

ON THE FREEZING-POINTS OF DILUTE SOLUTIONS. I.

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THE conflicting views in regard to the nature of solution arise largely from the fundamental disagreement in the results which different observers have found for the freezing-points of dilute aqueous solutions. The difficulties in making such determinations are so great that the results have been affected apparently by large errors. The methods which have been employed to overcome these difficulties are so uncertain in practice that different observers, even when using identical methods, have obtained radically different results, and these have furnished the material for the construction of the conflicting theories. While the estimated errors of the principal observers have been placed by themselves as low sometimes as $0^{\circ}.0005$ C., and seldom higher than $0^{\circ}.005$ C., the observed freezing-points of a given solution have differed by many times the latter amount. One may cite, for example, the case of an aqueous sugar solution, in middle concentration, say $\frac{1}{10}$ normal, or about 3.3 per cent. The observed freezing-points, together with the estimated error of the observer, are given in the following table. These results are obtained by interpolation, for the most part within narrow limits. The first determination of Raoult is reduced to numerical value from his curve of results, which is the only published data. To gain a clearer idea of the magnitude of these differences it must be remembered that the total depression of the freezing-point in a $\frac{1}{100}$ normal sugar solution does not exceed $0^{\circ}.02$. One seems warranted in believing that theories which require for their support such a degree of certainty in the freezing-point of a solution, that $0^{\circ}.001$ C. becomes critical, rest

so insecurely upon the present experimental data that they should be held with some little reservation, and at least advocated with no display of temper.

Observer.	Year of Publication.	Freezing-point.	Estimated error.
¹ Raoult, I.	1886	0°.24	0°.01 (<i>a</i>)
² Arrhenius, I.	1888	0°.210	0°.005 (<i>b</i>)
³ Traube	1891	0°.235	0°.005 (<i>c</i>)
⁴ Eykman	1891	0°.216	
⁵ Arrhenius, II.	1891	0°.204	
⁶ Tamman	1891	0°.206	
⁷ Pickering	1891	0°.202	0°.0005 (<i>d</i>)
⁸ Raoult, II.	1892	0°.205	0°.0020 (<i>e</i>)

Some two years ago, at the suggestion of Professor Dr. W. Hallwachs, I began to work upon the freezing-points of dilute solutions. The apparatus employed was the well-known one of Beckmann in its improved form,⁹ which commends itself so highly on account of its great ease of manipulation and large range of application. The results which I obtained, however, showed so little agreement among themselves, that it soon became evident that the desired degree of accuracy was not to be expected with this method. Not the least of the many difficulties which were encountered, and one which made me always suspicious of my own results, was the inability to free the observations from a large element of arbitrariness. The thermometer seemed to be incapable of assuming a fixed position, and when at times it did become stationary, the slightest incautious jar or change in the rate of stirring, or even continued stirring at a uniform rate, would disturb the mercury. Thus a slight increase in the vigor

¹ Ann. de Chim. et de Phys. (VI.) 8, 1886, p. 313. (*a*) same, (V.) 1883, p. 135.

² Zeit. Phys. Chem. II., 1888, p. 491. (*b*) same, p. 493.

³ Ber. Chem. Berichte, 1891, p. 1853. (*c*) same, p. 1854.

⁴ Ber. Chem. Berichte, 1891, p. 1783.

⁵ Ber. Chem. Berichte, 1891, p. 2255.

⁶ Ber. Chem. Berichte, 1891, p. 2287.

⁷ Ber. Chem. Berichte, 1891, p. 3328.

⁸ Comptes Rendus, 1892, p. 268.

⁹ Zeit. Phys. Chem. II., 1888, p. 638.

(*d*) same as ⁷, 1892, p. 1860.

(*e*) same as ⁸, 1892, p. 271.

of the stirring or its uniform continuation is attended by a steady *rise* in the thermometer, which becomes less and less as the stirring is gradually decreased, and finally the mercury becomes stationary at almost any prescribed point at which the stirring is allowed cautiously to cease altogether. Thus the danger that the bias of the observer may affect the results was so great that the method was finally abandoned.

