THE
PHYSICAL REVIEW.

ON THE FREEZING POINTS OF AQUEOUS SOLUTIONS
OF NON-ELECTROLYTES.

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THE object of the work which is presented in this paper has been to test the validity of the van't Hoff constant for dilute aqueous solutions of non-electrolytes. Much work has already been done in this region, but it has been mostly confined to the investigation of cane sugar, ethyl alcohol and urea. The results in general have not been in accord with the van't Hoff theory. While the great confusion which the earlier results presented has largely disappeared with the more recent advances in the methods of measurement, still there remains much disagreement in the latest observations of the most careful observers, even in cases where the apparent exactness of the methods had lead the observers to regard their results as final.

Thus Abegg¹ finds for the molecular depression in the case of

Cane Sugar,	1.86
Ethyl Alcohol,	1.79
Urea,	1.87
Dextrose,	1.81

While Raoult's² latest values give for

Cane Sugar,	1.87
Ethyl Alcohol,	1.83

These results can not be looked upon as *constant*, since the esti-

¹ Zeit. Phys. Chem., XX., 1896, p. 207.

² Zeit. Phys. Chem., XXVII., 1898, p. 617.

mated experimental errors are of a much smaller order than would be required for such a conclusion.

THE METHOD.

The apparatus is the same as that originally used by the writer, and described in the *PHYSICAL REVIEW*, Vol. I., 1893. The method is likewise unchanged in all essentials. It will be remembered that this method enabled the writer to overcome the most serious difficulty met with in attempts to measure the freezing points of solutions, namely, that of bringing the solution and its "ice" to their actual temperature of equilibrium. This difficulty is so troublesome and the experimental errors which arise in this connection are so great that I am not surprised that the complete solution of this difficulty after many months of the most tedious work left me entirely unarmed against another source of error much less difficult to overcome and of the most self-evident nature. This difficulty concerns itself with the manipulation of the *thermometer*. It was found necessary at the very outset to keep the thermometer at 0° C. when not in actual use. To effect this the thermometer was packed, *its whole length*, in ice in the ice cellar of the Strasburg Laboratory. Thus the *stem*, as well as bulb, was at 0° C. The temperature of the room in which the observations were made was on the average about 5° C., and it is thus obvious that the *stem* of the thermometer was gradually warming during the first series of observations each working day.

Hence these observations were lower than they would have been if the stem had come at once to the temperature of the room. These first observations were uniformly the ones which determined the zero point of the thermometer for the day, and thus all such zero points may be said to have been "too low." Since the stem range was $2^{\circ}.5$ C. and the thermometer was of the enclosed type with a thick glass wall, it is easy to believe that the error arising from this very obvious source could have reached as much as $0^{\circ}.001$ C. To avoid this it is, of course, only necessary to place the lower portion of the thermometer in ice and water and leave the "stem" at room temperature. This change was introduced at the beginning of the 1896 series. A second source of error arises also from the manipulation

of the thermometer. While it is of much less importance than the one already described, its discovery has led to a real simplification of the practice of the method, and so deserves attention. It relates also to the stem of the thermometer. That portion of the stem below the cork which supports the thermometer in the freezing vessel and above the surface of the solution must, of course, have a constant temperature if a series of independent observations on the freezing point of a given liquid are to agree. This was accomplished in the earlier work by keeping the freezing vessel with its contents for 20 minutes in a bath of ice and water before each observation of a freezing point. It was then transferred to a freezing mixture to induce freezing of the solution and then to the "protection bath" where the solution and its "ice" were allowed to come to equilibrium. While the great uniformity with which these changes were made would preclude the possibility of any very serious lack of constancy in the temperature of this intermediate portion of the stem, still there is a source of danger here. This becomes the more evident when it was discovered that, although the *length* of this unmarked portion of the stem is only that of 4 degrees on the thermometer, *actual measurement of the temperature range showed it to be 10 degrees*. This fact was unknown to me until after all the experimental work had been finished. It now seems probable that the small remaining experimental error of the present method will be eliminated when the difficulty is removed. Obviously it is necessary to have a thermometer made with the capillary reduced to the smallest possible size in this portion.

Without knowing at the time the real nature of the source of error I was always aware of its existence and overcame it by the long exposure of the whole apparatus to a temperature of 0° C. To still further overcome this difficulty and to facilitate the practice of the method the following change of procedure has been made. The freezing vessel, holding the thermometer and solution, is placed in a freezing mixture until an overcooling of $0^{\circ}.3$ C. is produced. It is then placed directly in the "protection bath," whose temperature is also $0^{\circ}.3$ C. below that of the freezing point to be observed. Here it is allowed to stand 15 minutes. It is then "touched off" with a tiny crystal of ice. The stirring and jarring are then begun and

continued for two minutes as usual. A reading of the thermometer is then made.

THE ACCURACY OF THE METHOD.

It is plain that a method which claims to have any high degree of exactness must fulfil two experimental conditions :

1. In a series of observations on a given freezing point, the various observations must have a narrow range of variation. The present method originally showed a range of about $0^{\circ}.0008$ C. in a series of five entirely independent observations. By lowering the room temperature to about 0° C. this variation was reduced to the average value, $0^{\circ}.0005$ C., in the 1896 series, while the slight change in the practice of the method which allows the freezing vessel to stand in the "protection bath" instead of the ice and water bath for the fifteen minutes preceding the observation has reduced this to $0^{\circ}.00046$ C. in the present series. Many series of observations on the zero point of the thermometer gave the same result for each individual observation, while in some cases of the more concentrated solutions the variation has amounted to as much as $0^{\circ}.0015$ C. It is to be noticed that the variation, which now remains, may be wholly accounted for by a lack of uniformity in the temperature of the middle portion of the stem of only $0^{\circ}.25$ C. I am of the opinion that when this source of error is wholly suppressed, this very slight lack of constancy in a series of successive observations will be reduced still further.

2. The observed zero points determined from day to day on the thermometer must show only small variation. An examination of such a series of zero points throws much light upon the exactness of the method, since it is evident that any lack of absolute constancy in such a series must be accounted for either by assuming experimental errors, or irregular changes in the thermometer itself. When the variation is large the method is proportionally inexact. Unfortunately these zero points are generally not published. The latest work of Abegg is, however, an exception, and this example will serve to illustrate the importance of this criterion of a method's accuracy. He publishes a series of eight such zero points, presumably in the order in which they were made, though he fails to give

the dates.¹ I allow myself the privilege of submitting the series together with the barometer at the time.

