.

" The chemical signs express always one volume of the substance. "When it is necessary to indicate several volumes it is done by adding the "number of volumes; for example, the *oxidium cuprosum* (protoxide of "copper) is composed of a volume of oxygen and a volume of metal, "therefore, its sign is Cu + O. The *oxidum cupricum* (peroxide of cop-"per) is composed of 1 volume of metal and 2 volumes of oxygen, there-"fore its sign is Cu + 2O. In like manner the sign for sulphuric acid "is S + 3O; for carbonic acid, C + 2O; for water, 2H + O.

" When we express a compound volume of the first order, we throw "away the +, and place the number of volumes above the letter; for "example, $\mathrm{CuO} + \mathrm{S}\overset{3}{\mathrm{O}}$ = sulphate of copper, $\mathrm{Cu}\overset{2}{\mathrm{O}} + 2\mathrm{S}\overset{3}{\mathrm{O}}$ = persulphate "of copper. These formulas have the advantage, that, if we take away "the oxygen, we see at once the ratio between the combustible radicles. "As to the volumes of the second order, it is but rarely of any advantage "to express them by formulas as one volume; but if we wish to express "them in that way, we may do it by using the parenthesis, as is done in "algebraic formulas; for example, alum is composed of 3 volumes of sul-"phate of alumina and 1 volume of sulphate of potash. Its symbol is "$3(\mathrm{Al}\overset{2}{\mathrm{O}} + 2\mathrm{S}\overset{3}{\mathrm{O}}) + (\mathrm{Po} + 2\mathrm{S}\overset{3}{\mathrm{O}})$. As to the organic volumes, it is at "present very uncertain how far figures can be successfully employed to "express their composition. We shall have occasion only in the following "pages to express the volume of ammonia. It is 6H + N + O, or $\overset{6}{\mathrm{H}}\mathrm{NO}$."

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THE DENSITIES OF CERTAIN DILUTE AQUEOUS SOLUTIONS BY A NEW AND PRECISE METHOD.[1]

BY ARTHUR B. LAMB AND R. EDWIN LEE.

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The density of liquids is a sharply defined and exactly measurable property; indeed, it can be determined with greater relative accuracy

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[1] Presented in part by R. Edwin Lee, as a thesis for the Degree of Doctor of Science at New York University.

and ease than any other specific property of liquids. To make such a determination, it is only necessary to weigh a known volume, or what amounts to the same thing, to compare the weight of a given volume of the liquid with the weight of the same volume of a known or standard liquid. Using a Sprengel pycnometer of 50 cc. volume and a thermostat bath, constant to two or three hundredths of a degree, it is easy to obtain, at room temperatures, results concordant to one unit in the fifth decimal place, or to 0.001%. Ostwald and Luther[1] estimate the accuracy, attainable with a Sprengel pycnometer of 200 cc. volume in a good thermostat, as ±0.002%, and the careful measurements of Tammann[2] by this method confirm these estimates. Kohlrausch and Hallwach's[3] modification of the displacement method affords still greater refinement. Using a float with a volume of 900 cc. and working under such conditions that temperature fluctuations were of little moment, Kohlrausch obtained results concordant to within two or three units in the seventh place of decimals, or to about one part in five million.

This high order of accuracy is amply sufficient for most purposes. We have, however, been engaged in a study of the densities of some very dilute solutions, and there, if the results are to have any significance, the very highest possible accuracy is desirable. This led us to a critical examination of the accurate methods of density determination at present available. The only ones to be seriously considered from this point of view are the above mentioned Sprengel pycnometer and Kohlrausch displacement methods, and, in addition, the submerged sinker method of Pisati and Reggiani.[4]

The pycnometer method has three fundamental drawbacks for measurements of the highest accuracy. In the first place, it is difficult to secure a constant and definit temperature inside a considerable volume of unstirred liquid. This difficulty could be lessened by use of some internal, electromagnetic stirring device, but this would in turn introduce several new difficulties and the manipulation would certainly not be simple. Secondly, glass vessels, because of the variation in the humidity of their surfaces, are always difficult to weigh with the utmost accuracy. Thirdly, the pycnometer with its contents puts a considerable load upon the balance arm, and so reduces the sensibility of the balance. All three of these unfavorable effects increase with increasing size of pycnometer, so that it is useless to attempt to increase the accuracy by increasing indefinitly the volume of the pycnometer.

The displacement method escapes these three objections, for the liquid

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[1] *Physico-chemische Messungen, Leipzig*, 1910, 178.

[2] *Z. physik. Chem.*, 16, 91.

[3] *Wied. Ann.*, 53, 14 (1894).

[4] *Rend. Reale Accad. dei Lincei*, [4] 7, 99 (1890).

is *outside* and is easily stirred; the submerged glass float, completely surrounded by the liquid at constant temperature, must soon reach a perfectly definit surface condition; and finally, since most of the weight of the float is neutralized by the buoyant effect of the liquid, the load on the balance arm is small and the sensibility correspondingly high. Unfortunately, a fresh difficulty arises; the surface tension on the suspension wire at the liquid-gas surface is pronounced, and like most surface-tension effects, is subject to large and irregular variations, probably due to exceedingly minute quantities of impurities. Kohlrausch[1] deposited platinum black on his fine platinum suspension wire, and found that this very greatly diminished these variations of the surface-tension effect. His excellent results, others by Ditjken,[2] and prolonged trials which we have carried out ourselves, have convinced us that this method is an excellent one, and makes possible results of decidedly greater accuracy than can be obtained with a pycnometer. Still, we have never been able to eliminate the surface-tension variations altogether, and it remains a serious obstacle to any further increase in the accuracy of this method.

The submerged sinker method of Pisati and Reggiani cuts, as it were, the Gordian knot of this difficulty, for it abolishes the suspension wire altogether. Two variations of this method were proposed and used in 1885 by these investigators, who were especially interested in the density of sea water. In one, a sinker of known specific gravity was employed and distilled water added to the solution under investigation, until the sinker hovered in the body of the liquid; in the other, this floating equilibrium was attained by the addition of platinum weights to the sinker. They secured results concordant to one part in several hundred thousand. The lower portions of a liquid at rest are always denser than the upper portions, partly because of the superposed weight of the upper portions of the liquid, but chiefly because of inequalities in temperature. The sinker thus comes to rest in a layer of the same average density as itself. Nansen,[3] in 1896, while studying the salinity of the sea water in the north polar basin, independently developed the same method, using chiefly, what corresponded to the second modification of Pisati and Reggiani. Weights were added to the sinker until equilibrium was nearly attained, the final adjustment being secured by slight variations of the temperature. Warrington[4] also proposed and used this method in 1899, obtaining again an accuracy of one part in several hundred thousand. Finally, Richards and Shipley[5] proposed a modification of this method where temperature was made the variable factor, and applied it with marked success

[1] *Wied. Ann.*, **56**, 184 (1895).

[2] *Z. physik. Chem.*, 24, 108 (1897).

[3] The Norwegian Polar Expedition, Vol. III, pt. 10, p. 78, London.

[4] *Phil. Mag.*, [5] 48, 498 (1899).

[5] THIS JOURNAL, **34**, 599 (1912).

to the quantitative analysis of solutions. They showed that with water it was sensitive to one part in five million, which corresponds to the degree of concordance of the best measurements of Kohlrausch. Moreover they showed that it could be used as a very quick and accurate empirical method of analysis without concern as to the actual density or the actual temperature of the solution.

The submerged sinker method is then evidently intrinsically superior to the displacement method, for it shares in all the latter's advantages and obviates its difficulty with variable surface tension. Its one drawback lies in the difficulty of varying the buoyancy of the sinker by small amounts. If this variation in buoyancy is to be secured by the addition or removal of weights, then it is necessary to use weights as small as a hundredth of a milligram, provided an accuracy equal to that of Kohlrausch is to be secured with a float of ordinary dimensions; this is evidently impracticable for any extended series of measurements. The relative buoyancy could also be changed by changing the temperature, but since each test of the sinker's buoyancy requires the utmost constancy of temperature, much time would have to be allowed after each change for the whole system to reach a steady state, and the method would become a time-consuming one. Its accuracy, too, if no other means were used for varying the buoyancy of the float, would never be greater than that with which the coefficient of expansion of the solution over that temperature interval was known.

Some immaterial, easily variable, easily measurable external force is wanted, which will produce displacements of the sinker in a vertical direction and thus fulfil the function of added weights. Two methods for securing such a force have occurred to us; first, to use a not too rigid sinker and to alter its buoyancy at will by changing the pressure of the air above the liquid; second, to enclose a piece of soft iron in the bulb of the sinker, and, by means of an electric current sent through a properly placed external circuit, to exert an electromagnetic attraction in a vertical direction upon the bulb. The first method is neither as convenient nor as elegant as the second, and besides, introduces a fresh complication due to the variation of solubility of the air in the liquid with the pressure.

We have, therefore, adopted the second method, and we present below a description of the instrumental arrangements which were adopted for its execution, of the experimental procedure followed, and finally, a summary of the results obtained.

Outline of the Procedure and of the Experimental Arrangements.

We first attempted to use a permanent magnet in the sinker and to produce an electromagnetic field of such a character in the body of the liquid that the sinker would tend to occupy a central position in the axis of the glass beaker. This would have eliminated any possibility of the sinker sticking to the sides of the beaker. A suitable vertical field could then have been superposed and the necessary upward or downward pull produced. We did not succeed in realizing a satisfactory centralizing field of this kind.