The only apparent way of avoiding this danger is to insure the presence of a large quantity of ice by allowing a large degree of overcooling to precede the freezing; but here, again, a still more serious difficulty presents itself, namely, the change in the concentration of the solution due to the freezing of a portion of the solvent. My experiments convince me that the corrections which thus become necessary are extremely uncertain, and when they amount, as some observers find, to more than 4 per cent. of the total depression, they cannot fail to produce utter confusion in the results.

My experience, however, with the Beckmann apparatus furnished the key to the method which finally developed itself, since it was during this time that it first became evident how marked was the influence of the temperature of the freezing mixture upon a mixture of ice and water obtained by exposing water in any suitable vessel to its action. The temperature of this partially frozen water, especially when the initial overcooling which always precedes the freezing does not exceed 1°C. , is always lower, within certain limits, the lower the temperature of the freezing mixture is chosen, reaching, however, a maximum depression when the freezing mixture becomes about -7°C. Beyond this point a surprising fact presents itself; for now the *lower* the temperature of the freezing mixture, the *higher* becomes the observed temperature of the ice and water mixture surrounded by it. The highest temperature is observed when the freezing mixture is reduced to about -15°C. All this is easily understood as soon as one observes that below a certain point, by no means, however, fixed, but rather dependent on the shape of the vessel and manner and rate of stirring, an ice sheath is formed on the wall of the vessel, which thus serves as a shield against the extreme cold of the exte-

rior bath. When this sheath is complete and compact in texture, the protection which it affords to the remaining ice and water mixture becomes complete, and the water assumes its true freezing temperature. Further reduction of the outside temperature beyond the point at which a complete ice sheath is formed has no appreciable influence upon the inner temperature. That this final temperature should be higher than it is when the freezing mixture is only -3°C. , for example, is plain, since at this much warmer temperature the stirring prevents the formation of an ice sheath, and the freezing water is exposed to the full action of the cold environment. It is equally plain that any circumstances which facilitate or hinder the formation of the ice sheath affect the course of these various phenomena, but in no way their general nature.

For similar reasons the temperature of freezing water is determined by the extent of the initial overcooling. When this overcooling is little, the quantity of ice which forms as a result is small, and the influence of the freezing mixture thus manifests itself strongly, while, on the other hand, an initial overcooling of more than 1°C. is followed by a rapid formation of a large quantity of ice throughout the water and the freezing mixture ceases to influence sensibly the thermometer.

That the temperature of an ice and water mixture is exceedingly sensitive to the temperature of its surroundings appears, however, more directly from a simple fact which every observer in this field must have noticed; namely, while allowing the ice to melt in the tube of a Beckmann apparatus, the usual practice is to hold it in the air until, with uninterrupted stirring, the ice is about to disappear. A glance at the thermometer in the meantime shows that as the ice has been melting, the thermometer has steadily risen, slowly at first while the quantity of ice is still relatively large, and finally with great rapidity as the ice nears the point of disappearing. We may safely say, when little ice is present, the effect of a cold freezing mixture or the warm air upon a mixture of ice and water is the same in kind and hardly less in degree than when no ice whatever is present.

This high sensitiveness of an ice and water mixture to the temperature of its surroundings is surpassed by that of a partly