Zero Point.	Barometer.
0°.7741	747 mm.
.7738	744.5
.7736	741
.7733	742
.7724	741
.7681	736.5
.7670	732.5
.7668	727.5

The total variation is 0°.0073 C. Reducing the readings to a common air pressure, say 740 mm. by use of a correction factor which the author himself experimentally determined (0°.0002 C. per 1 mm.). The series becomes

0.7727,	0.7729,	0.7734,	0.7729,
0.7722,	0.7688,	0.7685,	0.7693.

The range is thus reduced to about 0°.005. Thus of the original variation of some 0°.007 C. in *eight* observations, only 0.002 are accounted for in an experimental way, and yet he says of this series:

“Die Variationen der Einstellung rühren jedoch, wie eine nähere Betrachtung der Zahlen zeigt, sicher nicht allein von den Luftdruckänderungen her, sondern dürften auch kleinen zufälligen Verunreinigungen des destillirten Wassers zuzuschreiben sein, auf dessen genau gleiche Beschaffenheit kein besonderer Wert gelegt wurde.”

I have elsewhere remarked that it seems unwise to refer so great a variation in the observed zero point of the thermometer to accidental impurities of the distilled water used, since these impurities would need to be so great as to raise the water to the order of a $\frac{1}{1000}$ normal salt solution.

The series furthermore shows that the zero point of his thermometer was *falling*. During the six years that I have been observing the zero point on my thermometer, the zero point has been rising, whether it was in use or at rest. This is evident in every series except that of 1893, where the experimental errors were so great as to mask this rise of the zero point. I am persuaded that the greater part of

¹ Zeit. Phys. Chem., XX., 216.

these observed variations in the zero point of the thermometer are due to faulty methods.

The record of zero points for the series 1897, 1898 and 1899 is here submitted.

Date.	Observed zero.	Barometer.	Room Temp.	Zero point corrected to 760 mm. and 0°C.	Depressions observed on the given zero.
1897					
Feb. 26	0.0510	761	2°C.	0.0500	Butyric Acid.
" 27	0.0517	769	2	0.0494	Propyl Alcohol.
Mar. 7	0.0512	773	1	0.0486	Cane Sugar.
" 16	0.0518	771	2.5	0.0490	Ethyl Alcohol.
" 28	0.0505	759	3	0.0495	Normal Butyl Alcohol.
Apr. 21	0.0521	773	3.5	0.0506	Control for Sugar, M = 0.10.
1898					
Feb. 26	0.0520	760	3	0.0508	Part of Methyl Alcohol.
Mar. 31	0.0542	760	5	0.0522	Urea.
Dec. 29	0.0545	759	2.5	0.0537	Part of Chloral Hydrate.
1899					
Jan. 2	0.0569	781	1	0.0530	Chloral Hydrate and Acetone.
" 3	0.0558	773	1	0.0532	Ether and Mannite.
" 7	0.0552	763	2	0.0540	Urea.
" 10	0.0562	771	2	0.0536	Control for Urea.
" 19	0.0566	766	4	0.0541	Amyl Alcohol.
" 25	0.0555	750	3	0.0550	Part of Amyl Alcohol.
" 28	0.0557	760	2	0.0549	Aniline and MgSO_4 . ²
" 30	0.0556	759	2	0.0550	H_2SO_4 . ² and part of MgSO_4 . ²
" 31	0.0551	757	2	0.0548	No depressions measured.
Feb. 1	0.0566	766	2	0.0548	NaCl . ²
" 11	0.0570	771	2	0.0544	Acetamide. ²
Mar. 18	0.0556	757	4	0.0545	Control for Acetamide.

These zero points are represented graphically in Fig. 1.

Fig. 1.

¹ Results reserved for a subsequent paper.

It needs to be stated that the zero point at the end of the 1896 series was 0.045° . Thus the slow rising of the zero point which has been observed before is still going on, though the rate is noticeably less. It is worth noticing that the variation in the zero point is such as to be largely accounted for by the well-known changes which a thermometer undergoes—a slow rise of the zero point. The exact uniformity in the rate of this elevation of the zero point for the greater portion of the 1897 period is certainly not other than accidental, but the very nearly uniform rise in the first part of the 1899 period and its almost exact constancy during the latter portion of the same period, are clearly indicative of the high degree of exactness which the method has attained.

The range of variation for the 1897 series is seen to be 0.002° C. in six zero points, and in the 1899 series it is seen to be 0.002° in thirteen zero points, extending through a period of three months.

In each case the greater part of this variation is accounted for by the obvious fact that the zero point has been rising. The remainder of the variation I think represents the experimental errors.

It is not without interest to observe that this thermometer has experienced a total rise of the zero point during the six years that it has been in use since it was corrected at the Reichsanstalt, amounting to not less than 0.023° C. The rate has been about 0.0003° C. per month. The rise during the period of use is noticeably more rapid than this.

Further, any attempt to judge the exactness of any method must take notice of the facts which Nerst and Abegg¹ so clearly set forth in connection with their study of the disturbances which the equilibrium temperature of a mixture of water and ice undergoes on account of the temperatures of the surrounding bodies and the heat developed by the stirring. In the statement of their results they have introduced a temperature called the convergence temperature, which may be defined as that temperature which the water *without the ice* would assume when it has come into thermal equilibrium with its surroundings. They showed that in case the conditions of the experiment were not so chosen that this convergence temperature was identical with the true temperature of equilibrium

¹ Zeit. Phys. Chem., XV., p. 681.

of ice and water, then the observed temperature of the mixture when it has come into thermal equilibrium with its surroundings is not the true temperature of equilibrium of the ice and water sought, and that in certain cases the measurement of depressions of freezing points would be affected by grave errors unless the observations were corrected in a manner shown by the authors.