Instead, we replaced the permanent magnet in the sinker by a piece of soft iron, and attached a small helix of insulated copper wire to the bottom and outside surface of the beaker. In addition we sealed a fine platinum point into the lower end of the sinker, and, just above the helix, on the floor of the glass beaker, we cemented a small saucer designed to guide the platinum point of the sinker into a fixed central position as the float was drawn downward by the activated helix. After the liquid under examination had reached a constant temperature, platinum weights were added to the sinker till it barely floated. A current was then allowed to pass through the helix strong enough to send the sinker to the bottom and hold its platinum point in the platinum saucer. When this position had been maintained for some time, long enough to allow all eddies in the liquid to disappear, the current in the helix was slowly diminished until the platinum point just left the platinum saucer. The current reading at this point was carefully noted on a milliammeter in the circuit. This procedure was first carried through with the purest water, then a known quantity of stock solution was added to the water and the procedure repeated. From the weight added to the sinker, the weight equivalent of the current used, and the known volume of the sinker, the density of the solution could be calculated with reference to water.

The electromagnetic pull was only employed to produce the finer variations in buoyancy, platinum milligram weights being added to or taken from the float where larger variations were necessary. The utmost precaution had, of course, to be taken to maintain a constant, accurately known temperature, to avoid any jarring of the apparatus and to wait until all eddy currents in the liquid had ceased. The point of contact of the platinum wire with the platinum saucer had also to be observed with the greatest care, and we designed and had constructed a special form of microscope for this purpose.

Description of Apparatus.

The Sinker.—This was made from a round-bottom Jena glass flask of about 250 cc. capacity. A bar of soft iron was fitted inside the flask, a small quantity of mercury was introduced and a fine platinum point was sealed into the extreme tip of the closed neck. The relation of its various parts may be seen from Fig. I. The flask floated in an inverted position; a small depression was blown in its top to provide a place for the reception of the platinum weights. The bulb weighed *in vacuo* *234.5681* grams; it displaced 235.1089 cc. of water at 20.004° on the hydrogen scale.

The Weights.—The weights used on the sinker were of platinum and had been specially calibrated by the maker. We re-calibrated them to hundredths of a milligram by comparison, according to Richards' method, with a 100 mg. weight which had been standardized at the Bureau of Standards to 0.001th of a milligram.

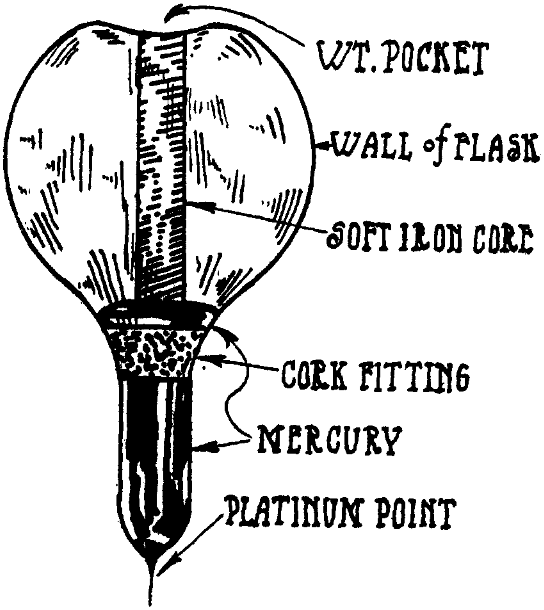

Fig. I.

Containing Vessel. — The water, or solution under investigation, was contained in a large, cylindrical vessel made by cutting off the rim of a four-liter Jena glass beaker. Very nearly the same volume of liquid was always used and it sufficed to fill this vessel to within a few centimeters of the upper edge. This containing vessel was placed inside a large, thick-walled, glass specimen jar. A heavy, lead disk resting on cork feet was put on the bottom of the specimen jar; the containing vessel was supported on rubber pads on top of the disk. There was an annular air space between the beaker and the jar $2^1/_2$ cm. in width. The heavy glass cover of the specimen jar was clamped on by four *brass* clamps and made water-tight by a rubber gasket between the ground glass surfaces. Five holes were drilled in this cover, and vertical brass tubes cemented into them; through these tubes passed a thermometer, a glass stirring rod, the reflecting microscope, and the lead wires to the helix on the bottom of the containing vessel. One tube served for the introduction of the nickel forceps used for the removal or addition of weights. Except for these tubes, the whole specimen jar was submerged three centimeters below the level of the water in the thermostat. (Fig. II.)

The Thermostat.—The thermostat was rectangular in shape, 80 liters in capacity and deep enough to submerge easily the specimen jar. It was electrically heated, and the temperature of the water with which it was filled was kept constant to within 0.005° without difficulty, by a large mercury-toluene regulator. Since the periodic fluctuations in the temperature of the thermostat were rapid, and the insulation of the liquid in the containing vessel was high, the lag of the inner liquid was great, and the temperature remained constant in it to within less than ±0.001° for relatively long periods of time. The thermostat was placed on a heavy concrete pier in the cellar of the laboratory. This was found necessary, as the very slightest jar was sufficient to start the sinker prematurely from the position with its platinum point resting in the platinum cup. The vibrations set up by the rotating propeller also had to be moderated by introducing a perforated sheet of brass as a shield between it and the specimen jar; but this did not entirely suffice, so that at the moment of taking an observation, the stirring was temporarily interrupted.

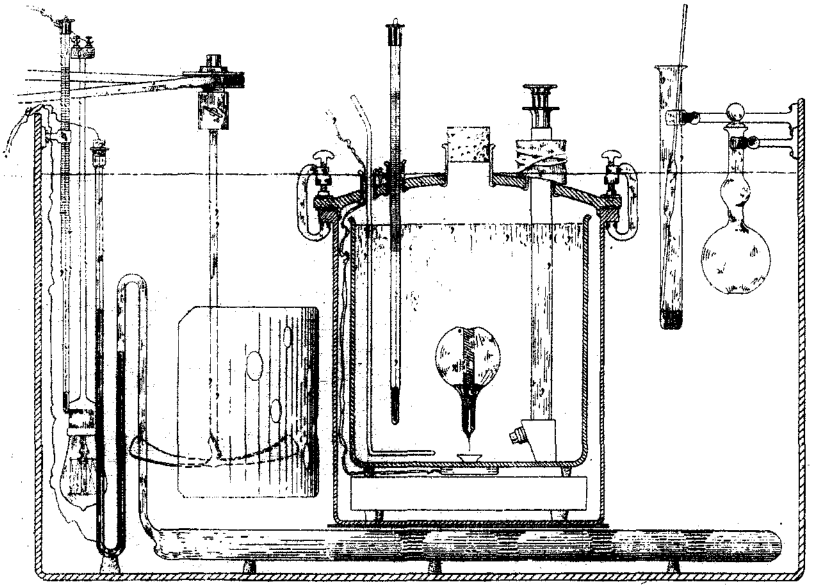

Fig. II.

In addition to this arrangement for maintaining a constant temperature in the liquid under examination, it was also found necessary, because of the several appliances which extended through the thermostat bath into the outer air, to maintain a constant temperature in the room. This was accomplished by a mechanism similar to that used in the thermostat itself, consisting of a fan, a mercury-toluene regulator and an electric relay and a heater. Fluctuations of more than 0.1° were prevented by this mechanism.

The Helix.—This consisted of forty turns of No. 27 (English Standard) insulated copper wire. The average radius of the helix was 1.25 cm.; the length, 1 cm. It was attached permanently to the middle of the lower surface of the beaker and was connected in series with a rheostat, a battery and an accurate milliammeter. The milliammeter had an open scale, and could be read even closer than one milliampere. It had been calibrated by the makers, and was re-calibrated in this laboratory.

The field of this helix was certainly far from uniform, but the end of the soft iron rod was always five or more centimeters from the top of the helix and at that distance the variations in the field must have been relatively small. Moreover, the contact cup, described below, with its center very nearly on the axis of the helix, kept the float automatically within one or two millimeters of the same place: that is within one or two millimeters of the axis of the helix. Under these conditions no lack of uniformity in the field was ever observed.

The Contact Saucer.—This was constructed of sheet platinum, was 6 mm. deep, 25 mm. in diameter at the top with sides gradually sloping to a tiny depression at the center. The slope of the sides was sufficient to guide the platinum point into this tiny central depression and yet not so great as to interfere with the observation of the platinum point through the submerged microscope. Platinum was found by trial to be preferable both to mercury or glass as a material for the contact surface, both because no sticking of the platinum point ever occurred with it and because the light reflected from its surface facilitated the exact observation of the platinum point.

The Observation Microscope.—Some instrumental assistance was necessary for noting the exact moment when the platinum point left the platinum cup, for the point and the cup were both quite out of sight from the top of the thermostat. For this purpose we designed and had made a microscope with its axis bent nearly at right angles. It consisted essentially of a small, brass box, on whose upper face the vertical observation tube carrying the eye piece was fitted; on one of its lateral faces was screwed the objective, its axis making an angle of about 15° with the horizontal. A small mirror was supported back of the objective in the brass box at such an angle as to reflect the vertical image of the objective directly into the eye piece. The focal length of the objective was two inches, that of the eye-piece was one inch, and the total tube-length was very nearly sixteen inches. This afforded a magnification of about fifty diameters. The whole microscope had to be entirely water-tight and was thoroughly gold plated. It was fitted into the brass tube in the cover of the specimen jar, and in this position the middle of the platinum cup and the platinum point, when there, were in sharp focus.

It was found that the large brass tube of the microscope conducted heat into and out of the liquid with great rapidity, so that slight fluctuations of the air in the room were reproduced on a smaller scale in the inside liquid. This difficulty was finally entirely remedied by surrounding the exposed portion of the metal tube with a felt pad which dipped into the water of the thermostat (Fig. II).

The Thermometer used to measure the temperature of the liquid under examination was of the Beckmann type, Goetze's make. It was selected from a number of similar instruments on account of the very great uniformity of its bore. The bulb was long and slender; the length of a degree was 5.1 cm., and each degree was divided into one hundred parts. Readings were made to 0.0005° with certainty by means of an attached microscope. The variations in bore, over the portion of the scale used, were never great enough to produce calibration corrections as large as 0.001° and were practically negligible.