frozen solution. The combined action of these disturbing influences has occasioned large errors in the results, and accounts, I think, in no small measure, for many of the great differences between the results of different observers,—differences which not infrequently amount to 40 per cent. I may perhaps venture to suggest one combination of these influences which accounts for the fact that the observed depressions have been commonly too large. Let us take, for example, a $\frac{1}{100}$ normal solution of any substance. To measure the depression of the freezing-point, we must first find the freezing-point of the solvent,—let us suppose water,—and then that of the solution itself. The difference is the desired depression. The freezing-point of the water is most accurately determined by allowing a large degree of overcooling, and thus insuring the formation of a large quantity of ice. As this in no way affects the validity of the observation, and contributes greatly to the ease and certainty in making it, a common practice has been to allow a large degree of overcooling. On the other hand, in taking the freezing-point of the solution, great care is exercised to confine this overcooling within certain narrow limits, so that the corrections which must be applied on account of the change in the concentration may be as small and uniform as possible. What the effect of this method of procedure is, becomes evident from what has already been said in regard to the influence of the freezing mixture, and its relation to the quantity of ice which is allowed to form; the observed freezing-point of the water, owing to the large quantity of ice present, will be approximately the true freezing-point, while the observed freezing-point of the solution will be too *low*, since the quantity of ice is too small to protect the solution from the action of the freezing mixture. The observed depression is thus too large. This error may easily reach a number of thousandths. As the depression for a $\frac{1}{100}$ normal solution must be multiplied by 100 to obtain the *relative* or so-called *molecular depression*, we observe that an error of a thousandth has the magnitude of a *tenth* of a degree on any chosen scale or curve of results. That some such error has played a prominent part in the various deter-

minations seems evident from a most casual glance at the successive results, from the first observations to the most recent. The observed depressions have steadily decreased, in seeming proportion as these errors have been eliminated, exactly as appears in the case of the $\frac{1}{10}$ normal sugar solution already mentioned.

Before entering upon a detailed description of the present method it needs to be observed that the central idea about which it has grown up lies in the fundamental conception of the freezing-point of a liquid. For the sake of clearness, let us confine ourselves to water as a type.

The freezing-point of water may be defined as *that temperature at which ice and water may exist in contact, and no reaction take place between them*. It is thus the temperature of equilibrium in a mixture of ice and water. However objectionable the term "freezing-point of water" may be when used to designate this temperature, the term "melting-point of ice" is certainly no less so, and I have uniformly used the former as less likely to produce confusion. It is to be observed that this state of equilibrium is exceedingly delicate, and that the mixture of ice and water is at its freezing-point only when this equilibrium is maintained. Thus the temperature of an ice and water mixture is higher when the ice is melting than when it is freezing, and the difference, which may be considerable in spite of thorough stirring, increases in proportion as the forces which tend to disturb the equilibrium become greater, and the extent of surface-contact between the ice and water becomes less. If this surface of contact is small, as is the case when little ice is present and massed in relatively large pieces, the temperature of the mixture may be made to vary many tenths of a degree, according as it is exposed to the temperature of the air or that of a freezing mixture. In the former case, the temperature rises much above the freezing-point, since, owing to the little ice-surface exposed, the melting cannot proceed fast enough to use up the large amount of heat which the mixture receives from the air; in the second case, the temperature is, on the contrary, much below the freezing-point, since, for the same reason, the freezing cannot take place fast enough to prevent the overcooling of the water.

The necessity, then, of protecting the liquid whose freezing-point is to be determined from the disturbing influences of outside temperatures is fundamental; and almost from the beginning, even while still using the Beckmann apparatus, I sought to accomplish this by making the freezing-tube much longer, and so remove the solution as far as possible from the air, and by using a secondary freezing mixture with a temperature only a few tenths below the freezing-point of the liquid to be examined, in which the apparatus was placed at the time of making an observation. This practice still remains a prominent feature of the new method.

The Apparatus.

It consists of a thermometer with enclosed scale divided in hundredths of a degree. Its dimensions are such that a hundredth measures about 0.4 mm. This instrument was made according to special order by Herrn R. Fuess, Berlin, and I may take this opportunity of thanking him for the masterly way in which he met all of my requirements. The scale is divided with the greatest precision, and in all my work with it I have observed no deformation of the mercury meniscus, which has given me so much trouble in other instruments of this class, and which appears to indicate an unclean capillary and impure mercury. This thermometer is held firmly by two paraffined corks in a large test-tube (28×3 cm.). One cork is fixed to the thermometer and serves as a stopper to the tube, while the other is placed a little way above the level of the liquid in the tube, and serves to guide the stirrer and maintain the thermometer in a central position. This test-tube has a simple modification which is fundamental to the success of the method. The bottom is bottle-shaped, *i.e.* rounding *inward*, and not outward, as is usually the case with test-tubes. This tube is set in a second test-tube of slightly larger dimensions so as to allow for a millimeter air space between the tubes. They are held together at their upper ends by a short piece of thin-walled rubber tubing of large calibre, while a small rubber band stretched over the inner tube keeps them apart at the bottom. The walls of the tubes should not exceed 1 mm., and the thermometer should reach to within about 2 cm. of the bottom.

