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TRANSACTIONS.

I.—*A New Method of Determining the Freezing points of very Dilute Solutions.*

By PERCY BENEDICT LEWIS.

Introductory Note by M. Wildermann.—Percy Benedict Lewis, who died on the 29th of March, 1894, at the early age of 23, had been for some time engaged in the investigation of a subject of importance from the point of view of physics, of practical value in organic chemistry, and of great importance in physical chemistry, namely, the best means of determining the freezing points of very dilute solutions. At his request, I have thoroughly tested and verified his method, and the results of his work are communicated in the following paper. Although valuable investigations on the same subject have been already made by Jones (*Zeit. physik. Chem.*, **11**, 110) and by Loomis (*Wied., Ann.*, **51**) Lewis' work is distinguished by greater experimental accuracy, and by the minute and judicious care with which the conditions necessary to secure the best possible results are investigated.

It was his wish that his thanks should be given to the authorities of Christ Church, and to Mr. A. G. Vernon Harcourt, for placing the resources of their laboratory at his disposal.

I have applied the method described to the more exact investigation of Arrhenius' law as to the connection between the depression of the freezing point and the electrical conductivity; of Van't Hoff's constant; and of Ostwald's law of dilution, forming, as they do, the foundation of modern theories of solution. For this purpose very dilute, aqueous solutions of phosphoric acid, cane sugar, phenol, urea, ethyl alcohol, dichloroacetic acid, trichloroacetic acid, and orthonitrobenzoic acid were

chosen; the agreement between the theory and the experimental results surpassing my expectations. The results thus far obtained will form the subject of a separate communication, and I intend to continue the investigation, and also to examine by the freezing point method cases in which the dissociation values for a mixture are affected by the presence of a common ion.—[M. W.]

The Method Employed.

The thermometer A, Fig. 1, used for delicate measurements was of Beckmann's form, and was graduated into thousandths of a degree; the mercury reservoir was 117 mm. long and about 20 mm. in diameter, and the expansion at the top of the capillary tube, *i*, was large enough for the thermometer to be used over a range of temperature from -20° to 30° . The whole scale, whose length was 220 mm., corresponded to 0.58° C. The thermometer was of Jena glass, and was made by the same instrument-maker (Götze, of Leipzig) as the one used by Jones. This thermometer was fixed in a very thick cork *k*, and by its side in the same cork, was a second Beckmann thermometer B, divided into 100ths of a degree, also made by Götze. A piece, *b*, was cut out of the cork (see Fig. 2), after a hole *a*, of a suitable size, had been bored, and the large thermometer with the india-rubber ring *c'* was placed in the hole which was closed again with the piece *b*. The thermometer was thus almost rigidly fixed, so that when the cork was gently tapped it could move only slightly, whilst the mercury in the upper reservoir was but just moved. The small thermometer was merely put through a hole *d*, in the cork, the india-rubber ring *c''* being fastened on it. The vessel which held the solution under investigation was a beaker D, of about 1600 c.c. capacity, and the quantity of solution used for each observation was 1250 c.c. The beaker, which stood in a zinc vessel E to serve as an air-chamber, rested on a mat of thick felt, *l*, which was encased in gutta-percha tissue to keep it dry; the beaker was covered with a glass plate through which the thermometers and a stirrer passed without friction. Between the sides of the beaker and those of the zinc vessel was an air space about 40 mm. wide; the zinc vessel had a cover of the same material in which a round hole was cut, and in this the thick cork with the thermometers was fixed; the stem of the stirrer, C, passed through a third hole, *n*, in the cork.

The stirring of the liquid was effected by means of a double porcelain stirrer, *c*, Figs. 1 and 3, consisting of two porcelain plates 100 mm. in diameter, placed parallel to one another at a distance of 15 mm., and fastened together by four small porcelain rods, and the large rod *a*. In the middle of each of the porcelain plates was an oval hole, *i* (36 mm. broad, and 51 mm. long), so that they could easily pass over both

thermometers, and the liquid could be easily and thoroughly stirred without disturbing the thermometers. There were besides eight

circular holes in each plate, so arranged that the holes in the upper one were not immediately over those in the lower; by this arrange-

ment, side currents were caused to flow in all directions through the liquid, so that even when the stirrer was moved but gently at the bottom of the beaker, the liquid was very perceptibly mixed even in the top-most layers. On moving the stirrer up and down, currents are sent in opposite directions. Stirrers of various materials (gutta-percha, heavily gilt copper, &c.) were tried, but the best results were obtained with the porcelain stirrer, especially when dealing with acids and alkalis. We did not try a platinum stirrer, which would have been not only heavy but costly. This porcelain stirrer was specially made for the purpose; but stirrers of the same kind can now be obtained at Messrs. Townson and Mercer's, London.