This thermometer, set to read temperatures of about 20°, was carefully compared with a standard rod thermometer of record number 21667 which had been made and standardized by H. I. Green, of Brooklyn, N. Y., especially for this work, and which had also been standardized to thousands of a degree by the Bureau of Standards at Washington. The length of a degree on this thermometer was 4.3 cm.; an ice-point was provided. It's pressure coefficient was determined and the necessary correction was applied.

The Calibration of the Current Readings in Terms of Weight.

With the float immersed in pure, boiled water at very nearly constant temperature, the weight upon the sinker was varied in ten milligram steps, and the current necessary barely to hold the sinker in place, was determined. The slight changes in buoyancy, due to temperature differences in successive experiments, were eliminated by means of the results given in the next section, and the readings were all referred in this way to a uniform temperature (3.000° on the Beckmann thermometer). Several series

TABLE I.—CALIBRATION OF CURRENT READINGS IN TERMS OF WEIGHT.

Series No.	Temperature. Degrees.	Weight on sinker. Milligrams (apparent).	Weight on sinker + buoyancy correction to 3.000°. Milligrams (true).	Current, milliampere.	Milligrams per milliampere.
1	2.982	120	113.648	287	0.04761
1	2.995	130	123.743	75	
1	3.000	120	114.422	270	0.04775 0.04768
1	3.007	130	124.259	64	
1	3.007	110	105.188	464	
2	3.010	110	105.317	461	0.04768 (0.04813)[1]
2	3.010	130	124.388	61	
2	3.011	120	114.895	260	
3	3.023	130	124.947	49	0.04796
3	3.025	120	115.497	246	

Average, 0.04772

Average deviation, ±0.00014

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[1] This value was omitted in taking the mean, but was included in the average deviation.

of results obtained in this way are given in Table I. Many other similar measurements were made, but they all yielded results practically identical with these.

The Correction Factor for Temperature Variations.

The temperature could easily be maintained constant to a thousandth of a degree during a density measurement, as has been shown above: however, the temperature of different measurements often varied by several thousandths of a degree, and it was necessary to correct all the measurements to a common temperature (20.004° on the hydrogen scale). The correction factor for this purpose was determined by simply finding the changes in weight and in current which were necessary to retain the sinker in equilibrium in the same water when a wide variation was made in the temperature.

Repeated determinations with pure water gave 22.691° for the temperature of floating equilibrium on the hydrogen scale when no weights or current were used. To retain the sinker in equilibrium in the same water at 20.004° required 120 mg. (apparent weight) and 214 milliamperes. The joint effect of these two forces was equivalent to a total true weight of 124.65 mg., according to the conversion factors established in the preceding paragraphs. This number, divided by the temperature interval, gave 0.04639 gram as the mean change in buoyancy of the sinker per degree at the midway temperature of 21.347°. Dividing this result again by the volume of the sinker at this temperature (235.1 cc.) gave 0.000,-197,3 for the change in buoyancy per cc., per degree. This evidently represents the difference between the coefficients of cubical expansion of water and of the glass bulb. The coefficient of cubical expansion of water at this temperature (21.35°), obtained by differentiating the interpolation equation of Theisen, Scheel, and Disselhorst,[1] is 0.000,220,4. It follows from this that the coefficient of cubic expansion of the glass bulb was 0.000,023,1. This does not, however, represent exactly the true coefficient of thermal expansion; the increase in the internal gaseous pressure must have caused a secondary expansion of the bulb. From our data on the compressibility of the bulb, this is readily found to amount to 0.000,000,9 per degree, giving then for the real coefficient of thermal expansion 0.000,022,2. The cubical expansion of the Jena "geräte" glass of which the bulb was made, is given by the manufacturer as 150×10^{-7}. This value doubtless refers to massive glass, while ours was determined from the change in volume of a thin-walled flask. The difference between these values is decidedly greater than the experimental error. It would have been instructive to determin the coefficient of expansion of another bulb of the same glass by an independent method, but unfortunately at this point of our investigation, we had no more such flasks. The best

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[1] *Ann. Phys.*, **60**, 340 (1897); *Wiss. Abh. physik.-tech. Reichsanst.*, 111 (1900).

we could do was to determin the coefficient of expansion of a 100 cc. pycnometer made of Jena "geräte" glass. This we did by determining its volume carefully at 4.76° and 21.87°, respectively, using values for the density of water from the same source as before. In this way a coefficient of expansion of 24 x 10^{-6} was obtained. This value, though subject to greater error than our previous value, strongly corroborates it as compared with the value furnished by the manufacturer.

The correction factor at 20.004° can now be readily calculated, making the reasonable assumption that the coefficient of expansion of the glass does not change perceptibly over this small range. The coefficient of expansion of water at this temperature, calculated from the Thiesen, Scheel and Disselhorst formula, is $0.000,206_5$; subtracting the above value for the coefficient of expansion of the glass gives $0.000,183_4$ for the change in buoyancy per cubic centimeter per degree. Multiplying this by the volume of the sinker gives 0.0431_2 mg. as the change in buoyancy of the sinker per 0.001°. This correction factor only applies strictly to pure water, but as no solution we have measured has had a relative density greater than 1.0009, and the temperature differences have never exceeded 0.008°, we have applied it without hesitation to all our results.

Correction for the Variations in the Barometric Pressure.

Any variation in atmospheric pressure affects the observed density in three ways: (1) It changes the volume of the glass sinker, and in the sense that an increase in pressure decreases the volume and thus indicates too *low* a density. (2) It alters the reading of the thermometer, and in the sense that an increase in pressure causes an apparent rise in temperature, and, therefore, indicates too *high* a density. (3) It directly affects the density of the liquid itself, and in the sense that an increase in pressure compresses the liquid and thus indicates too *high* a density. Of the three effects the third is the only one which can be calculated in advance; it evidently depends only upon the coefficient of compressibility of the liquid; for water, this would amount to an increase of 0.000,000,6 in density for every increase in barometric pressure amounting to 10 mm. of Hg.

It was simplest, however, not to separate the first and third effects, but to determin their joint action by actual density measurements on water at widely different pressures. It was not convenient to exhaust the specimen jar in our apparatus for this purpose, so the sinker was transferred to a smaller jar filled with distilled water and provided with a cover, through which there were openings for a manometer, a stirring rod, a thermometer, and a tube connecting with the vacuum pump. The whole was sunk in a constant temperature bath, the sinker was brought to floating equilibrium by the use of milligram weights, and the temperature taken. A known excess weight was then added to the sinker, the jar closed and lowered till it rested on the bottom of the thermostat. The pressure was now gradually reduced until the bulb was again in floating equilibrium. The reading of the manometer at this point was recorded, the pressure was restored to atmospheric and the temperature was again taken. The cover was then taken off and the process checked by again attaining the original floating equilibrium at the same temperature by the removal of weights. This process was repeated a number of times, until a pressure range up to 200 mm. Hg had been covered.

The weight equivalents in milligrams per millimeter of Hg pressure, thus secured, were concordant at the same pressure to within about one per cent. (or less than one ten-thousandth of a milligram) and showed a steady decrease with increasing pressure, as would be expected. Extrapolated to zero pressure, the value 0.0792 mg. per mm. Hg was obtained. A small correction must be applied to this number for the negative heat of compression, due to the slight expansion of the liquid when the partial vacuum was applied. This expansion must have been nearly adiabatic, because of the absence of stirring inside the large suction flask. Its magnitude can easily be calculated[1] and is found to be ×0.00008° per mm. Hg increase in pressure which would produce an apparent decrease in weight of 0.0034 mg., thus giving a net decrease in apparent weight of 0.0758 per mm. Hg increase in pressure. The same correction as before for the heat of compression must be subtracted giving an apparent rise in temperature of 0.00157 per mm. Hg increase in pressure.

The magnitude of the second effect, that is, the alteration in the reading of the Beckmann thermometer with the pressure, was then determined in a similar fashion by inserting the thermometer in a suction flask sunk in the thermostat and connected with a suction pump and a manometer. The constancy of the temperature was assured by readings taken before the application and after the release of the partial vacuum. Pressure lowerings of between 60 and 210 mm. Hg were applied, and these altered the reading of the thermometer from one to three-tenths of a degree; so an accuracy of one to 2% could be secured in the temperature change per mm. variation in pressure. Here again the change decreased with increasing pressure, as would be expected. When the results were extrapolated to zero pressure a value of 0.00165° change per mm. Hg was obtained.

This change in temperature reading produced by a 1 mm. change in pressure, can be expressed in milligrams of weight applied to the sinker by means of the correction factors for temperature variation, given on the preceding page. This factor was found to be 0.0431 mg. per thousandth of a degree. The apparent increase, then, in the weight required for the

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[1] Kohlrausch, *Lehrbuch d. pr. Physik;* 11 Aufl., p. 232, Leipzig, 1910.

sinker would be 0.0431 × 1.57 = 0.0677 mg. per mm. Hg. This nearly cancels the decrease of 0.0758 mg. per mm. Hg found above for the effect of pressure on the sinker. The difference of 0.0081 mg. per mm. of Hg would correspond to an error in the density of about three units in the eighth place of decimals. A variation of 1 mm. Hg in pressure would then be negligible, but one of 2–3 mm. would require the application of a correction. However, in all the final experiments and in all the experiments here recorded, measurements were made only on quiet days when the barometer was constant within 1 mm. throughout the experiment.

Discussion of the Sources of Error, and How They May be Lessened.

Errors in the Weights.—As the small platinum weights were calibrated to hundredths of a milligram and were kept immersed in the partially exhausted liquid under investigation, errors, either due to an inaccuracy in the weights themselves, or to a film of air on their surfaces, must have been no more than one or two hundredths of a milligram, which corresponds to an uncertainty in the density of five units in the eighth decimal place. It would be possible to reduce these errors somewhat, but an accuracy ten times as great, which would correspond to an uncertainty in the density of one unit in the ninth decimal place, would be almost as far as one could reasonably expect to go, and so apparently sets a limit to the future attainable accuracy, at least for solutions so much denser than water that the electromagnetic force, which could be accurately measured, would not be sufficient to hold the sinker at the bottom.