They conclude that the observed freezing point of any liquid is never its true "freezing point" unless one of two conditions are met; either the convergence temperature must be coincident with the true freezing point, or the *rate* at which a liquid comes to temperature equilibrium when once it begins to freeze must be infinitely great. This may be accepted without hesitation. Then they express themselves in these words:

"Since the former condition has never yet been exactly fulfilled, it has been assumed in the earlier investigations that the equilibrium between the solid and liquid solvent takes place at an infinite velocity."¹

I have elsewhere said that the "convergence temperature" played no rôle in the method which I have used.² From the very beginning of the work the disturbance which the temperature of a mixture of ice and water suffers on account of the temperature of its surroundings and the heat due to the stirring was well known to me, and the entire development of the method was always in the direction of eliminating these disturbances. Thus in the first brief notice of the work³ I express myself on this point as follows:

"A fundamental difficulty lies in the fact that the temperature of a mixture of ice and water is influenced by the temperature of the surroundings, * * * * and a further difficulty consists in the fact that this influence, which is caused by the heat exchanges between the mixture and its surroundings, *and also by the heat developed by the stirring*, varies with the quantity and fineness of the ice present. In order thus that the temperature of a mixture of ice and water may be as nearly as possible the (true) freezing point (of the water), that is, the temperature at which the ice and water alone would be

¹Zeit. Phys. Chem., XV., p. 683. 1894.

²Jour. Phys. Chem., I., p. 224.

³Ber. Berichte, 1893, XXVII., p. 798.

in equilibrium, it is necessary that these disturbing influences be eliminated." In the fuller publication of the work¹ stress is laid upon the success with which this was accomplished, and data are then presented which enabled one to conclude that "the disturbing influences of the freezing bath and surrounding air have been so far eliminated that the *actual* freezing point of water, and so too of a solution, may be determined." This conclusion was drawn from a series of observations on the freezing point of water in which about one-half the individual observations were made with very large amounts of ice present, while the remainder were made with only traces of ice present. It was found that the average values of these two portions of the series were the same. But Abegg² reminds me that my conclusion that the convergence temperature was thus shown to be identical with the true freezing point under observation does not follow necessarily. Since, as he says, the same result would be found if the rate at which a mixture of ice and water comes to its equilibrium temperature is very great. The theory requires this rate to be infinitely great. Now simply put, this rate depends upon nothing save the rate at which the ice melts or the water freezes, and there is little need to talk about this rate being "very great" to say nothing about its approaching an infinite value. It is necessary to observe that my conclusion that the "convergence temperature" of my apparatus was coincident with the true freezing point of the solutions was the result of long experimental work which had no other aim than to bring about this essential result, and I have never had the slightest ground for doubting the soundness of my conclusion. It is for this reason that I have not thought it necessary to reopen this part of the investigation. But Abegg has kindly urged upon me the value of some direct test of the matter, and on March 7, 1899, I made the following experiment:

Room temperature $3^{\circ}.5$ C., barometer 742 mm. The observed freezing point of water was $0^{\circ}.0520$. To find the convergence temperature of the apparatus it is only necessary to proceed exactly as though a determination of the freezing point of the water were to be observed except that the water is not "touched off," so that the

¹ PHYS. REV., 1893, I., p. 213.

² Wied. Ann., 64, p. 490.

water comes to thermal equilibrium with no ice present. After a few minutes the thermometer showed $0^{\circ}.056$, and this was the final reading after ten minutes of stirring. Thus the convergence temperature of the apparatus when the air is at $3^{\circ}.5$ C. and the protection bath is $0^{\circ}.3$ C. is $0^{\circ}.004$ C. above the true freezing point of water. This difference between the convergence temperature of the apparatus and the freezing point of the water under observation is many times smaller than is necessary to insure the exactness of the method. The result of this experiment is exactly what I had every reason more than six years ago to believe was the fact: The convergence temperature plays no rôle in the results obtained by use of the present method. It should be added that sufficient uniformity in the stirring is had by keeping time to a "sing-song" the exact words of which have little scientific interest.

TABLE I.

1 Compound.	2 <i>m</i>	3 Grams per liter of the solution.	4 Sp. gr. of the solution in (3) $\frac{15^{\circ}}{4^{\circ}}$	5 Sp. gr. of the solution <i>m</i> = 0.20.	6 Source of the material.	7 Manner of Preparing Solution in (3).
Methyl Alcohol.	1.	32.02	0.9928	0.9975	Prepared in Lab.	By direct weight, after drying.
Ethyl Alcohol.	1.	46.04	0.9901 ¹	0.997	Squibb's 99.89%.	" " "
<i>n</i> -Propyl Alcohol.	1.	60.05	0.9894	0.9967	Kahlbaum.	" " " " "
<i>n</i> -Butyl Alcohol.	1.	74 .06		0.997 ⁷	Kahlbaum.	" " " " "
Amyl Alcohol.	0.1	8.81		0.997 ²	Kahlbaum.	" " " " "
Glycerine.	1.	92.04	1.0203	1.003	Eimer & Amend.	Gerlach's Tables. ³
Dextrose.	0.9834	177.08	1.0664 ⁴	1.0125 ⁴	Merck & Co.	Fresenius' Tables. ⁵
Cane Sugar.	1.	342.1	1.1294	1.024	Rock Candy.	By direct weight, after drying.
Mannite.	0.5	91.04	1.0304	1.012	Merck & Co.	" " " " "
Ether.	0.5	37.03	0.9911	0.996	Squibb's Abs.	" " " " "
Acetone.	1.	58.04	0.9908	0.997	Kahlbaum.	Squibbs' Tables. ⁶
Chloral Hydrate.	1.	165.4	1.0722	1.0159	Kahlbaum.	Direct weight.
Aniline.	0.2	18.61		0.9995	Kahlbaum.	" " after drying.

¹ Sp. gr., $\frac{20^{\circ}}{4^{\circ}}$.² *m* = 0.10.³ Landolt and Börnstein Tabellen, 1895, p. 230.⁴ Sp. gr., $\frac{17.5^{\circ}}{4^{\circ}}$.⁵ Zeit. Anal. Chem., 1883, XXII., p. 454.⁶ Ephemeris, VII., p. 541.⁷ Assumed.

The present investigation includes the non-electrolytes, which are tabulated with the usual accompanying data in the opposite table.

METHYL ALCOHOL, 1896.