It was found to be absolutely necessary, not only that the thermometers should be kept continuously at 0° for some months before they were in a condition fit for using in these experiments, but also during the time which elapsed between one experiment and another; for if the thermometer be allowed to remain for several hours at the ordinary temperature of the room, it must be kept at 0° for two or three days before it can be used for another experiment. In order to provide for this, a second zinc vessel, similar to that which held the liquids under observation, was placed in the ice bath, and in it was a beaker containing pure distilled water, partly frozen, and in this the thermometers were kept immersed during the intervals between the experiments; the temperature of this distilled water showed variations of only some hundredths of a degree above or below 0° . When actually experimenting, it is necessary to keep the thermometer for as short a time as possible in the liquid which is cooled below its freezing point; that is to say, that the freezing had to be determined as soon as possible by the introduction of a little fragment of ice. Moreover the mercury was never allowed to enter far into the upper reservoir, so as to insure that it should always recede completely on cooling. The temperature of the cooled solution was always read off directly on the smaller thermometer alone, the scale of which was divided into hundredths of a degree.

Both the zinc vessels, holding respectively the experimental liquid and distilled water, stood in a large zinc vessel, *m*, serving as an ice bath, and this again in a still larger vessel, *n*, with an air space of several centimetres between them; the outer vessel, moreover, stood upon a thick mat of felt, and was also covered with a thick coating of felt. Both the tops of the ice-bath and of the outer vessel were covered with pieces of thick asbestos cardboard, *r r*, up to the central cork.

It will be seen that the object of the whole arrangement is to maintain the temperature of the ice bath for a length of time as con-

stant as possible; the temperature of the bath being adjusted in such a way that the solution to be cooled down is only exposed to exceedingly slow changes of temperature. Direct experiments with a freezing mixture at -2° to -2.3° in the bath, and a temperature of $12-18^{\circ}$ in the room, proved that the rate of cooling, when the stirrer is but occasionally and slightly moved, is from 0.013° to 0.017° in five minutes, and when the stirrer is moved continuously but quietly, from 0.0085° to 0.01° . If ice has been already formed in the solution, and is thoroughly mixed with it, the fresh ice, which is formed during the 15–20 minutes of the experiment, will make the solution only about 0.03 or 0.04 per cent. more concentrated—a difference which is immaterial. If, however, the ice cannot be thoroughly mixed with the solution, as happens when the bath is too cold, then even if the temperature of the bath has only sunk to -2.3° , the liquid itself continually cools down, and a constant temperature can no longer be obtained. The above observations and also the experiments made by Loomis (*Ann. Phys. Chem.*, **51**, 519) show that a constant temperature in a mass of liquid may be obtained with greater ease and certainty by means of an air bath than with a liquid bath; for the latter, even if it is only -0.3° below the freezing temperature of the solution, always affects the vessel of liquid placed in it with comparative rapidity.

It was found that if the temperature of the air was from 12° to 18° , the best results were obtained when the temperature of the cooling bath was -1.8° to -2° , but if the temperature of the room rose to 24° , the bath had to be cooled to -2.1° or -2.2° .

The cooling bath is prepared by placing a considerable number of small pieces of ice in water, stirring well, and then adding salt in small quantities until the necessary temperature is obtained; if too much salt be added, this can be corrected by diluting with water; before using the mixture, it should be well stirred until the temperature is the same at different levels. Under these conditions, the variation of temperature in the mixture in the course of two hours will be less than 0.1° . After the bath is in working order, the liquid to be investigated must be cooled below its freezing point at least 0.55° or 0.6° in order that enough ice may be formed on freezing; in a good determination, this super-cooling should lie between -0.7° and -1° , and should be maintained as constant as possible throughout a whole series of determinations, both with water and with the aqueous solutions.

