micaceous scales, melting-point 51.5°, easily soluble in methyl or ethyl alcohols, in chloroform, carbon bisulphide, benzene, acetone, very difficultly soluble in boiling water, difficultly soluble in cold naphtha or kerosene but easily soluble in these solvents when boiling.

NOTE.—Since writing the above, an article has appeared by Delépine,[1] in which he describes the methyl, ethyl, normal and isopropyl, benzyl and *p*-nitrobenzyl dithiocarbamates, and gives the melting-point of the normal propyl compound as 58°.

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THE FREEZING-POINTS OF DILUTE SOLUTIONS.

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THE difficulties which attend the accurate determination of the freezing-points of dilute solutions, according to the ordinary method of procedure, are well known. A brief perusal of the work of Jones,[2] Loomis,[3] Nernst and Abegg,[4] and Raoult[5] is enough to convince even a hasty reader that besides the common errors of thermometry, and of quantitative work in general, the process is especially complicated by the slowness with which the equilibrium is attained. This complication results in either supercooling or superheating, according as the system is being cooled or warmed. Nernst and Abegg performed a valuable service in calling attention to this danger, and the latter of the two, as well as Loomis and Raoult, carried out a few accurate determinations guarding especially against it. Unfortunately, however, their precautions were so elaborate that few experiments were made, and the difficulty seems to have deterred other workers in the same field.

It is easy to see that another method may be used, a method which overcomes the chief difficulty in a simpler manner; and the

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[1] *Bull. Soc. Chim.*, **3**, 29-30, 48 (1903).

[2] Jones: *Ztschr. phys. Chem.*, 11, 110 and 529; **12**, 623 (1893).

[3] Loomis: *Wied. Ann.*, **51**, 500 (1894); also *Ztschr. phys. Chem.*, **32**, 578 (1900); **37**, 407 (1901).

[4] Nernst and Abegg: *Ztschr. phys. Chem.*, **15**, 681 (1894); also Abegg: *Ibid.*, **20**, 207 (1898).

[5] Raoul: *Compt. Rend.*, **125**, 751 (1897).

present paper has as its object the brief presentation of this simpler method.

As has been said, the prime difficulty is the delay in attaining the true equilibrium. Since this equilibrium is one between two phases, it can be adjusted only on the surface between the two. The speed is therefore proportional to the extent of surface. In order then to avoid the danger of superheating or supercooling, one must have as much ice present as possible, instead of as little as possible. Nothing could be easier than the carrying out of the process under these new conditions. It is true that the solution surrounding the ice must be analyzed, but this may often be done volumetrically or simply by evaporating portions to dryness, and the labor thus involved is vastly less than that involved in the older method.[1]

While the Beckmann apparatus may be thus used with a large excess of ice, fairly accurate results may be obtained more simply as follows. A tall beaker of at least half a liter capacity is filled with finely cracked ice. In many cases a slight impurity present in the ice will not cause a serious error, unless the impurity present is such as to influence the degree of dissociation of the substance to be studied, or chemically to combine with it. It is important in this case, however, that the water at first surrounding the ice should have the same amount of impurity as the ice itself; hence, it is well to use a melted sample of the same material for this purpose. The beaker is surrounded by a protection of wool or cotton several centimeters thick, in order to delay the melting. The temperature of the melting ice is then taken by means of a deeply immersed accurate thermometer, allowing the zero point to become constant. A small portion of the substance to be studied, dissolved in a small volume of the same water, is added and the mixture is stirred with a pipette until the temperature has become approximately constant, and then the pipette is freed from the little cold liquid which it contains and quickly used to draw out its volume of liquid from the immediate neighborhood of the thermometer bulb. The thermometer, which of course should be gently tapped before each reading, remains surprisingly constant during this process, since the slow melting takes place only on the sides and top of the beaker, and the diffusion through the inter-