Errors in Electromagnetic Weighing.—The uncertainty in the readings of the milliammeter, due to errors of calibration, or of observation, was certainly less than one-half a milliampere, which corresponds to an error in weight of about 0.02 mg. or about eight units in the eighth decimal place in the density. The average deviation in the experimental determination of the conversion factor was, as stated above, one ten thousandth of a milligram per milliampere. As the difference in our current reading scarcely ever exceeded 150 milliamperes in any single series, this uncertainty in the conversion factor never involved an uncertainty in the density of more than five units in the eighth decimal place, and usually much less than this. The total uncertainty in the density, due to the electromagnetic weighing of the sinker, could not have greatly exceeded one unit in the seventh place of decimals, and was probably less. This error could easily be reduced to one-tenth of this magnitude, by adjusting the buoyancy of the float more closely with small platinum weights and using a weaker current and a lower reading current-meter. Indeed, we can say that, if desirable, the error in the electromagnetic weighing of the sinker can always be kept down to the error in the platinum weights themselves; that is, for practical purposes at present, to one or two thousandths of a milligram.

The Temperature Error.—The very greatest care is necessary to determin actual temperatures to within 0.001–0.002° with a mercury thermometer. But in this method, where the density of the solution is referred to that of pure water, only the small *differences* in temperature between the water and the resulting solution actually need to be known and these can be measured to 0.001° without special difficulty. The temperature was practically stationary within a thousandth of a degree for hours, and the largest difference in temperature to be measured was eight thousandths of a degree. Under these conditions errors in calibration were practically eliminated and so were errors due to thermometric lag. Moreover, constant hydrostatic pressure and a constant exposure of mercury threads were provided for, and an automatic correction, as explained above, was made for barometric fluctuations. As a matter of fact, most of the readings recorded in this paper were made independently by two observers, and their results rarely differed by as much as 0.001° and never by more. The maximum error in the differences of temperature may be taken as 0.0005°, which corresponds at 25°, to an error in the density of water or of a dilute solution of nine units in the eighth decimal place.

The accuracy of the temperature measurements cannot be greatly increased without considerable difficulty. The simplest procedure would be to follow Kohlrausch, and work at a temperature such that the coefficient of expansion of the water would be equal to that of the float. At that temperature the buoyancy of the sinker would be almost independent of the temperature. In other words, by choosing a suitable temperature, it will be possible to reduce the error in density due to inaccuracy in the thermal measurements to any desired extent.

Errors Due to Pressure Changes.—This has already been discussed under the heading "Correction for Variations in Atmospheric Pressure." It was shown there that, owing to a fortunate cancellation of several pressure effects, the correction factor is negligible with our apparatus for pressure variations up to one mm. of Hg. As in all the experiments here cited the variation in pressure was no greater than this, a correction factor has not been applied, and we may consider the error on this score to be negligible. For any greater accuracy than we have attempted, either the above correction factor could be applied, or a sinker secured which would afford a still more perfect neutralization of pressure effects.

Errors in the Concentrations of the Solutions.—Errors in concentration are of relatively slight importance in the very dilute solutions; thus in a 0.0001 N solution of sodium chloride, whose density was 0.998,235,36, an error of one-tenth of a per cent. would correspond to an error in the density of but four to eight units in the ninth place of decimals. In concentrated solutions, on the other hand, this source of error becomes important and in 0.01 N solutions, the most concentrated ones which were studied, one-tenth of a per cent. error in concentration would correspond to an error in density of two to eight units in the seventh place of decimals. The accuracy of our concentration measurements was, however, certainly not less than one-tenth of a per cent., as can be seen from the analytical results printed in the paragraph on the preparation of the solutions, so that the corresponding errors in density were probably less, and usually much less, than *one* unit in the seventh decimal place.

The accuracy of the concentration data could, of course, be brought in most cases to as high as the one-hundredth of a per cent. without excessive trouble, but it would be difficult to go much beyond this. Errors in concentration could thus be made negligible in measurements up to hundredth normal; above one-tenth normal they would determin the accuracy of the method.

Summary.—From this discussion of the sources of error it appears that none of the errors singly, even in unfavorable cases, should affect the density results by more than one unit in the seventh decimal place. If all of these maximum errors should displace the density values in the same direction, the total error would amount to some three units in the seventh decimal place. However, it is equally unlikely that all of the errors would have this maximum value, or that all would lie in the same direction, so that the probable error is much less than three units in the seventh place. Indeed, as can be seen by examining the duplicate determinations given in the tabulated results, the agreement is usually within a few units in the *eighth* decimal place.

It also appears from the above discussion that without extraordinary difficulty, at least if measurements were made at a more favorable temperature, the accuracy of this method could probably be increased to five or ten times its present value for solutions of low concentrations.

Preparation of the Solutions.

The materials used in the preparation of the solutions evidently did not have to be of the very highest purity. Impurities, other than water, in the salts would surely be of approximately the same density as the salts themselves and would exert approximately the same effect upon the density of the water, and so would have but little influence on the final data. Impurities in the water would be of still smaller consequence, for in every case, the density of each solution was referred to the density of the water of which it was composed. Nevertheless, precautions were taken to secure solutions of high purity. The initial material from which our salts were made was in every case the "Analysed C. P." brand of the Baker and Adamson Chemical Co. The procedure employed for the further purification of each substance will be found below.

Water.—The water was twice redistilled, first from an alkaline permanganate solution, for which the laboratory supply of distilled water was used, and then a second time, after the addition of a trace of sulfuric acid. The water was distilled in each case from a glass-stoppered, side-neck, Jena glass flask through a block tin condenser into a Jena glass receiving vessel. The first quarter of each distillate was rejected. Neither rubber nor cork was used in assembling the apparatus. The water prepared by this procedure was then heated to incipient boiling, and finally evacuated by means of a water pump.

Even with these precautions the density of various samples differed by as much as eight units in the seventh decimal place, an amount easily measurable by our method. However, as above pointed out, these differences cancelled out in the final calculation of the density of the solutions.

Magnesium Sulfate.—The original salt was certified to contain but a trace of calcium, 0.0015% of chlorine, 0.0006% of iron, and to be free from the hydrogen sulfide metals. After two crystallizations from hot water, it was used to prepare the stock solution. This solution was analyzed, first, for magnesium by precipitation as magnesium ammonium phosphate, and then a second time for sulfate by precipitation as barium sulfate. The content of 500 cc. of solution expressed in grams of $MgSO_4$ was found to be as follows:

Average from $Mg_2P_2O_7$ determinations..........	10.5708
Average from $BaSO_4$ determinations............	10.5710
Average..................................	10.571

A standard solution of the salt was prepared from this by dilution.

Zinc Sulfate.—The original salt was certified to contain: 0.0006% iron, 0.0012% chlorine, no calcium, and no metals of the hydrogen sulfide group. It was recrystallized three times from hot water. The crystals were drained by suction and slowly dried, with frequent stirring, at about 300°. A stock solution was prepared of approximately the desired concentration. This solution was then analyzed for zinc by precipitation as zinc ammonium phosphate, and for sulfate by precipitation as barium sulfate. 500 cc. of this solution were found to contain the following amount in grams of $ZnSO_4$:

Average from $Zn_2P_2O_7$ determinations...........	13.4509
Average from $BaSO_4$ determinations............	13.4513
Average..................................	13.451

Sodium Carbonate.—The original salt was certified to contain the following impurities: SiO_2 0.0018%, Fe_2O_3, Al_2O_3, etc., 0.0061%, and no sulfur, or metals of the hydrogen sulfide group. It was twice recrystallized from a saturated solution prepared at 34° by cooling to about 2°. The crystals were drained by suction and dried over strong sulfuric acid.

A portion of this salt was placed in a platinum crucible supported within a larger one so as to provide an air chamber. The outer crucible was heated to dull redness and the salt stirred with a platinum rod. A standard solution was prepared by weight from this salt.

Sodium Chloride.—The original salt was certified to contain no sulfates, alkaline earth metals, heavy metals nor metals of the hydrogen sulfide group, and to dissolve clear in water. It was twice reprecipitated from a nearly saturated solution by washed hydrogen chloride gas. The crystals were collected upon a Büchner funnel, washed with a little water, and ignited in a platinum dish. A standard solution was made by weight from this salt. The strength of the solution was also controlled by evaporation of several known volumes. Ten cubic centimeters were found to contain in each of two determinations 0.20505 grams of salt; according to its preparation it should have contained 0.20503 grams.

Potassium Chloride.—The original salt was certified to contain but a trace of sodium and to be free from sulfates, alkaline earth metals, heavy metals, and the metals of the hydrogen sulfide group. Samples of this salt were precipitated twice from solution with hydrogen chloride gas, were washed with hydrochloric acid, dried, then dissolved in boiling water, and recrystallized at about 6°. The crystals obtained by this procedure were then washed with water and dried by gentle ignition. A flame test showed no sodium. In preparing the standard solution this salt was again ignited to incipient fusion before weighing. The strength of the solution was controlled by evaporating portions of it to dryness. The content in 10 cc. expressed in grams was found to be 0.25148, 0.25152, and 0.25146 in successive experiments, while according to its preparation it should have contained 0.25157 grams in this volume.