When the above conditions are observed, a satisfactory determination of the freezing point can be obtained; the reading of the thermometer remains constant for 10 to 15 minutes after it has reached

its maximum, and the mercury in the thermometer has ample time to acquire the temperature of the liquid.*

It may be further noted that the choice of a beaker for the experiment is of importance; it should be as cylindrical as possible throughout its whole length; if the diameter of the stirrer is 100 mm., the diameter of the beaker should be between 107.5 and 109 mm. If it be as little as 106 mm., it is impossible to get a good determination with certain concentrations of solution, as the ice formed cannot pass freely between the stirring rod and the walls of the beaker, but is pressed into compact masses against the beaker and removed from the solution almost completely, or else it forms a compact mass on the bottom of the beaker. If, on the other hand, the beaker be wider than 109 mm., it becomes difficult to stir the liquid effectually. Before starting on a series of determinations, this point should be carefully ascertained by direct experiment with a few selected beakers.

It is impossible to insist too strongly that neither the constancy of the thermometer reading in one experiment nor the agreement of the thermometer readings in successive experiments, affords in itself a sufficient guarantee that a correct determination of the freezing point has been obtained. It is absolutely necessary to examine the solution at the end of the experiment, and to make sure that it contains a sufficient quantity of finely-divided ice, uniformly distributed, and that there is no accumulation of compact ice either round the thermometer or on the walls of the beaker. This precaution is absolutely necessary, but if the operation be carefully performed, and all the precau-

* These conditions also bring about a convenient formation of ice in the form of fine flakes distributed uniformly throughout the whole liquid. A curious difference in the mode of separation of ice under different circumstances may here be noticed. In solutions which show a depression of freezing point of about 0.02° , ice almost always forms throughout the liquid, but that is not the case with pure water. With the latter, the ice forms in fine crystals throughout the liquid, but at once aggregates, forming a cap round the bulbs of the thermometers, and settling in a thick layer round the stirrer.

There is no doubt that the correct freezing point can only be obtained when ice is formed in fine flakes throughout the solution; and it is equally certain that it cannot when an ice-cap forms round the bulb of the thermometer. Comparative experiments, in which the formation of an ice-cap was sometimes allowed to take place, and sometimes prevented, gave uniformly lower readings for the freezing point in the former case. From this it will be seen that the agreement of readings in successive experiments is no guarantee that the freezing point observed is the true one. There can be no doubt that a correction must be applied in the determination of the freezing point of water for a constant error due to the formation of an ice-cap round the bulb of the thermometer: the accurate determination of this correction is a matter of great importance, and will form the subject of a later communication.—M. W.

tions indicated be observed, an unsuccessful experiment will be of rare occurrence.

The Two Thermometers (0.01° and 0.001°).

In stating the conditions under which an accurate determination of the freezing point of a solution is possible, it has been assumed that a thermometer divided to $1/1000^{\circ}$ C. has been used, because with such a thermometer more delicate and accurate determinations of freezing points can be made than with a thermometer divided only to $1/100^{\circ}$ C. Nevertheless, all the experimental precautions described above should be taken in order to obtain a good determination with the $1/100^{\circ}$ thermometer; by the use of the more delicate thermometer, the conditions necessary for a successful determination have been more definitely ascertained and controlled. Kohlrausch (*Ann. Phys. Chem.*, **51**, 527—528) has recently adduced several *à priori* objections to the use of the more delicate instrument. The best way to judge of the force of his objections is by simultaneous observations with the two thermometers. The description of the precautions required in the execution of the experiment makes it clear to what extent the doubts of Kohlrausch and of Dieterici (*Ann. Phys. Chem.*, **50**, 78) are justified.

One difficult question remains to be answered, namely, what is the effect of a variation in the barometric pressure on the reading of the thermometer? Any variation of the actual freezing temperature due to variation of barometric pressure may be neglected.