The solution $m = 1$ was prepared from methyl alcohol which had been made by the saponification of methyl oxalate crystals with ammonia water in a manner which is described below. The tables of specific gravity furnished by Dittmar and Fawsitt¹ were used. But the specific gravity of the resultant normal solution was 0.99313 at 15° 56C. and the solution according to these tables was thus 5 % too strong.² The observed depressions were accordingly corrected by this amount, reducing the observed molecular depressions to the almost constant value 1.73. This result was so surprising that it could not be accepted until all possibility of error in the concentration of the solutions was set aside. To this end nothing would avail except the attempt to prepare *pure methyl alcohol*. This I undertook to do. The work, however, was so great and was so slow of accomplishment that the publication of the large part of the experimental material of the years 1896, 1897 and 1898 had to be delayed to the present time. This will account for the confusion in the dates of the various series of observations. To prepare methyl alcohol the following method was used: The best methyl alcohol of commerce is converted into methyl oxalate by adding 800 cc. of the alcohol to a solution of 1000 gr. oxalic acid crystals in 400 cc. of sulphuric acid. When this is allowed to stand in a cool place the methyl oxalate separates out in an abundant crop of colorless crystals, which are drained and *washed with ice cold water*. The product has a marked "mouse nest" odor. The crystals are now digested with a strong solution of ammonia in water, using a glass flask provided with an "inverted condenser." This leads to the saponification of the methyl oxalate with the regeneration of methyl alcohol. It is then distilled and all of the distillate collected that will come over from a bath kept at 100° C. The product is about half water, the greater part of which is removed by the use of dry K_2CO_3 and

¹ Edinburgh Trans., XXXIII., p. 509.

² In the Princeton Bulletin, May, 1896, in publishing the value for a .1 normal methyl alcohol solution I used a correction factor of 3 per cent. by mistake.

CaO in the order named. The yield is scanty, and large quantities of the materials have to be employed, for the product must again be put through the oxalate process.

After this has been done the methyl oxalate has lost its odor. The resultant methyl alcohol is dried as before and then subjected to a long series of successive distillations from metallic sodium. The distillations were made backwards and forwards between two distillation flasks, each of which served in turn as distilling flask and condenser.

In this way no pouring of the alcohol from one vessel to another was necessary. Between each distillation the specific gravity of the alcohol was observed. Some twenty such distillations from small bits of sodium were made before the specific gravity had been reduced to a constant value. I think much of this work would have been unnecessary if I had learned earlier in the work that methyl alcohol when nearly *dry* takes water from the air, in spite of ordinarily careful stoppering, so rapidly that its specific gravity goes up three or four points in the fourth place of decimals during a single night. When this fact became known the exclusion of the moisture of the air received the utmost care, and the determinations of the specific gravity were made in a pyknometer so arranged that the alcohol could be transferred to it from the condensing flask without contact with the air's moisture. In this way the specific gravity was reduced to a constant value.

At 10° the specific gravity = 0.80065.

At 20° the specific gravity = 0.79133.

Water at 4°C. = 1.

The boiling point of this methyl alcohol

At 766.74 mm. is 64°.70C.

At 752.92 mm. is 64.23.

Thus at 760 mm. it is 64°.5C. (Gasthemometer, Reichsanstalt).

It needs to be observed that the boiling point was taken as usual with the entire stem exposed to the vapor and the bulb about 4 cm. above the liquid. A quantity of glass beads was put in the flask to insure uniform boiling. The entire product, except the last frothing traces, went over at the temperatures given above. I find that the slight rise of 0°.1—0°.2 which occurs at the last moment

is no indication of an impure product, but results wholly from the unavoidable "overheating" when any small quantities of the substance are in the flask. Thus I find that the *purest water* behaves in the same way.

While the specific gravity and boiling point of methyl alcohol have thus been very much lowered below the hitherto accepted values, I have no reason for thinking that a *dry* product has yet been obtained. Only the limit which the apparatus and drying method used in the present work have fixed has been reached. It is worth mentioning that I find that sodium continues to dry methyl alcohol long after dry copper sulphate and P_2O_5 have ceased to act. It is probable, then, that Carrara,¹ in his attempt to measure the dissociation of water in methyl alcohol did not succeed in getting a *dry* alcohol as the basis of his work.

The methyl alcohol prepared in the way described above *has lost all traces of its characteristic odor*. I am of the opinion that a slight odor still remains, though some who have examined the product do not admit this. The details of this purely incidental work will perhaps be given at some future time in case opportunity arises to measure some other important constants of pure methyl alcohol, some 40 grams of which I still have left.

From this alcohol a gram-molecular solution was made by direct weighing. Its specific gravity at 18° C. was found to be 0.99281 and at 15°.56 C. it was 0.99318. Thus my suspicion that the tables of Dittmar and Fawsitt are faulty in the region of great dilution is confirmed. Using this final normal solution I then prepared a tenth normal solution for the purpose of determining its freezing point as a control to the observations made in 1896. The result was exactly 1% higher than the value found in 1896, and I should accordingly correct the entire series by this amount. But unfortunately a confusion exists in the original notes which forces me to regard the specific gravity of the normal solution prepared in 1896, as probably wrong, so that I am unable to say as I should like to that the 1896 solution was 1% weaker than the final one used in the "control." I can do no more than to give the 1896 series and say that they may be 1% too small. At the first opportunity I shall repeat the entire series.

¹ Gazz. Chim. Ital., 1897, XXVII., p. 1.

Methyl Alcohol, Feb. 17, 1896.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0183	1.83	0.321	0.01	1.83
0.02	0.0362	1.81	0.641	0.02	1.81
0.03	0.0548	1.83	0.963	0.0301	1.82
0.05	0.0910	1.82	1.605	0.0502	1.81
0.10	0.1818	1.82	3.216	0.1005	1.81
0.20	0.3655	1.83	6.457	0.2018	1.81

Fig. 2.

In the tables throughout this paper m denotes the number of gram-molecules per liter of the solution; Δ , the depression of the freezing point, and Δ/m is what is generally known as the *molecular depression*.

By the help of the specific gravity of the solution $m = 0.20$, it is easy to reduce the values of m to the values m' which denote the number of gram-molecules per 1000 grams of water in the solution. To this end the calculated number of grams of the substance per 1000 grams of water is given under P in the tables. m' equals of course the quotient of P divided by the molecular weight.

The graphic representation of the results is presented with each table, using my usual method, in which the ordinates represent the the values of Δ/m , and the abscissas the values of m . The dotted line gives the values of Δ/m' .