The stirrer is a most important part of the apparatus. Of the many forms which I have used, one alone gives complete satisfaction. This is the common "ring" stirrer, with this essential alteration: around the outside of the platinum ring a stripping from a goose feather is bound with platinum wire in such a way that the edge of the feather border just rubs the wall of the tube. This gentle and uniform friction against the wall of the tube, together with the peculiar shape of the bottom of the tube itself, prevents the troublesome massing of the ice between the bulb of the thermometer and the bottom of the tube, and obviates all tendency of the ice to freeze in a sheath. The glass rod of this stirrer runs through openings in the two corks, which act as guides to its motion and so prevent its striking against the bulb of the thermometer. It may be added that in using this stirrer, no tendency has been observed in the ice to mass itself together and float at the surface.

For the sake of clearness and brevity, this double tube with its thermometer and stirrer will be referred to as the *freezing-tube*.

At the time of an observation, this stands up to its neck in a thick mixture of salt water and finely powdered and sifted ice (snow answers the purpose admirably) in such proportions as to have a temperature of $0^{\circ}.30$ C., below the freezing-point of the liquid to be observed. This mixture is contained in a copper vessel 35 cm. high and 6 cm. wide. This is also provided with a ring stirrer and is closed at its mouth with a flat cork through the opening in which the freezing-tube is set. To render the temperature of this mixture as constant as possible, the copper vessel is placed in a thick jacket of felt. This copper cylinder, with its weak freezing mixture and felt jacket will be uniformly referred to as the *protection-bath*. This rests upon the base of an ordinary retort-stand, the vertical rod of which supports the framework of a small electric hammer (*H*) similar to those used in common electric call-bells. The coils of this hammer have a combined resistance of about 10 ohms, and are supplied with the current from two accumulators (in series) of about 2 volts each. The blows of this hammer are thus energetic and are delivered directly upon the upper end of the thermometer. Uniform and

vigorous jarring of the instrument is thus maintained during an observation. In addition, two other baths are employed,—one a salt and ice freezing mixture at -10° C., contained in a glass battery jar about 30 cm. high, which the mixture fills to a depth of about 14 cm., or, more exactly, to such a depth that it reaches up to the level of the solution in the freezing-tube when this is placed in it.

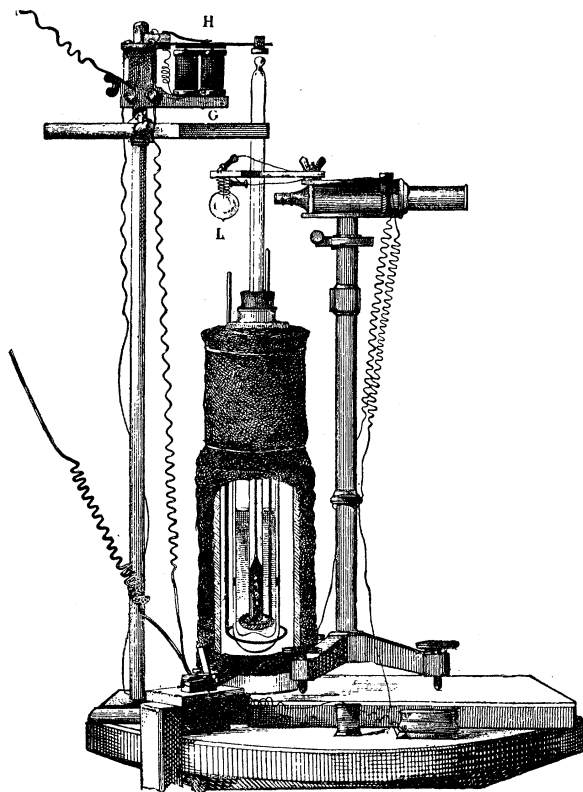


Fig. 1.