Lithium Chloride.—The original material was certified to contain no metals of the hydrogen sulfide group, and traces only of the heavy metals, of sulfates of other alkali and alkaline earth metals. Although a number of methods for the purification of this salt have been proposed, Richards and Willard[1] point out that they are either inadequate or extremely wasteful. The last traces of the alkalies and the alkaline earth metals and particularly of sodium, are very difficult to remove. However, they call attention to the fact that the amount of sodium "steadily decreased upon successive recrystallization until only a trace remained." Although this method of purification was, indeed, found to be very wasteful, owing to the great solubility of the salt, it was used in purifying the above-mentioned commercial salt. It was subjected to three recrystallizations of this kind. The resulting salt showed no evidence of sodium by the flame test. Most of the water was driven off from the resulting material by heating in a platinum crucible on an electric hot plate. Persistent heating

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[1] THIS JOURNAL, 32, 19 (1900).

caused a loss of hydrochloric acid. A stock solution was, therefore, first prepared from the nearly anhydrous salt. This solution was wholly neutral to litmus; when analyzed for chlorine, two successive determinations gave 0.14878 and 0.14867 grams of salt per 10 cc. A standard solution was prepared from this by dilution.

Ammonium Chloride.—The original material was certified to contain 0.0004% of iron and no sulfates, no metals of the hydrogen sulfide group nor any non-volatil matter. It was recrystallized three times from hot water. The salt was then dried by heating in an open platinum dish in a current of hot air at 122–125°. The content of the stock solution made by weight from this salt was determined by precipitation with silver nitrate. The standard solution was prepared by dilution.

TABLE II.—DENSITIES OF DILUTE SOLUTIONS OF MAGNESIUM SULFATE.

Mol. wt. of $^1/_2MgSO_4$, 60.215. Wt. of bulb *in vacuo*, 234.5681 grams.

Bar., 731 mm. (cor.). Vol. of bulb at 20.004°, 235.1095 cc.

First Determination.

Gm. equiv. per liter at 20.004°.	Temp. (cor.) of observation.	Load.		Total buoyant effect.		Density H_2O at 20.004° C=0.998231.	Rel. density H_2O at 20.004° C=1.00000000.	Deviation of rel. density from empirical formula × 10^8.
		Wt. on bulb in mg.	Milliamperes.	Observed.	Red. to 20.004°.			
Water	....	...	...	234	234	....	....	...
....	20.010	120	213	$.69268_6$	$.69294_4$	0.998231	1.00000000	...
0.00010000	20.010	120	245	$.69421_1$	$.69446_9$	0.9982374_9	0.0000065_0	+1
0.00019993	20.009	120	278	$.69578_1$	$.69599_6$	0.9982439_8	0.0000130_0	+3
0.00049942	20.008	120	374	$.70035_6$	$.70052_8$	0.9982632_6	0.0000323_2	—8
0.0009974	20.006	130	335	$.70802_6$	$.70810_7$	0.9982954_9	0.0000646_0	—3
0.0019892	20.013	150	244.5	$.72278_6$	$.72317_3$	0.9982595_7	0.0001288_0	+6
0.0049313	20.011	190	378	$.76729_5$	$.76759_5$	0.9985485_2	0.0003180_8	—1
0.009726	20.009	270	289	$.83933_8$	$.83955_3$	0.9988545_7	0.0006246_8	0
							Average,	±3.1

Second Determination. Bar., 730 mm. (cor.).

Water	20.010	120	215	$.69277_4$	$.69303_2$	0.998231	....	...
0.00010000	20.012	120	245.1	$.69420_9$	$.69455_4$	0.9982374_8	0.0000064_9	0
0.00019993	20.007	120	281.7	$.69595_4$	$.69608_4$	0.9982439_8	0.0000130_0	+3
0.00029982	20.009	120	311.5	$.69737_4$	$.69758_9$	0.9982503_8	0.0000194_1	—3
0.00039965	20.010	120	342.5	$.69885_2$	$.69911_0$	0.9982568_5	0.0000259_0	—2
0.0004994	20.011	120	373.2	$.70031_6$	$.70061_7$	0.9982632_7	0.0000323_2	—8
0.0009974	20.009	130	334	$.70800_6$	$.70819_8$	0.9982955_0	0.0000646_1	—2
							Average,	±3.0

Relative density $= 1 + 0.06488c - 0.086c^2 + 1.93c^3$.

The Experimental Results.

The experimental results for the above mentioned seven salts have been collected in Tables II—XV. Two tables are given for each salt; one contains the actual observations and the densities calculated from them at the observed concentrations, as well as the deviation of the relative densities from the requirements of an empirical formula computed for each

TABLE III.—MAGNESIUM SULFATE.

Data at Round Concentrations.

Concentration. Gram equivalents per liter at 20.004°.	Density H_2O. 20.004° = 1. From empirical formula.	Density H_2O, 20.004°, from Kohlrausch.[1]	Change in volume of water per gram equivalent solute, cc.	Total change in volume on solution. Cc.	
				Per gram equiv.	Per gram.
Water	1.000,000,0	1.000,000,0	(—4.55$_9$)	(—27.15$_9$)	—0.4510$_3$
0.0001	1.000,006,4$_9$	....	—4.5$_5$	—27.1$_5$	—0.451$_0$
0.0002	1.000,012,9$_7$	1.000,012,9$_6$	—4.5$_6$	—27.1$_6$	—0.451$_0$
0.0003	1.000,019,4$_6$	....	—4.5$_5$	—27.1$_5$	—0.451$_0$
0.0004	1.000,025,9$_4$	....	—4.5$_3$	—27.1$_3$	—0.450$_5$
0.0005	1.000,032,4$_2$	1.000,032$_4$	—4.5$_2$	—27.1$_2$	—0.450$_4$
0.0010	1.000,064,8$_0$	....	—4.4$_8$	—27.0$_8$	—0.449$_7$
0.0020	1.000,129,4$_8$	1.000,129$_9$	—4.39$_5$	—26.99$_5$	—0.448$_3$
0.0050	1.000,322,4$_9$	1.000,322$_4$	—4.17$_7$	—26.77$_7$	—0.4446$_9$
0.0100	1.000,642,1$_3$	1.000,642$_4$	—3.89$_2$	—26.49$_2$	—0.4399$_5$

TABLE IV.—DENSITIES OF DILUTE SOLUTIONS OF SODIUM CARBONATE.

Mol. wt. of $^1/_2Na_2CO_3$, 53.00.

Bar., 730 mm. (cor.).

Gm. equiv. per liter at 20.004°.	Temp. (cor.) of observation.	Load.		Total buoyant effect.		Density H_2O at 20.004° = 0.998231.	Rel. density H_2O at 20.004° = 1.00000000.	Deviation of relative density from empirical formula × 10^8.
		Wt. on bulb in mgs.	Milliamperes.	Observed.	Red. to 20.004°.			
......	....	..	..	234	234	....	....	...
Water	20.010	120	214	.69273$_0$	.69298$_8$	0.998231	1.00000000	...
0.00009552	20.007	120	243.3	.69312$_2$	.69425$_2$	0.99823637	0.0000053$_8$	+1
0.00019102	20.009	120	268	.69530$_4$	.69552$_7$	0.9982417^0	0.0000107$_8$	+3
0.00038184	20.010	120	320	.69778$_3$	.69804$_1$	0.9982524$_9$	0.0000215$_3$	+4
0.00057245	20.011	120	372	.70026$_2$	.70056$_2$	0.9982632$_2$	0.0000322$_8$	+6
0.0007628	20.012	130	223.5	.70271$_8$	.70306$_8$	0.9982738$_7$	0.0000429$_3$	—2
0.0009530	20.010	130	278	.70531$_6$	.70557$_4$	0.9982845$_3$	0.0000536$_3$	—4
0.0019005	20.008	140	343	.71795$_0$	.71812$_3$	0.9983379$_0$	0.0001071$_0$	—4
0.003780	20.009	170	265.5	.74286$_1$	.74308$_1$	0.9984440$_4$	0.0002134$_2$	+1
0.004714	20.011	180	324	.75518$_6$	.75549$_3$	0.9984968$_3$	0.0002663$_1$	0
0.009294	20.009	240	400	.81602$_1$	.81624$_0$	0.9987552$_1$	0.0005251$_4$	0
							Average,	±2.5

Relative density = $1 + 0.05625c + 0.073c^2 - 5.0c^3$.

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[1] Recalculated to 20.004°. See *Wied. Ann.*, **53**, 14 (1894).

TABLE V.—SODIUM CARBONATE.

Data at Round Concentration.

Concentration. Gm. equiv. per liter at 20.004°.	Density H_2O, 20.004° = 1. From empirical formula.	Density H_2O, 20.004° = 1, from Kohlrausch and Hallwachs.[1]	Volume change of water per gm. equiv. solute, cc.	Total change in volume on solution. Cc. Per gram equiv.	Per gram.
Water	1.000,000,00	1.000,000	(—3.15$_6$)	(—24.55$_6$)	(—0.4633$_2$)
0.0001	1.000,005,6$_3$	....	—3.1$_6$	—24.5$_6$	—0.463$_4$
0.0002	1.000,011,2$_5$	....	—3.1$_7$	—24.5$_7$	—0.463$_6$
0.0004	1.000,022,5$_1$	....	—3.1$_8$	—24.5$_8$	—0.463$_8$
0.0005	1.000,028,1$_4$	....	—3.1$_9$	—24.5$_9$	—0.464$_0$
0.0010	1.000,056,3$_2$	....	—3.2$_2$	—24.6$_2$	—0.464$_5$
0.0020	1.000,112,7$_5$	1.000,112$_4$	—3.28$_2$	—24.68$_2$	—0.4657$_0$
0,0020	....	1.000,112$_2$	.....	......	....
0.0040	1.000,225,8$_5$	1.000,224$_7$	—3.36$_8$	—24.76$_8$	—0.4673$_2$
0.0050	1.000,282,4$_6$	1.000,281$_3$	—3.39$_6$	—24.79$_6$	—0.4678$_5$
0.0100	1.000,564,8$_0$	1.000,564$_7$	—3.38$_6$	—24.78$_6$	—0.4676$_6$
....	....	1.000,565$_0$	.....	......	....