The "curve" turns out to be a straight line. The observed values do not in any case differ from those that such a straight line would require by more than $0^{\circ}.0003$ C. The molecular depression is thus seen to be 1.82 in extreme dilution, increasing slowly to 1.83 in the region of greater concentration.

ETHYL ALCOHOL, MARCH 16, 1897.

The solution, $m=1$, was made by direct weight from Squibb's "absolute alcohol." Dr. Squibb was kind enough to determine the

specific gravity of the product which he sent me directly before the can was sealed. He found specific gravity $\left(\frac{15^{\circ}.6}{15^{\circ}.6}\right)$, 0.79386. According to his table¹ the strength was 99.89%. The solution $m = 1$ had a sp. gr. $\left(\frac{26^{\circ}}{4^{\circ}}\right)$ 0.99005.

Ethyl Alcohol, March 16, 1897.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0181	1.81	0.460	0.01	1.81
0.02	0.0368	1.84	0.921	0.02	1.84
0.05	0.0920	1.84	2.312	0.0502	1.83
0.10	0.1849	1.85	4.633	0.1007	1.84
0.20	0.3707	1.85	9.314	0.2024	1.83

Fig. 3.

The comparison of these results with those of 1892² is instructive. For this purpose the earlier results are given below:

Ethyl Alcohol, Dec., 1892.

m	Δ	$\frac{\Delta}{m}$	Corrected Values.
0.01	0.0172	1.72	1.74
0.02	0.0351	1.76	1.78
0.04	0.0729	1.82	1.84
0.05	0.0894	1.79	1.81
0.10	0.1825	1.83	1.85
0.16	0.2927	1.83	1.85

Before making the comparison it must be remembered that the solutions of 1892 were known to be 1% too weak (see note, p. 282,

¹ Ephemeris, II., p. 541.

² PHYS. REV., I., p. 199.

l. c.). Applying this correction to the series we get the values shown in the last column of the table. The values at $m = 16$, $m = 0.10$ and $m = 0.04$ are identical with those in the new series. The values at $m = 0.01$, $m = 0.02$ and $m = 0.05$ fall below those of the new series. This comparison of the two series furnishes a very striking confirmation of the conclusion which has been reached in regard to the error which arose in the earlier work on account of packing the whole thermometer in ice when out of use. The zero point is therefore uniformly made too low and the curve of molecular depressions, which was found to be straight in the region of greater concentration, is made to curve considerably downward in the region of great dilution where the error in the zero point would be most felt. A second matter of interest appears in the very singular value for $m = 0.04$. In the paper of 1892, this observation is looked upon as incorrect only because it was so out of accord with the rest of the series, and I was forced to assume the possibility of an error amounting to $0^{\circ}.0015$ C., an error which, apart from this single observation, I had no right to admit.

It now appears that this one observation was the only one that was right in the region of extreme dilution. The observations at that time required generally a whole day for the determination of the zero point of the thermometer and the freezing point of the solution, so that it is easy to believe that this single determination could have been so made as to escape the influence of the usual source of error.

As in the case of methyl alcohol the graphic representation of the results is best effected by a *straight line* which shows, allowing for errors in no case greater than $0^{\circ}.0003$, that the molecular depression is 1.84 in *extreme dilution*, and that it increases uniformly to 1.85 at $m = 0.20$.

It is a matter of very great importance as well as gratification that the last results of Raoult,¹ are so exactly in accord with these values that it is impossible to distinguish the two series when graphically represented on the scale of the present curves. Although my work was done some time before Raoult published his results, Raoult had no knowledge of it until after the publication of his work. The two series have been made by different observers.

¹ Zeit. Phys. Chem., XXVII.

in entire independence and *without the guiding hand of any theory* and must be looked upon as affording the most strikingly confirmation of each other.

PROPYL ALCOHOL, FEBRUARY 27, 1897.

The solution $m = 1$ was made by direct weight from Kahlbaum's product. The product was successively distilled from sodium as in case of methyl alcohol, though with much less care. The boiling point of the middle portion of a final distillate was constant within $0^{\circ}.1$ C.

The specific gravity of this portion, at 15° C., was 0.80798; at 20° C., 0.80406.

Its boiling point at 760 mm. is $97^{\circ}.2$ C. These values, as with methyl alcohol, are much lower than those hitherto accepted, due simply to the greater dryness of the present products.

n-Propyl Alcohol, Feb. 27, 1897.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0189	1.89	0.601	0.01	1.89
0.02	0.0371	1.86	1.201	0.02	1.86
0.05	0.0936	1.87	3.015	0.0502	1.86
0.10	0.1858	1.86	6.015	0.1008	1.84
0.20	0.3723	1.86	12.191	0.2031	1.83

Fig. 4.

The graphic representation again is best effected by a straight line. The errors which must be assumed in drawing this conclusion do not exceed $0^{\circ}.0003$ C.

The molecular depression is seen to be 1.87 in extreme dilution and to fall uniformly to 1.86 in the region of greatest concentration.

N-BUTYL ALCOHOL, MARCH 28, 1897.

The solution $m = 1$ was made by direct weight from Kahlbaum's product. The quantity at my disposal was so small that no drying was possible. I assumed that there was 1% water present and made allowance for this in making the weighings. Its specific gravity at 20° with a Mohr balance was 0.8095 ± 0.0002 . An attempt to dry a sample obtained afterwards from the same source, with the hope that a "control" determination of the freezing point would enable one to "correct" the original series resulted in failure; since, in spite of the utmost care in the successive distillations from Na, the product did not show a constant boiling point within 5° C. I am unable to find that *n*-butyl alcohol has ever been prepared with such a degree of purity that the boiling point is any more constant than this, and I abandoned the idea of making any control determinations. I found the specific gravity of the product when dried with Na to be 0.8082 at 20° C. What degree of error there may be in the given values of the various concentrations I have no means of knowing. That the results are in accord with the rest of the alcohol series, of course, furnishes no ground for any conclusion in this matter.

n-Butyl Alcohol, Mar. 28, 1897.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0189	1.89	0.741	0.01	1.89
0.02	0.0368	1.84	1.482	0.02	1.84
0.05	0.0926	1.85	3.72	0.0503	1.84
0.10	0.1863	1.86	7.47	0.1009	1.85
0.20	0.3723	1.86	15.08	0.2037	1.83

Fig. 5.