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[1] Roloff thus analyzed concentrated solutions. *Ztschr. phys. Chem.*, 18, 572 (1895). A. A. Noyes has kindly suggested to me the use of electrical conductivity as a convenient means of analyzing the solution without withdrawing it.

stices of the ice is too slow to have an important effect. If this withdrawn pipetteful measured 10 cc. and is titrated by means of an N/10 solution, the number of cubic centimeters of titrating solution divided by 100 gives at once the approximate equivalent normality of the freezing solution. For the greatest accuracy, of course, allowance should be made for the contraction of the glass and of the solution at the low temperature; but for approximate results these complications are not necessary. By means of this very simple apparatus it is easy to obtain a depression of half a degree within half a per cent. of its true value.

When it is desired to obtain a result accurate to within less than the thousandth of a degree, greater precautions of all kinds must be taken. The thermometer must become seasoned to the low temperature by remaining for hours, or even for days, in melting ice, in order that the slow rise of the zero point due to the slow internal adjustment of the glass may have ceased; the pressure due to the atmosphere and the height of the liquid should be carefully observed, since the bulb is compressible; the thermometer should be carefully calibrated with reference to the international hydrogen scale; the inflow and outflow of heat should be reduced to a minimum, and pure ice must be used. No thermometer can ever give an accurate reading of a temperature which is not constant for many minutes, because the thermometer possesses heat capacity, and its temperature must therefore inevitably lag behind that of its changing environment.[1]

The inflow or outflow of heat may easily be prevented by immersing the experimental vessel in a mixture possessing a temperature, within a few hundredths of a degree, the same as that inside. Such a mixture is very easily made with pounded ice and small portions of any soluble salt, added in solution until an auxiliary thermometer graduated into tenths of a degree indicates a sufficient approach to the temperature desired.[2] An air jacket, such as is used in Beckmann's apparatus, is an advantage, if it can be entirely immersed in this bath, but if it allows the convection of warm air it is rather a disadvantage than an advantage. A Dewar flask might answer well. For results of the greatest accuracy, the vessels should all be large. If these principles are heeded, almost any form of apparatus will yield good results.

[1] This error greatly complicates the correction for cooling in calorimetric experiments, but is usually disregarded.

[2] Nerns d Abegg used constant temperature-baths of this kind (*loc. cit.*).

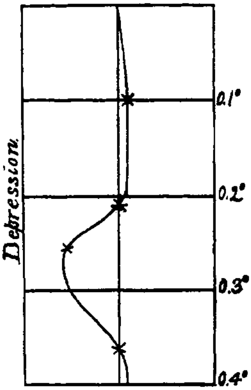
The determinations recorded below were conducted as follows: A Jena flask holding somewhat over a liter, was fitted with a rubber stopper containing three holes. One of these received the thermometer (which was arranged so as to come no nearer than a centimeter to the bottom of the flask), another a short fine funnel-tube for admitting the salt solution, and the third a short, wide glass tube large enough to admit the long stem of a 20 cc. pipette. This pipette was used for withdrawing portions of the solution, its point was always allowed to remain several minutes in the ice, and the liquid remaining in it was always expelled, before it was filled by suction. If the flask has not a wide neck, the stem of the pipette should be slightly bent just below the bulb, otherwise this bulb collides with the projecting thermometer stem.

During an experiment, the flask was somewhat more than half-filled with carefully washed, cracked ice, and at first contained enough ice-water to reach about a centimeter above the top of the thermometer bulb,—enough to render the pieces of ice easily mobile. The flask was then immersed in a large bath of similar cracked ice, and was packed in cotton wool and cloth and left with the thermometer stem projecting for forty-eight hours. In this time, the arbitrary zero point of the thermometer rose from a minimum of 3.805 to 3.820, where it remained during the experiments, so long as there was no large change in the pressure on the bulb. When the zero point had been established, successive portions of potassium chloride solution were added, and the corresponding positions of the mercury thermometer were read after suitable agitation and delay. The contents of the flask were easily mixed by removing it from the ice-bath and giving it a rotary motion. As already suggested, the ice-bath was provided with an essentially isotonic solution by stirring in dilute salt solution until an auxiliary thermometer indicated about the same depression in the outside bath as that exhibited by the accurate thermometer within the flask. Constancy was usually reached within five or six minutes from the introduction of the dissolved substance. The successive change in concentration might be most conveniently effected by adding successive portions of the solution, having the same volumes as that previously removed by the pipette. If the solution were cooled before its introduction, the amount of ice would remain nearly constant, although hardly constant enough to dispense with the analysis of the solution.