TABLE VI.—DENSITIES OF DILUTE SOLUTIONS OF SODIUM CHLORIDE.

Mol. wt. of NaCl, 58, 46. Bar., 731 mm. (cor.). First Determination.

Gm. equiv. per liter at 20.004°.	Temp. (cor.) of observation.	Load. Wt. on bulb in mgs.	Milliamperes.	Total buoyant effect. Observed.	Red. to 20.004°.	Density H_2O at 20.004° = 0.998231.	Rel. density H_2O at 20.004° = 1.0000000.	Deviation of relative density from empirical formula × 10^8.
......	....	...	....	234	234	....	....	...
Water	20.010	120	217	.69286$_1$	.69311$_9$	0.998231	1.00000000	0
0.00010000	20.009	120	239	.69390$_9$	.69412$_4$	0.9982352$_7$	0.0000042$_8$	0
0.00019999	20.009	120	260	.69491$_1$	.69512$_6$	0.9982395$_8$	0.0000085$_5$	—1
0.00049942	20.007	120	324.8	.69800$_0$	.69812$_9$	0.9982523$_1$	0.0000213$_4$	—3
0.0009974	20.009	130	227.5	.70289$_7$	.70311$_3$	0.9982735$_0$	0.0000425$_8$	—2
0.0019892	20.008	140	236	.71283$_7$	.71301$_0$	0.9983156$_0$	0.0000847$_5$	+3
0.004931	20.010	170	245	.74187$_3$	.74213$_1$	0.9984394$_6$	0.0002088$_4$	—1
0.009725	20.007	220	246	.78959$_7$	.78972$_6$	0.9986419$_0$	0.0004116$_3$	+1
								±1.4

Second Determination. Bar., 731 mm. (cor.).

Gm. equiv. per liter at 20.004°.	Temp. (cor.) of observation.	Load. Wt. on bulb in mgs.	Milliamperes.	Total buoyant effect. Observed.	Red. to 20.004°.	Density H_2O at 20.004° = 0.998231.	Rel. density H_2O at 20.004° = 1.0000000.	Deviation of relative density from empirical formula × 10^8.
....	....	...	...	234	234	....	....	...
Water	20.010	120	216	.69281$_8$	.69307$_6$	0.998231	1.00000000	0
0.0004951	20.008	120	322	.69787$_1$	.69804$_3$	0.9982521$_3$	0.0000211$_7$	—2
0.0009900	20.008	130	226	.70283$_0$	.70300$_2$	0.9982732$_2$	0.0000422$_9$	+1
0.0019787	20.010	140	231	.71260$_4$	.71286$_2$	0.9983151$_6$	0.0000843$_1$	+3
0.0039531	20.008	160	243	.73224$_6$	.73241$_8$	0.9983983$_4$	0.0001676$_3$	—3
0.0049385	20.009	170	246.3	.74193$_4$	.74214$_9$	0.9984397$_2$	0.0002090$_9$	—6
0.009849	20.007	220	271	.79079$_3$	.79092$_5$	0.9986471$_7$	0.004169$_0$	—1
								±2.3

Relative density $= 1 + 0.04285c - 0.150c^2 + 9.863c^3$.

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[1] Recalculated to 20.004°.

salt; the other table contains data at round concentrations calculated from the empirical formulas including both relative densities and the volume changes per gram and per gram equivalent when solution takes place. In addition, comparable density measurements of other observers are added whenever such exist.

The relative densities at the observed concentrations were obtained by dividing the total weight of the sinker in the various solutions by its total weight in pure water at the same temperature; the absolute densities were

TABLE VII.—SODIUM CHLORIDE.

Data at Round Concentrations.

Concentration. Gm. equiv. per liter, 20.004°.	Density H_2O, 20.004° = 1. From empirical formula.	Density H_2O, 20.004° = 1. From Kohlrausch and Hallwachs.[1]	Vol. change of water per gm. equiv. solute. cc.	Total change in volume on solution. Cc. Per gram equiv.	Total change in volume on solution. Cc. Per gram.
Water	1.000,000,00	1.000,000,00	(15.71$_4$)	(—11.32$_0$)	(—0.1936$_4$)
0.0001	1.000,004,2$_8$	....	15.7$_5$	—11.2$_8$	—0.192$_9$
0.0002	1.000,008,5$_6$	....	15.7$_6$	—11.2$_7$	—0.192$_8$
0.0005	1.000,021,3$_9$	....	15.7$_8$	—11.2$_5$	—0.192$_4$
0.0010	1.000,042,7$_1$	....	15.8$_5$	—11.1$_8$	—0.191$_2$
0.0020	1.000,085,1$_8$	1.000,085$_6$	15.97$_4$	—11.06$_0$	—0.1891$_9$
0.0040	1.000,169,6$_3$	....	16.15$_6$	—10.87$_8$	—0.1861$_8$
0.0050	1.000,211,7$_3$	1.000,210$_8$	16.21$_8$	—10.81$_6$	—0.1850$_1$
0.0050	....	1.000,213$_6$	....	......	....
0.0100	1.000,423,3$_6$	1.000,423$_8$	16.22$_8$	—10.80$_6$	—0.1848$_5$
0.0100	....	1.000,427$_0$	....	......	....

TABLE VIII.—DENSITIES OF DILUTE SOLUTIONS OF POTASSIUM CHLORIDE.

Mol. wt. of KCl, 74.56. Bar., 730 mm. (cor.).

Gm. equiv. per liter at 20.004°.	Temp. (corr.) of observation.	Load. Wt. on bulb in mgs.	Load. Milliamperes.	Total buoyant effect. Observed.	Total buoyant effect. Red. to 20.004°.	Density H_2O at 20.004° = 0.998231.	Rel. density H_2O at 20.004° = 1.00000000.	Deviation of relative density from empirical formula × 10^8.
....	....	....	...	234	234	....	....	...
Water	20.010	120	215	0.69277$_3$	0.69303$_1$	0.998231	0.00000000	...
0.00009616	20.010	120	238	0.69387$_0$	0.69412$_8$	0.9982356$_7$	0.0000046$_8$	+1
0.00019227	20.009	120	262	0.69501$_8$	0.69522$_8$	0.9982403$_4$	0.0000093$_6$	+2
0.00048030	20.007	120	332.7	0.69838$_5$	0.69851$_5$	0.9982543$_3$	0.0000233$_6$	+2
0.0009592	20.009	130	245.5	0.70376$_2$	0.70397$_7$	0.9982775$_5$	0.0000466$_3$	+2
0.0019128	20.009	140	273	0.71460$_9$	0.71482$_4$	0.9983236$_9$	0.0000928$_5$	—8
0.00472	20.008	170	350	0.74679$_7$	0.74705$_7$	0.9984607$_8$	0.0002302$_0$	+1
0.009353	20.007	230	246	0.79913$_9$	0.79926$_9$	0.9986828$_7$	0.0004526$_7$	+1
							Average,	±2.4

Relative density = $1 + 0.04859c - 2.24c^3$.

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[1] Recalculated to 20.004°.

then found by multiplication with the factor 0.998231, the true density of pure water at 20.004° according to the results of Thiesen, Scheel and Disselhorst,[1] and of Chappuis.[2] This factor, to be sure, is probably less accurately known than the relative densities of the solutions, so the absolute densities as given are probably less accurate than the relative densities; but these can of course be revised without difficulty whenever a more accurate value for the density of water at this temperature shall have been obtained. The application of the correction for temperature changes has been previously explained. The comparative data of other investigators

TABLE IX.—POTASSIUM CHLORIDE.

Data at Round Concentration.

Concentration. Gm. equiv. per liter, at 20.004°.	Density H_2O, 20.004° = 1. From empirical formula.	Density H_2O, 20.004° = 1. From Dijken.[3]	Vol. change of water per gram equiv. solute, cc.	Total change in volume on solution. Cc.	
				Per gram equiv.	Per gram.
Water	1.000,000,00	1.000,000,00	(26.10_0)	(—11.39_0)	(—0.1527_6)
0.0001	$1.000,004,8_6$	....	26.1_0	—11.3_9	—0.1527_6
0.0002	$1.000,009,7_2$	....	26.1_0	—11.3_9	—0.1527_6
0.0005	$1.000,024,2_9$	....	26.1	—11.3_9	—0.1527_6
0.0010	$1.000,048,5_9$	....	26.1_0	—11.3_9	—0.1527_6
0.0020	$1.000,097,1_6$	....	26.11_1	—11.37_8	—0.1525_0
0.0050	$1.000,242,6_7$	....	26.15_8	—11.33_2	—0.1519_8
0.0100	$1.000,483,6_6$	$1.000,483_5$	26.19_4	—11.29_6	—0.1515_0

TABLE X.—DENSITIES OF DILUTE SOLUTIONS OF LITHIUM CHLORIDE.

Mol. wt. of LiCl, 42.40. Bar., 730 mm. (cor.).

Gm. equiv. per liter at *20.004°*.	Temp. (corr.) of observation.	Load.		Total buoyant effect.		Density H_2O at 20.004° = 0.998231.	Rel. density H_2O at 20.004° = 1.00000000.	Deviation of relative density from empirical formula × 10^8.
		Wt. on bulb in mgs.	Milliamperes.	Observed.	Red. to 20.004°.			
....	....	...	...	234	234	....	....	...
Water	20.010	120	216	$.69281_8$	$.69307_6$	0.998231	1.00000000	0
0.00010002	20.010	120	228.5	$.69341_4$	$.69367_2$	0.99823353_3	0.0000025_4	0
0.00019999	20.011	120	240	$.69396_1$	$.69426_4$	0.99823606_6	0.0000050_6	—1
0.0004997	20.008	120	280.2	$.69587_8$	$.69605_0$	0.9982436_5	0.0000126_7	+1
0.0009977	20.009	120	341.5	$.69880_1$	$.69901_6$	0.9982562_6	0.0000253_0	+6
0.0019897	20.009	130	264.5	$.70466_5$	$.70488_0$	0.9982812_0	0.0000502_9	+2
0.004932	20.008	150	229	$.72204_3$	$.72221_5$	0.9983549_4	0.0001241_6	0
0.009726	20.010	180	218	$.75012_5$	$.75038_3$	0.9984747_4	0.0002441_8	0
							Average,	±1.3

Relative density = $1 + 0.02535c - 0.048c^2 + 2.35c^3$.