Again the graphic representation is a straight line. This conclusion requires the assumption of an error in no observation exceeding

0°.0003 C. The molecular depression in extreme dilution is 1.86 and this is the value also for all the concentrations.

AMYL ALCOHOL, FEBRUARY 27, 1897.

The original product was Kahlbaum's "amyl alcohol" and is the ordinary amyl alcohol of fermentation. It was dried with Na. The final product had a boiling point constant within 1°.1 C. Its specific gravity was 0.8121 at 18° C. The solubility of amyl alcohol in water does not permit the solution $m = 0.20$.

Amyl Alcohol, Feb. 27, 1897.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0185	1.85	0.883	0.01	1.85
0.02	0.0372	1.86	1.766	0.02	1.86
0.05	0.0926	1.85	4.431	0.0503	1.84
0.10	0.1845	1.845	8.922	0.1013	1.82

Fig. 6.

The graphic representation is again a straight line, with practically no error in any observation. The molecular depression in extreme dilution is 1.86 and this falls to 1.84 at $m = 0.10$.

GLYCERINE, FEBRUARY 13, 1896.

The solution $m = 1$ was made by use of Gerlach's tables of specific gravity.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0186	1.86	0.922	0.01	1.86
0.02	0.0372	1.86	1.845	0.0201	1.85
0.05	0.0929	1.86	4.622	0.0502	1.85
0.10	0.1869	1.87	9.280	0.1008	1.85
0.20	0.3758	1.88	18.688	0.2031	1.85

Fig. 7.

The graphic representation is a straight line, and this conclusion requires no appreciable errors to be admitted. The molecular depression is 1.86 in extreme dilution and rises to 1.88 at $m = 0.20$.

DEXTROSE, FEB. 22, 1896.

The product was from Merck and Co. It was not true to their label in regard to dryness, and so an approximate solution, $m = 1$, was made by weight and then corrected by use of the Fresenius tables.¹ The specific gravity of the approximate solution was 1.0664,

Dextrose, Feb. 22, 1896.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.0098	0.0185	1.88	1.774	0.0098	1.87
0.0197	0.0363	1.84	3.559	0.0198	1.84
0.0492	0.0916	1.86	8.927	0.0496	1.85
0.0983	0.1850	1.88	17.95	0.0997	1.86
0.197	0.3745	1.90	36.30	0.2016	1.86

Fig. 8.

and was thus 1.66% too weak according to these tables. The concentrations in column (m) are corrected by this amount.

A true $m = 1$ solution, prepared from Kahlbaum's fine crystalline product, when freed from its bare trace of water by most careful drying, has been found to have a specific gravity at $\left(\frac{17.5}{17.5}\right)$, 1.0684.

¹ Zeit. An. Chem., XXII., p. 454.

and at $\frac{18^\circ}{4^\circ}$, 1.0669. This is so nearly in accord with the Fresenius tables that I have accepted them with confidence.

The graphic representation is again a straight line, a conclusion which requires the admission of experimental errors reaching to $0^\circ.0004$ C.

The molecular depression is 1.85 in extreme dilution and rises to 1.90 at $m = 0.20$.

CANE SUGAR, MARCH 7, 1897.

The solution $m = 1$ was made by direct weight from carefully selected crystals of "rock-candy." These were pulverized and dried over sulphuric acid. The solutions were made immediately before the observations on their freezing points.

Cane Sugar, March 7, 1897.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0187	1.87	3.432	0.01	1.87
0.02	0.0378	1.89	6.879	0.0201	1.88
0.05	0.0947	1.89	17.312	0.0506	1.87
0.10	0.1918	1.92	34.962	0.1022	1.88
0.20	0.3960	1.98	71.599	0.2093	1.89

Fig. 9.

The graphic representation is again a straight line if an error of $0^\circ.0004$ be assumed at $m = 0.02$.

The molecular depression in extreme dilution is 1.86. It rises rapidly to 1.98 at $m = 0.20$.

These results should be compared with the series of 1892. It appears that, barring the downward curvature in the region of extreme dilution, which all the early series exhibited, the new re-

sults are exactly 1 per cent. higher than the old. The solutions however were not of the same strength, as appears from their specific gravity. Thus the solution $m = 1$, at $17^{\circ}.5$ C., has a specific gravity at 18° , 1.1294. The solution used in 1892 ($m = 1$ at 4° C.) had a specific gravity at 18° , 1.1285.¹ Accordingly, using the tables of specific gravity in the Kohlrausch Leitfaden, eighth edition, the old solutions were 0.6 per cent. too weak. The two series then are *parallel* and differ by 0.4 per cent., a difference probably less than the experimental errors of the method.

The latest values found by Raoult² are exactly parallel with these results when they are computed on like definition of a gram-molecular solution, but are exactly 1 per cent. higher. The agreement, while falling short of complete identity, as in the case of ethyl alcohol, is still not less striking, since the two series agree in that they confirm each other in the *fact of a uniform increase in the value of the molecular depression* with increase in the concentration. It is to be observed that the results of Raoult are expressible by a straight line without the smallest trace of an error, say at $m = 0.03$, when the error reaches $0^{\circ}.0003$ C. It is to be regretted that he did not examine solutions more dilute than $m = 0.03$, since his method clearly would justify this.

The two series are represented graphically in the annexed figure, in which m is the number of gram-molecules per 1000 grams of water (m' in the tables).

Fig. 10.

MANNITE, JANUARY 3, 1899.

The solution $m = 1$ was made by weight from Merck's product after drying at 100°C. to constant weight.

¹ The published value was 1.1286. This was reckoned without making allowance for air displacement, which is now done.

² Zeit. Phys. Chem., XXVII., p. 617.

Mannite.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0185	1.85	1.821	0.01	1.85
0.02	0.0371	1.86	3.656	0.0201	1.85
0.05	0.0931	1.86	9.169	0.0504	1.85
0.10	0.1874	1.87	18.44	0.1013	1.85
0.20	0.3807	1.90	37.33	0.2061	1.85
0.50	0.9835	1.97	96.92	0.5323	1.85

Fig. 11.

The results are again in a straight line if an error of $0^{\circ}.0005\text{C.}$ be assumed in the observations at $m = 0.10$ and $m = 0.20$. The molecular depression is 1.86 in extreme dilution. It must be remarked that the results in the present case could be expressed by a curve slightly convex on the upper side and given a value for the molecular depression 1.84 in extreme dilution. I am of the opinion, however, that this is due to the distribution of the experimental errors in spite of the fact that an error of $0^{\circ}.0005\text{C.}$ has to be admitted to make the results expressible by a straight line.