The thermometer used in these experiments was one of the Beckmann type, made by F. O. R. Götze in 1895, divided into hundredths of a degree. In order to make certain of the value of its degree, it was compared with thermometer Baudin 15275, which was made and standardized with the greatest precision by the Bureau International des Poids et Mesures for this purpose.[1] The following table and accompanying diagram gives the results of this comparison, which was made after both thermometers had been in ice for a long time. The bath in which they were compared consisted of properly protected and stirred ice fragments immersed in suitably dilute solutions of salt. The readings were made with an accurate Geneva microscope-micrometer.

Beckmann thermometer.	Standard thermometer (corrected).
3.820°	+0.107°
3.817°	+0.104°
3.718°	+0.004°
3.604°	—0.110°
3.559°	—0.148°
3.456°	—0.257°
3.100°	—0.617°

Correction to be applied to Beckmann.
—0.01° ← correction → +0.01°.



This table was verified by measuring lengths of short mercury columns in various places, a process which indicated a narrow place in the bore between 3.60° and 3.50°; but nevertheless this question of calibration is the most serious difficulty in the whole matter. Its import is so great as to make the present paper a preliminary one rather than a final statement of the depressions corresponding to definite solutions. According to the method described there is no difficulty in attaining a great degree of constancy in the thermometer readings; but to determine the true temperature from these readings is a far more difficult problem. The thermometer bulb was not allowed to become warm throughout the series of experiments, for fear of changing the settled structure of the cold glass. The correction for the projecting thread of the thermometer was eliminated by the constancy of the conditions.

Potassium chloride was chosen as the substance to be studied in order to facilitate comparison with the work of other experi-

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[1] See *Proc. Am. Acad.*, **38**, 434 (1902).

menters, who have nearly always used it as one of their substances. The specimen employed was precipitated by hydrochloric acid from a pure solution, and thoroughly dried. The amounts present in the respective solutions were determined by a modified form of Vohard's method, titrating the excess of standard silver nitrate with sulphocyanate, after filtering off the precipitated silver chloride, which otherwise disturbs the reaction by its solubility. The solutions were standardized in a similar way with pure fused potassium chloride. Since the solutions were N/5, and the instruments were accurate,[1] the reading for the silver nitrate divided by 100 gives at once the normality of the freezing solutions.

Below is given a table of data and results which are enough to indicate the satisfactory constancy of the readings. An hour elapsed between the first and third experiments, as well as between the eighth and tenth. The atmospheric and hydrostatic pressure on the thermometer bulb were essentially constant.

No. of experiment.	Concentration of solution (normal standard).	Observed depression.	Corrected depression.	Molar depression.
1	0.1256	0.433°		
2	0.1261	0.433°	0.433°	3.42
3	0.1258	0.432°		
	0.1258	0.433°		
4	0.0944	0.330°	0.328°	3.48
5	0.0944	0.330°		
	0.0944	0.330°		
6	0.0386	0.136°	0.137°	3.52
7	0.0388	0.136°		
	0.0387	0.136°		
8	0.0311	0.112°		
9	0.0309	0.111°	0.112°	3.59
10	0.0307	0.111°		
	0.0309	0.111°		

These results are near those of other experimenters, who needed much more labor than that expended in the present case. For example, Abegg found, for the concentrations 0.0469 and 0.0354, molecular depressions of 3.47 and 3.50 respectively, results but slightly lower than those given above.