This will be known as the *freezing-bath*. The other is merely a mixture of water and coarsely broken ice, in a similar jar, which it fills to such a depth that the freezing-tube may be entirely immersed in it. This is the *melting-bath*. Each of these baths are protected by a heavy wrapping of felt and closed with thick wooden covers, openings in which admit the freezing-tube.

The Reading of the Thermometer.

This is effected with a microscope having a micrometer scale in its eyepiece. The lenses and micrometer are so selected that exactly ten divisions of the micrometer correspond to one scale division of the thermometer. Thus the thousandths of a degree may be directly read and the *ten-thousandths* easily estimated. As the thermometer scale is back of the mercury column, it is obviously impossible to see distinctly the scale and mercury through the microscope at the same time. To read the thermometer, it thus becomes necessary to focus the microscope on the thermometer scale, and bring the micrometer scale into coincidence with it; and then, by a slight sliding backwards of the entire microscope stand, bring the meniscus into focus, in which position the thermometer may be read off on the micrometer scale. To avoid the errors which might possibly arise from this necessary disturbance of the microscope, the stand was made massive and the levelling-screws which supported it rested upon a pane of plate glass which was itself firmly cemented in place. Whatever inconvenience is occasioned by this arrangement is more than compensated for in the fact that, during the interval in which the mercury is coming to its stationary position, no idea may be obtained of what this final position may be, and hence there is no possibility that the observer's bias may affect the result through the unconscious changes in his rate and vigor of stirring, which this bias may induce. To the microscope stand is also attached a small incandescent lamp on the free end of a movable arm, so that it may be readily swung around behind the thermometer, directly in line with the axis of the microscope. The lamp, mercury, and microscope always occupy the same relative position, and errors arising from a variable illumination of the meniscus are avoided. The lamp is only used when the daylight becomes insufficient, and then only during the moment of reading the thermometer. The arrangement of the various parts and the minor details necessary for the few simple adjustments are easily gathered from Fig. 1, taken from a photograph. The figure shows in addition the interior of the protection-bath and freezing-tube.

The Thermometer Corrections.

The thermometer was furnished with a certificate from the German government scientific laboratory at Berlin (Reichsanstalt in Charlottenburg near Berlin), from which the corrections for 0° and -4° —the limits of the scale—were taken. Then by the most careful calibration with a detached mercury column, whose average length in thermometer scale-divisions was $0^{\circ}.9886$, it was found that the interval 0° to 1° was $0^{\circ}.0015$ too great, or instead of being a true degree it was in fact $1^{\circ}.0015$. Owing to the great uniformity in the capillary tube in this region, it was assumed that this error was uniformly distributed over the interval, and thus a correction proportional to the depression had to be added to the observed depression. For the greatest observed depression, namely, $0^{\circ}.7688$ in the case of the $\frac{2}{10}$ - H_2SO_4 solution, this correction amounts evidently to $0^{\circ}.00116$. For depressions of less than $0^{\circ}.1$ this correction almost vanishes.

The corrections for variations in the atmospheric pressure are more considerable. The thermometer with its large bulb and minute capillary is a true aneroid barometer, and has a sensitiveness determined by the thickness of the bulb walls and the relations of its other dimensions. In this case, according to the Berlin certificate, a change of 6 mm. in the barometer corresponds to a change of $0^{\circ}.001$ in the reading of the thermometer. Thus this correction may easily exceed $0^{\circ}.002$. To avoid the possible errors which might arise from applying such a large and partly uncertain correction, care was exercised to make all observations on the very *dilute* solutions immediately before or after the determination of the freezing-point of water.