ACETONE, JANUARY 2, 1899.

The solution $m = 1$ was made from Kahlbaum's "Aceton aur der Bisulfitverbindung," by use of Squibb's tables of specific gravity.

Acetone.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0185	1.85	0.580	0.01	1.85
0.02	0.0372	1.86	1.163	0.02	1.86
0.05	0.0932	1.86	2.914	0.0502	1.86
0.10	0.1846	1.85	5.851	0.1008	1.83
0.20	0.3706	1.85	11.78	0.2030	1.83
1.00	1.914	1.91	62.22	1.072	1.79

Fig. 12.

The representation of the *entire* series by a straight line is impossible. A curve, with its convex side downward, beginning at 1.86 in extreme dilution and running nearly straight in the region between $m = 0.01$ and $m = 0.20$ represents the results best. The errors necessary to this conclusion are inappreciable, while a straight line would require errors of $0^{\circ}.001$ at $m = 0.20$, and $0^{\circ}.007$ at $m = 0.05$.

The molecular depression is again 1.86 in extreme dilution and rises to 1.91 at $m = 1$.

CHLORAL HYDRATE, JANUARY 2, 1899.

The solution $m = 1$ was made from Kahlbaum's product by direct weight, after exposure to sulphuric acid. The powdered crystals are volatile and it is impossible to bring the compound to a constant weight.

Chloral Hydrate.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0186	1.86	1.655	0.01	1.86
0.02	0.0373	1.87	3.318	0.0201	1.86
0.05	0.0924	1.85	8.315	0.0503	1.84
0.10	0.1875	1.87	16.696	0.1009	1.86
0.20	0.3760	1.88	33.66	0.2035	1.85
1.00	2.050	2.05	182.40	1.1028	1.86

Fig. 13.

The graphic representation of the *entire series* shows that the results cannot be expressed by a straight line unless an error of more than $0^{\circ}.001$ be assumed at $m = 0.10$ and $m = 0.20$. As I have no right to assume so large an error, it must be said that here also a curved line with slight convexity on its lower side and practically straight in the region between $m = 0.01$ and $m = 0.20$, best represents the results. The necessary error for this conclusion is $0^{\circ}.0005$ C. in the observation $m = 0.05$.

The molecular depression is 1.86 in extreme dilution and rises to 2.05 at $m = 1$.

ANILINE, JANUARY 28, 1899.

Kahlbaum's product was distilled twice from sodium and made into a solution $m = 0.20$ by weight. The specific gravity of the aniline after the distillation was, at 15° C., 1.0260 and at 20° C., 1.0215.

Aniline.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0185	1.85	0.931	0.01	1.85
0.02	0.0372	1.86	1.867	0.0201	1.85
0.05	0.0914	1.83	4.681	0.0503	1.82
0.10	0.1811	1.81	9.407	0.1011	1.79
0.20	0.3549	1.77	18.97	0.2038	1.74

Fig. 14.

The results lie in a straight line, with an assumed error of $0^{\circ}.0005$ at $m = 0.10$.

The molecular depression is 1.86 in extreme dilution and falls rapidly to 1.77 at $m = 0.20$.

ETHER, JANUARY 3, 1899.

Squibb's "absolute ether" was distilled twice from sodium. It was then found to be no longer acted on by this drier. Its spe-

cific gravity at 15° C. was 0.7193, and its boiling point was 34°.3 C. at 760 mm. These values are much lower than the accepted values for these constants, save only the specific gravity, as found by Squibbs,¹ namely, 0.7189 at 15°.

Ether.

m	Δ	$\frac{\Delta}{m}$	P	m'	$\frac{\Delta}{m'}$
0.01	0.0162	1.62	0.741	0.01	1.62
0.02	0.0336	1.68	1.486	0.0201	1.67
0.05	0.0856	1.71	3.724	0.0503	1.70
0.10	0.1734	1.73	7.486	0.1011	1.72
0.20	0.3468	1.73	15.10	0.2038	1.70

Fig. 15.

The graphic representation is a curve line with a pronounced convex side on the upper side. The molecular depression in extreme dilution can be obtained only by a very uncertain extrapolation which gives, say, the value 1.50. The molecular depression becomes constant at $m = 0.10$, with the value 1.73.

GENERAL DISCUSSION.

It is well known how van't Hoff has shown that the freezing point of a solution of any non-electrolyte in any solvent is theoretically capable of calculation by the formula,

$$\Delta = \frac{0.002 T^2}{\lambda} \cdot \frac{G}{M}.$$

Where Δ denotes the difference between the known freezing point of the pure solvent and that of the given solution. T is this known freezing point of the solvent on the absolute scale, while λ is its heat equivalent of fusion. G denotes the number of grams of the solute

¹ Ephemeris, II., p. 678.

per liter of the solution, and M is its molecular weight. It is convenient to call G/M the number of gram-molecules per liter, and to denote it by m .

Thus in the case of aqueous solutions, using the value accepted by van't Hoff as the most probable for λ , we have, for the lowering of the freezing point due to any non-electrolyte:

$$\Delta = \frac{0.002(273)^2}{79} \cdot m,$$

and accordingly the value of the molecular depression is

$$\frac{\Delta}{m} = \frac{0.002(273)^2}{79} = 1.89.$$

This is the *van't Hoff constant*.

The early work of Raoult covered a large range of organic substances. The average value of the molecular depression of the *entire* series is as high as 1.85.¹ But the series comprises a large number of the *organic acids* which are known to be electrolytes.

Omitting these, since they have no right to be classed with the non-electrolytes, as everybody knows, the average value of the molecular depression of all the non-electrolytes examined by Raoult is 1.75, with aniline giving the value 1.53, and inverted sugar 1.93. This misrepresentation of Raoult's results is now quite general in the literature and for that reason I call attention to the matter.

More recent attempts to test the validity of the van't Hoff constant have been largely confined to ethyl alcohol, sugar and urea, which unfortunately constitute about the worst trio which could have been chosen for that purpose, since each presents an exception to the theory in question. Thus, sugar conforms to the theory only in solutions so dilute that the difficulty of determining the freezing point is very great. Ethyl alcohol does not conform to the theory at all, while urea seems to be so unstable in aqueous solutions that two attempts to repeat the work done by me on this compound in 1893 have been fruitless. For this reason no results for urea are found in the present paper.