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[1] *Wiss. Abh. physik.-tech. Reichsanst.*, III, 68 (1900).

[2] *Trav. et Mem. Bur. int.* **13** *D*, **30** (1907).

[3] *Zeit. phys. Chem.*, **24**, 108 (1897).

had to be secured, as a rule, by interpolation; in every case the concentrations were corrected to 20°.

The agreement of our density results with those of previous investigators is as good as could be expected. Little can be gained from such a comparison, for scarcely any of these investigators even tried for an accuracy such as we have apparently attained. The only exception to this has been Kohlrausch, who, in his later measurements on magnesium sulfate, acetic acid, sulfuric acid and sugar,[1] claims an accuracy of two or three units in the seventh decimal place. Magnesium sulfate is the only one of these substances whose solutions we have studied, and the agreement here is certainly excellent; the average deviation amounts to but two

TABLE XI.—LITHIUM CHLORIDE.

Data at Round Concentrations.

Concentration. Gm. equiv. per liter. 20.004°.	Density H_2O, 20.004° = 1. From empirical formula.	Volume change of H_2O per gram equiv. solute. cc.	Total change in volume on solution. Cc.	
			Per gram equiv.	Per gram.
Water	1.000,000,00	(17.12_5)	(—3.36_8)	(—0.0794_3)
0.0001	$1.000,002,5_3$	17.1_2	—3.36	—0.0792
0.0002	$1.000,005,0_7$	17.1_4	—3.35	—0.079_0
0.0005	$1.000,012,6_6$	17.1_5	—3.34	—0.078_8
0.0010	$1.000,025,3_0$	17.1_7	—3.32	—0.078_3
0.0020	$1.000,050,5_8$	17.21_0	—3.28_5	—0.0774_3
0.0050	$1.000,125,8_4$	17.30_7	—3.18_6	—0.0751_4
0.0100	$1.000,251,0_5$	17.37_0	—3.12_2	—0.0736_5

TABLE XII.—DENSITIES OF DILUTE SOLUTIONS OF AMMONIUM CHLORIDE.

Mol wt. of NH_4Cl, 53.502. Bar., 731 mm. (cor.).

Gm. equiv. per liter at 20.004°.	Temp. (corr.) of observation.	Load.		Total buoyant effect.		Density H_2O at 20.004° C = 0.998231.	Rel. density H_2O at 20.004° C = 1.00000000.	Deviation of relative density from empirical formula × 10^8.
		Wt. on bulb in mgs.	Milliamperes.	Observed.	Red. to 20.004°.			
....	....	...	...	234	234	....	....	...
Water	20.010	120	217	$.69286_1$	$.69311_9$	0.998231	1.00000000	0
0.00009838	20.007	120	228.8	$.69342_3$	$.69355_3$	0.9982338_4	0.0000018_4	0
0.00019670	20.007	120	237.8	$.69385_2$	$.69398_2$	0.9982346_6	0.0000036_7	0
0.00049134	20.009	120	263	$.69505_4$	$.69526_9$	0.9982401_4	0.0000091_5	+1
0.0009812	20.008	120	308.5	$.69722_3$	$.69739_5$	0.9982491_9	0.0000182_2	+1
0.0019570	20.007	120	397.8	$.70148_1$	$.70161_0$	0.9982671_1	0.0000361_8	+1
0.004851	20.007	140	256	$.71379_0$	$.71392_0$	0.9983194_7	0.0000886_3	—2
0.009568	20.008	160	269	$.73348_1$	$.73365_4$	0.9984034_1	0.0001727_2	+1
							Average,	±0.8

Relative density = 1 + $0.01865c - 0.0925c^2 + 3.10c^3$.

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[1] *Ann. Phys.*, **56**, 184 (1895).

units in the seventh decimal place, which is within the limit of accuracy claimed by Kohlrausch. The agreement of our results among themselves is even more gratifying. This is shown in two ways. First, the average deviation from the empirical formulas computed for each salt averages less than three units in the *eighth* decimal place. Second, where a duplicate series of measurements has been made (Tables II, VI) the agreement with the empirical formulas is equally good, although the formula in every such case was computed solely from the results of the first series.

Our conclusion, therefore, in the paragraph devoted to an examination of the accuracy of the measurements, that the probable error was much less than three units in the seventh decimal place has certainly been justi-

TABLE XIII.—AMMONIUM CHLORIDE.

Data at Round Concentrations.

Concentration. Gm. equiv. per liter, 20.004°.	Density H_2O, 20.004° = 1. From empirical formula.	Volume change of H_2O per gm. equiv. solute, cc.	Total change in volume on solution. Cc.	
			Per gram equiv.	Per gram.
Water	1.000,000,00	(34.94_7)	0.02_4	0.000_5
0.0001	$1.000,001,8_6$	34.9_6	0.0_4	0.000_7
0.0002	$1.000,003,7_3$	34.9_6	0.0_4	0.000_8
0.0005	$1.000,009,3_0$	34.9_9	0.0_7	0.001_3
0.0010	$1.000,018,5_6$	35.0_4	0.1_2	0.002_3
0.0020	$1.000,036,9_5$	35.1_2	0.2_0	0.0037_4
0.0050	$1.000,091,3_2$	35.33_3	0.41_0	$0.007,6_6$
0.0100	$1.000,180,3_5$	35.56_2	0.63_9	$0.011,9_4$

TABLE XIV.—DENSITIES OF DILUTE SOLUTIONS OF ZINC SULFATE.

Mol. wt. of $^1/_2ZnSO_4$ = 80.72. Bar., 730 mm. (cor.).

Gram equiv. per liter at 20.004°	Temp. (corr.) of observation.	Load.		Total buoyant effect.		Density H_2O at 20.004° = 0.998231.	Rel. density H_2O at 20.004° = 1.00000000.	Deviation of rel. density from empirical formula × 10^8.
		Weight on bulb in mgs.	Milliamperes.	Observed.	Red. to 20.004°.			
....	....	...	...	234	234	....	....	...
Water	20.010	120	214	$.69273_0$	$.69298_8$	0.998231	1.00000000	...
0.00009502	20.008	120	256.2	$.69471_2$	$.69491_4$	0.9982391_9	0.0000082_1	—1
0.00018999	20.010	120	294.5	$.69656_7$	$.69682_5$	0.9982473_2	0.0000163_5	—7
0.00047457	20.009	130	216.5	$.70238_4$	$.70259_9$	0.9982718_8	0.0000409_5	—5
0.0009480	20.008	140	218.5	$.71201_4$	$.71218_6$	0.9983126_6	0.0000818_0	—5
0.0018955	20.010	160	218.5	$.73108_5$	$.73134_3$	0.9983941_4	0.0001634_3	+3
0.0046865	20.011	210	394	$.78712_9$	$.78742_9$	0.9986326_9	0.0004024_0	+2
0.0056086	20.009	230	382.5	$.80565_1$	$.80586_6$	0.9987111_0	0.0004809_5	—6
0.009244	20.009	310	303.5	$.87819_1$	$.87839_5$	0.9990195_7	0.0007899_9	0
							Average,	±3.4

Relative density = $1 + 0.08648c - 0.0155c^2 + 4.64c^3$.

fied. However, the deviations of single measurements sometimes amounted to nine units in the eighth decimal place. We should, therefore, estimate the probable error of any single measurement as perhaps five units in the eighth decimal place, or about one part in twenty million.

TABLE XV.—ZINC SULFATE.

Data at Round Concentrations.

Concentrations. Gm. equivalents per liter at 20.004°.	Density H_2O 20.004 = 1.	Density H_2O, 20.004 = 1. From Kohlrausch and Hallwachs.[1]	Change in volume of water per gram equivalent solute, cc.	Total change in volume of solution. Cc. Per gram equiv.	Per gram.
Water	1.000,000,00	1.000,000	(—5.61$_7$)	(—28.74$_6$)	(—0.3561$_2$)
0.0001	1.000,008,6$_5$	....	—5.60	—28.7$_3$	—0.355$_9$
0.0002	1.000,017,2$_6$	....	—5.5$_8$	—28.7$_1$	—0.355$_6$
0.0005	1.000,043,2$_1$	....	—5.5$_6$	—28.6$_9$	—0.355$_4$
0.0010	1.000,086,3$_3$	1.000,086$_0$	—5.4$_7$	—28.6$_0$	—0.354$_3$
0.0020	1.000,172,3$_8$	1.000,172$_8$	—5.3$_2$	—28.4$_5$	—0.352$_5$
0.0050	1.000,429,1$_0$	1.000,427$_5$	—4.95$_8$	—28.08$_7$	—0.3479$_6$
0.0060	1.000,514,3$_0$	....	—4.85$_4$	—27.98$_3$	—0.3466$_7$
0.0100	1.000,853,9$_4$	1.000,853$_7$	—4.53$_1$	—27.66$_0$	—0.3426$_7$

The Volume Change on Solution.

The numbers in the column headed "Change in Volume of Water per Gram Equivalent Solute" in the tables giving data at round concentrations, represent the change in volume which the water experiences, assuming that the dissolved substance occupies no space; they also represent what is often called the "Molecular Volume" of the solute in solution, on the assumption that the *water* undergoes no change in volume.

The variations of this volume change with the concentration are not without interest; in every case, except one, it becomes smaller (algebraically) with decreasing concentration. In other words, when the volume change is positive, that is, when the water expands during the process of solution, the expansion is smaller in dilute solution; when the volume change is negative, that is, when the water contracts as the solute is dissolved, the contraction is greater in dilute solution.