The Method.

The best idea of the practical details of the method may be obtained from a description of the determination of the freezing-point of water, which must be made daily to eliminate the errors due to changes in the thermometer. Further, to render these changes as little as possible, the thermometer is kept during the entire

period of the observations at about 0° . The freezing-tube is filled to the depth of 10 cm. (about 70 cm^3 .) with distilled water of a high degree of purity, which is then cooled to the freezing-point and the thermometer put in place. The freezing-tube is now placed in the protection-bath, whose temperature is previously reduced to about $-0^{\circ}.32$ by the addition of proper quantities of ice or salt. Here it is allowed to remain twenty minutes to insure the cooling of the entire apparatus to the vicinity of 0° .¹ During this interval the temperature of the protection-bath has generally risen to the required $-0^{\circ}.30$. The freezing-tube is now removed to the "freezing-bath" (-10° C.), where it is kept, with uninterrupted stirring, until the freezing begins. It is then placed in the "melting-bath" (0° C.), and there, by the mere mechanical energy of vigorous stirring, the ice is brought almost to the point of disappearing.² This may be known by observing the thermometer itself. It rises slowly so long as considerable ice remains, and more rapidly as the melting proceeds. When but little ice remains, the rise becomes very rapid. A little experience enables one to judge with great certainty when the ice has been melted to the required degree. In the case of water it is generally when the thermometer has reached $+0^{\circ}.17$.³

At this moment the freezing-tube is placed in the freezing-bath where the temperature rapidly falls, until, after an overcooling of between $0^{\circ}.10$ and $0^{\circ}.20$, freezing begins, and the thermometer rapidly rises. At this instant the freezing-tube is thrust into the protection-bath, the electric hammer set in motion, and after two

¹ This precaution is absolutely necessary, since otherwise the first determinations are too high, owing to the warm walls of the freezing-tube and part of the thermometer above the surface of the liquid. This error may amount to more than $0^{\circ}.004$, and has led some observers *arbitrarily* to reject the first observations. When the source of error is discovered, its elimination becomes easy, and the first observations no longer show any irregularities.

² For obvious reasons, then, the melting of the ice is accomplished in the "melting-bath" instead of in the warm air, since the disturbing influences of the air and hands give rise to very considerable errors.

³ This warming of a liquid and its "ice" above its freezing-point may be denoted by the term *overwarming*; while, on the other hand, the cooling of such a mixture below its freezing-point may be denoted by the term *overcooling*. The fact that this latter term is commonly used to denote the cooling of a liquid alone, below its freezing-point before freezing is induced, can hardly lead to confusion.

minutes, during which the stirring has been vigorously maintained, the thermometer is read. In this interval the mercury uniformly reaches its highest point, and remains stationary so long as the jarring and stirring are maintained. After the stirring and jarring are stopped, the mercury continues perfectly stationary from one to two minutes, and then without exception begins slowly to sink. A jar, however, will cause it to drop suddenly much sooner. To obtain a second reading the freezing-tube is again placed in the melting-bath, and the ice again brought to the point of disappearing, at which moment it is transferred to the freezing-bath, and after freezing has again begun, it is placed as before in the protection-bath, when a second reading is made. This is repeated six to ten times, and the middle of the results taken as the required observation. It must not be forgotten that the stirring is to be maintained continuously, from the time that the freezing-tube comes in the freezing-bath, until the thermometer is to be read. The "strokes" should reach from the bottom of the tube to within a few millimeters of the surface of the liquid. The wooden fork (*G*) may be used as an index to control the height to which the stirrer should be lifted. In case the overcooling exceeds $0^{\circ}.20$, it may be known with certainty that the overwarming in the melting-bath was carried too far, and in the following observations the overwarming should be lessened, say to $0^{\circ}.15$. Should, now, the overcooling fall short of $0^{\circ}.10$, one knows with equal certainty that the overwarming was not carried far enough, and this overwarming must be cautiously increased until the subsequent overcooling is brought within the prescribed limits. This relation between the degree of overwarming in the melting-bath and the overcooling in the freezing-bath is most interesting. The experiments show that the greater the overwarming, the greater will be the following overcooling. Thus, one may effect almost any desired amount of overcooling by properly varying the degree of overwarming. In the case of water, for reasons still unknown to me, the degree of overwarming necessary to confine the overcooling within the prescribed limits ($0^{\circ}.10 - 0^{\circ}.20$) is changeable; sometimes, for example, after having remained for many weeks at $0^{\circ}.15$, it may rise to $0^{\circ}.22$, or perhaps fall as low as $0^{\circ}.08$, and