¹Ostwald's Chem., II., p. 751.

DISCUSSION OF THE PRESENT RESULTS.

1. It is shown by the experimental results that a large number of widely different compounds in extreme dilution all have exactly *the same value for the molecular depression, namely 1.86*. This remarkable series comprises *n*-propyl alcohol, *n*-butyl alcohol, amyl alcohol, glycerine, acetone, dextrose, cane sugar, mannite and aniline.

The exceptions to this general conclusion are shown by

Methyl Alcohol,	1.82,
Ethyl Alcohol,	1.84,
Ether,	1.50.

These exceptions are well established by the experimental results.

Thus the van't Hoff requirement that the molecular depression for non-electrolytes in great dilution should be constant is fulfilled in a large range of compounds, *with the constant value 1.86*.

It is to be observed that the formula given by van't Hoff required the value 1.89. But the factor 0.002 which the formula contained is now known to be too high. It should be, according to present knowledge, 0.00198. With this correction the value of the van't Hoff constant would be 1.87, while the present experimental results require it to be 1.86. I believe that it will be found that the value for λ , namely the heat equivalent of fusion for ice, which appears in the formula and to which van't Hoff assigned the value 79 as the most probable will be found by experiment to be 79.3 such at least is the value required by the experimental facts presented in this paper, provided the exact validity of the van't Hoff constant is allowed.

2. It appears as the concentration of the various solutions increases, the greatest diversity in the values of the molecular depression comes to light.

Thus, in the case of cane sugar, the molecular depression has rapidly increased to 1.98 at $m = 0.20$; in other cases it has shown little change; while in others, noticeably aniline, the molecular depression has fallen rapidly to 1.77 at $m = 0.20$. The significance of this change in the value of the molecular depression is evident when we remember that the van't Hoff equation is deduced on the as-

sumption that the dissolved substance behaves exactly as if it were in the state of an ideal gas with a volume equal to that of the solution. That is, it is assumed that the substance obeys the laws of Boyle and Gay Lussac *exactly*, which require $p v = RT$. Now no known gas does this perfectly. The familiar correction introduced by van der Waal by which the value of v is so corrected as to make allowance for the space actually taken up by the molecules themselves is known to render the product $p v$ more nearly constant. The introduction of this correction in connection with a substance dissolved in any solvent is easily effected by defining the concentration of the solution not in terms of gram-molecules per 1000 cc. of the solution, but in gram-molecules per 1000 cc. of the *solvent* instead. This definition is the basis of the value, m' , given in column 5 of each table. By referring to the tables, under the heading Δ/m' , it is found that the molecular depression has become constant in the case of methyl and ethyl alcohol, glycerine, dextrose, mannite and chloral hydrate. In the light of the van't Hoff theory this amounts to saying that these substances in aqueous solution behave exactly as if they were in the state of a gas.

In the remaining cases the application of this correction to m does not suffice to render the molecular depression constant for all concentrations. In the case of sugar the correction seems to be too small to render the depressions constant, while in the rest of the cases this correction is too large to bring this about. The failure of this correction to bring the substances into accord with the requirement that they behave as gases is conspicuous in the case of aniline alone. It is the one case which I have examined where it seems possible to believe that the molecules of the dissolved substance combine themselves into molecular aggregates, more and more numerous in proportion as the concentration of the solution is increased. Anomalous as the aniline certainly is in the region of greater concentration it is the more important to observe that it is in exact accord with the demands of the theory when the dilution becomes extreme.

3. It will be remembered that the only exception to the general law that the molecular depression of non-electrolytes in *extreme dilution* is constant, was exhibited by methyl alcohol, ethyl alcohol

and ether. The exceptions here presented are pronounced and cannot possibly be explained by the assumption of unusual experimental errors. More experimental knowledge of these substances must be had before any explanation of their behavior in aqueous solution may be finally made. I wish merely to be permitted to suggest that the low values for methyl and ethyl alcohol is more than likely due to the fact that they evaporate rapidly from their aqueous solutions. To test this suspicion, I undertook to investigate the behavior of ether in this relation. The results confirm the suspicion, but exhibit an additional difficulty, namely, the values of the molecular depression are found not to increase or decrease uniformly with the increase in the concentration as is the case in the other compounds, but the change is according to a much more complex law. This appears best in the graphic representation. I have no explanation for this.

4. Before concluding this discussion of the results the important relation which they bear to the values found by the writer for the molecular depressions in the case of a large number of inorganic electrolytes must be pointed out. In general these values for the electrolytes have been about 2% lower than the dissociation theory of Arrhenius could account for. In making comparison between the experimental results and the requirements of this theory the van't Hoff constant plays a fundamental rôle, and I have always accepted the value 1.89 as the most probable theoretical value for this constant. According to the results of the present work it appears that this value is *too high* by 1.6%. Making use of the new value it turns out that the very large number of electrolytes which the author has examined are brought into full accord with this important generalization of Arrhenius.

SUMMARY.

1. The method of determining the freezing points of dilute solutions introduced by the author in 1893 is shown to conform to the fundamental requirement of all exact cryroscopy, that the convergence temperature of the apparatus must be coincident with the *true freezing* point to be observed.

2. A source of error in the early practice of the method has

been discovered. This error arose from the fact that in order to keep the thermometer when not in use at the temperature of $0^{\circ}\text{C}.$, the whole instrument was packed in ice. It is now known that only the lower part should be so treated, the upper part should be kept always at room temperature. This error is shown to account for the slight downward curvature which the graphic representation of the early results for the non-electrolytes.

3. The method is used to find the molecular depressions of a large number of other non-electrolytes in aqueous solution. It is found that the van't Hoff constant is exactly verified in all the cases examined except methyl alcohol, ethyl alcohol and ether. The experimental value is found to be 1.86.

In conclusion I wish to say that a few remaining non-electrolytes which should be investigated before a general conclusion may be drawn in regard to the validity of the van't Hoff constant will be studied as soon as the opportunity presents itself, and it is hoped that the additional knowledge so acquired may throw light upon the exceptions already found.

PRINCETON UNIVERSITY, July 5, 1899.