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[1] The most important burette, that used for the silver nitrate, was unusually fine in bore and in graduation, having been marked only after careful preliminary calibration by the author.

While the study of a single electrolyte furnishes too meager a basis for extended theoretical conclusions, especially when the possible inaccuracy of the thermometer introduces a wide range of possible error, it may not be out of place to compare these molar depressions with those calculated from the conductivity. In order to make this comparison, it would be necessary to know the average molar depression caused by a non-electrolyte with an equal degree of accuracy. For the present the value, 186° taken from the average of many previous investigations, is sufficiently accurate. On this basis the degrees of dissociation of the four solutions whose depressions are recorded above are easily calculated as 0.84, 0.87, 0.89, and 0.93 respectively.

The most accurate data concerning the electrolytic conductivity of aqueous solutions are perhaps those of Kohlrausch and Maltby,[1] but unfortunately these do not apply in the present case, since the temperature used was 18°, not 0°. Next to these comes the work of Whetham,[2] who worked with very great care at the required temperature. He found the equivalent conductivity of potassium chloride to be 75.2 when diluted to 33 liters per mol, and to attain a maximum of 80.7 when diluted to 2000 liters. This leads to the value 0.93 for the degree of dissociation of the former solution, a solution which corresponds exactly to the last one named in the preceding paragraph.

The agreement between these two results (0.93 according to both the depression of the freezing-point and the electrical conductivity) is closer than would be expected from the possible errors of the results compared. So far as it goes, therefore, it is satisfactory to the adherent of the modern theory of solution; but many more comparable results with other substances should be obtained before the subject is allowed to drop.

The constancy of the thermometric readings obtained in this way from mixtures of ice with dilute solutions suggests the availability of such mixtures as a means of calibrating thermometers below the freezing-point. If an accurate curve were plotted, comparing the normality of the solution with the actual depression of the freezing-point, all that would be necessary in order to determine the error of a given point in a thermometer would be to place

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[1] *Wiss. Abh. phys. tech. Reichsanstalt*, **3**, 157 (1900).

[2] *Ztschr. phys. Chem.*, **33**, 344 (1900). The work of Déguisne at 2° indicates essentially the same value as that of Whetham. (Inaug. Diss., Strassburg, 1895.) Unfortunately Déguisne has not presented his data, but has concealed them in quadratic equations.

it in pure ice and then to stir into the ice an increasing amount of the standard solute until the desired point on the thermometer was reached and maintained. An analysis of the commingled solution, with the help of the curve, would then at once give the temperature which the thermometer ought to have recorded, and hence the error of the given point on the thermometer. Hydrochloric acid would perhaps be the best substance for this purpose, since it is easily prepared in a pure state and may be determined volumetrically in a variety of ways.

Such a means of calibrating thermometers would be theoretically as exact as any other, for according to the phase rule, with two components, four conditions must be fixed in order to fix a point. In the present case, the four conditions would be two phases, pressure, and the concentration of the dissolved substance. The experience gained in the trials recorded above seems to indicate that this method is practically feasible as well as theoretically sound, and in the near future more accurate data concerning the true course of some such curve will be obtained here.

Besides this, it is my object to study with the help of the new method a number of electrolytes and non-electrolytes with all possible accuracy, using a platinum resistance thermometer.

SUMMARY.

It is pointed out that in the presence of much ice the equilibrium concerned in the freezing-point of solutions is obtained with great speed and convenience. Several forms of apparatus are suggested for this determination, and results are given, showing that the plan is capable of practical execution. The exactness seems to be so great that the method may be of use in standardizing thermometers. The few data found are consistent with the hypothesis of ionization.

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DERIVATIVES OF NEW COMPLEX INORGANIC ACIDS.[1]

BY ALLEN ROGERS.

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THE splendid research work upon complex inorganic acids, by Dr. Wolcott Gibbs, has brought to view numerous classes of most

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[1] From the author's thesis for the Ph.D. degree presented in June, 1902.