there remain constant for a longer or shorter time. On the contrary, with a solution, this degree of overwarming is very constant, and by varying it the overcooling may be *controlled* to the hundredth of a degree.¹

It is not without interest to observe that the overwarming necessary to effect the same degree of overcooling in a solution is less than in the case of water, and decreases uniformly as the concentration is increased and with different rates in solutions of different substances.

Thus in a $\frac{1}{10}$ normal solution it is $0^{\circ}.06$ for sugar, while it is only $0^{\circ}.04$ for sulphuric acid. I have not studied this phenomenon systematically enough to warrant me in proposing any explanation of it. To return to the method, we have still to determine in exactly the same way as already described for water, the freezing-points of the solutions,—always remembering that the temperature of the protection-bath must be successively lowered so that for each solution its temperature is $0^{\circ}.30$ lower than the freezing-point of the solution under observation. The difference between this and the freezing-point of water is the observed depression.

It should be added that the various details of the method were developed during a long series of experiments relative to the freezing-point of water alone. In fact, several thousand determinations of the freezing-point of water were made before the various sources of error were so far discovered and suppressed that such a freezing-point could be determined with absolute certainty to the fraction of a thousandth of a degree; and what was more important, that this extreme accuracy could be attained when only the barest traces of ice were present,—a vital condition with solutions to avoid the increase in the concentration which the presence of much ice involves. To indicate to what extent success was attained in this latter respect, a random selection from my note-book may be made.

¹ It is to be noticed that in case ice is once allowed to form in "lumps," as is not infrequently the case with water before the required degree of overwarming is found, all that has been said about the relation between the degree of overwarming and overcooling has no longer any application, and the overcooling can no longer be made to exceed about $0^{\circ}.08$, and is independent of the amount of overwarming. The troublesome lump must be entirely melted by persistent and vigorous stirring in the melting-bath, before further progress may be made.

No.	Overwarming.	Overcooling.	Quantity of ice.	Reading for freezing-point.
1	+ (?)	- 0°.45	Much ice	+ 0°.0274
2	0°.21	0°.07	Little ice	0°.0273
3	0°.22	0°.05	Very little ice	0°.0283
4	0°.23	0°.065	Little ice	0°.0273
5	0°.23	0°.065	Little ice	0°.0270
6	0°.24	0°.070	Little ice	0°.0274
7	0°.34	0°.100	Little ice	0°.0274
8	0°.60	1°.0	Very much ice	0°.0278
9	0°.60	0°.6	Much ice	0°.0273
10	0°.60	0°.9	Very much ice	0°.0278

Middle of 6 observations, little ice present, + 0.02745.

Middle of 4 observations, much ice present, 0.02758.

It thus appears that the disturbing influences of the freezing mixture and air have been so far eliminated that the actual freezing-point of water, and so too that of a solution, may be determined with the greatest certainty even when only a trace of ice is present. *Not until this had been accomplished were any observations on solutions made.*

Although the observations are thus so largely independent of the quantity of ice present, for the sake of a last degree of accuracy, I have always confined the overcooling in the case of water, as is the necessity in the case of solutions, to the limits, 0°.10 to 0°.20. The conditions are thus identical with water and the solutions.

(*To be concluded.*)