This indicates that the compression, either of the water or of the solute, or both, is greatest at high dilutions. The variation beyond 0.001 normal is, however, very small, indicating that the limit of compression must be nearly reached at 0.0001 normal concentration.

This practical constancy at low concentration agrees with the views of Kohlrausch and Hallwachs,[2] Drude and Nernst,[3] Heydweiller,[4] and others that the compression of the water is produced, at least in part, by the ions; for dissociation is steadily increasing with dilution, and except per-

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[1] Recalculated to 20.004°.

[2] *Ann. Phys.*, [3] **50**, 125 (1893).

[3] *Z. physik. Chem.*, **15**, 79 (1894).

[4] *Ann. Phys.*, [4] **30**, 885 (1909).

haps in the case of zinc and magnesium sulfate, must be practically complete at 0.0001 normal. The only case where the change in volume does not show the above regularity is that of sodium carbonate. There, the volume change varies in a normal fashion in the more concentrated solutions, but in the dilute solutions it turns in the opposit direction and becomes less and less negative as dilution progresses. This can be best seen from Fig. III, where the variation of the volume change with the concentration is shown, the curve being based on our own values at low concentrations and on those of Kohlrausch and Hallwachs at the high ones.

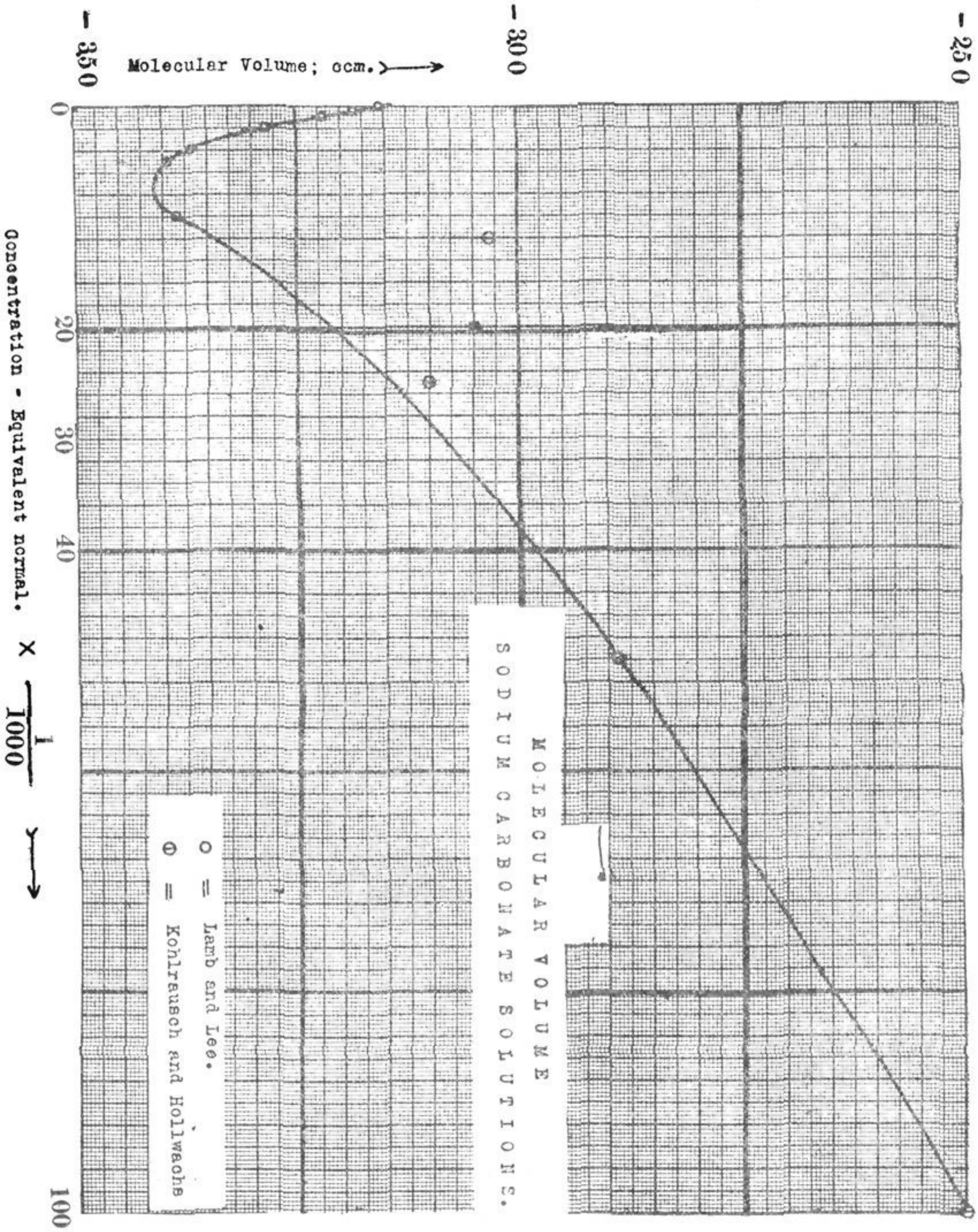

Fig. III.

This salt differs from the other salts studied in being greatly hydrolyzed in solution. If this hydrolysis were accompanied by expansion, it would furnish a reasonable explanation of the anomalous variation in the volume change, for the percentage hydrolysis must increase with increasing dilution.

The difficulty is that hydrolysis must in general produce the *opposit* effect, for it is well known that expansion occurs in the reverse process of neutralization. However, it has been found in the neutralization of weak organic acids by strong bases that the expansion is much smaller than usual, and this suggested that perhaps the neutralization of the still weaker carbonic acid might produce a *contraction* instead of an expansion. On the other hand, these same organic acids give nearly the normal expansion when neutralized in very dilute solution, and this pointed in the opposit direction.

Fortunately, this suggestion can be subjected to the test of experiment, for Blümke[1] has measured the density of carbon dioxide solutions of various concentrations. Interpolating and extrapolating from his data and using those of Kohlrausch,[2] Tammann,[3] and Cameron and Robinson[4] for sodium carbonate and sodium hydroxide we obtained the following values (Table XVI) for the volume change when one gram equivalent of carbonic acid is neutralized by sodium hydroxide at 20° at different concentrations.

TABLE XVI.—VOLUME CHANGE ON NEUTRALIZATION OF $^1/_2H_2CO_3$ BY NaOH AT 20°.

Concentration equiv.	Volume change per liter. cc.	Volume change per g. equiv. cc.
1.0	—27.3	—27.3
0.1	— 3.0_8	—30.0_8
0.01	— 0.3_0	—30.0
0.005	— 0.15	—30.0

Evidently there is a very decided contraction during the neutralization of carbonic acid, and this contraction remains fairly constant over a wide range of concentrations.

This proves, then, that the progressive hydrolysis of sodium carbonate as dilution increases may indeed be the reason for the anomalous variation of the volume change during solution at low concentrations.

Summary.

A precise method for measuring the densities of very dilute solutions has been described, and the densities of solutions of seven salts at concentrations from 0.0001 to 0.01 equivalent normal have been measured, with a probable error of less than one unit in the seventh decimal place.

The variations in the volume changes during solution indicate, in general,

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[1] *Ann. Phys.*, [3] **23**, 404 (1884).

[2] *Ibid.*, [3] **50**, (1893).

[3] *Z. physik. Chem.*, **16**, 91 (1895).

[4] *J. physic. Chem.*, **14**, 1, 569 (1910).

a progressively increasing compression as the dilution becomes greater; but an approximate constancy is reached at dilutions where the electrolytic dissociation is practically complete. Of the solutions studied, sodium carbonate alone presents an anomalous behavior in this particular, for in very dilute solution the contraction becomes less rather than greater; but it has been shown that this can be explained on the basis of the unusual contraction which is found to occur during the neutralization of carbonic acid.

THE PHENOMENA OF EQUILIBRIA BETWEEN SILICA AND THE ALKALI CARBONATES.

By Paul Niggli.

Received September 22, 1913.

In a previous publication[1] we have discussed a ternary system, made up of one volatil and two involatil components, in which no compounds occur. Such systems have been investigated chiefly by Smits, to whom we owe our present somewhat limited knowledge of their behavior; they are very important in view of the existence of similar complex systems in liquid magmas. The magma contains a number of substances which appear as gases or vapors in volcanic exhalations; of these the most important are H_2O, CO_2, S, and the mutual reaction products of these substances. Such vapors can unite with the involatil constituents of the magma to form compounds which are still liquid at temperatures lower than the general solidification temperature of the magma. That, under those conditions, compounds of this type actually exist has been established by petrographic investigation, which has shown that minerals containing water or fluorine, and in all probability minerals such as calcite and cancrinite, have in some cases crystallized directly out of the magma.[2] It is evident, therefore, that a more extended knowledge of the behavior of systems of volatil and involatil components, which can interact to form compounds, is very desirable.

Such a system is the system, *alkali oxide, silica, carbon dioxide;* it can be readily investigated, and at the same time it is of importance (at the least, indirectly) in connection with magmatic processes. The complete investigation of this ternary system would require a very long time; apart altogether from the technical difficulties associated with work at high pressures and high temperatures. Consequently, the work here recorded deals with only a limited portion of the whole field; it treats of the phenomena of equilibrium between R_2O, SiO_2 and CO_2 in melts at temperatures of 900–1000° under a pressure of 1 atm. CO_2. The relation of the

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[1] P. Niggli, *Z. anorg. Chem.*, **75**, 161; **77**, 321 (1912).

[2] See *e. g.*, F. D. Adams, *Am. J. Sci.*, [3] **48**, 14 (1894); O. Stutzer, *Centr. Min. Geol.*, **1910**, 433; R. Workman, *Geol. Mag.*, **1911**, 193, etc.