Before considering this point, however, a question which has been recently brought forward by Kohlrausch must be dealt with. Kohlrausch writes in reference to the freezing point determinations made by H. C. Jones:—"If the glass of the bulb of the $1/1000^{\circ}$ thermometer were very thin, the following difficulty must be considered. The thermometer was allowed to remain in the solution even when it was cooled 1.2° below the freezing point. At the moment of solidification the mercury rose in the stem by about 20 cm., so that the increase in the length of the mercury column would cause an increase of pressure of about a quarter of an atmosphere on the inside of the bulb. It is possible that the consequent expansion due to the elasticity of the glass may cause a gradual variation in the reading." Kohlrausch proposes to settle this question by simply inclining the thermometer; but this method would be inapplicable for large variations of pressure, because it is only possible to obtain a definite freezing temperature under very definite conditions and with very special precautions, and in this case, where the effect to be measured is necessarily very small, no conclusions could be drawn from a rough experiment. The thickness of the cork in the apparatus above de-

scribed made it possible to incline the thermometer to an extent corresponding to a difference of pressure of 10 to 15 mm., but no change in the reading of the thermometer could be detected. Further information on this point was obtained in the course of the investigation of the effect of different degrees of super-cooling on the readings in the case of water. As no variations of concentration can occur in the case of water, the observations on this point can be extended over wider limits than in the case of solutions (*e.g.*, 0.6° to 1.2° or 1.3°). Now, if the wall of the bulb be thin enough for the elastic effect to become obvious, the observed freezing point would depend on the extent of the preceding super-cooling.* In the following observations the thermometer was left for as short a time as possible in the super-cooled liquid.

Super-cooling read off on the $1/100^{\circ}$ thermometer.	Freezing point of water read on the $1/1000^{\circ}$ thermometer.
0.497°	0.4875°
0.607	0.4875
0.647	0.4873
0.827	0.4873

These results seem to show that the thickness of the glass bulb was sufficient to confine within the customary limits of experimental error (one, two, or three thousandth of a degree) the variations due to the two causes mentioned above, namely, the elastic effect caused by the internal pressure, which was applied only for a very short time, and the contraction due to variations in the amount of super-cooling of the liquid examined.

But the case is different if the excess of pressure and the lowering of temperature be allowed to persist for any length of time, in which case the effect on both thermometers was observable. If the $1/1000^{\circ}$ thermometer be kept at the temperature of the room for some hours, and afterwards used for a series of freezing point determinations under constant or almost constant atmospheric pressure, the observed freezing point shows a continuous rise in consequence of the gradual contraction of the glass bulb. A similar rise is observed when the atmospheric pressure is gradually increased, so as to diminish the volume of the mercury bulb. In the following experiments, which were performed at various times, the water used was not always the same in each pair of corresponding observations, but the mercury was not allowed to rise into the upper reservoir during any pair of experiments.

* The capillary tube from 0.58° to the mercury reservoir is about 330 mm. and the difference in the pressure will be about 150 mm.

Atmospheric pressure.	Difference.	Reading of 1/1000° thermometer.	Difference.
749·5 mm. 759·3 „	} + 9·8 mm. {	0·4855(6) 0·4819	} + 0·0036°
750·2 mm. 756·5 „	} + 6·3 mm. {	0·4832 0·4848	} + 0·0016°
752·6 mm. 761·3 „	} + 8·7 mm. {	0·4839(40) 0·4865	} + 0·0026°
752·6 mm. 758·8 „	} + 6·2 mm. {	0·4840 0·4859	} + 0·0019°
749·0 mm. 758·5 „	} + 9·2 mm. {	0·4830(1) 0·4857(8)	} + 0·0027(8)

From these observations, it appears that an increase of 1 mm. in the atmospheric pressure acting for some time causes a rise of about 0·0003° in the freezing point as observed on the 1/1000° thermometer. The difference between observations made at the same time with the 1/100° thermometer amounted to 0·004° for a difference of pressure of +9·8 mm., 0·002° for a difference of +6·3 mm. These differences in the readings of the small thermometer include the errors of observation, which may amount to 0·001°, to 0·002° if the pressure remains unaltered.

It was found that the use of a microscope with micrometer scale, such that 10 divisions of the scale corresponded to one division of the thermometer scale, was of very little use, as it was impossible to read the thermometer scale and the mercury meniscus at the same time. It is still uncertain what correction should be applied for an alteration of 1 mm. in atmospheric pressure if the change of pressure affects the mercury bulb for one or two hours only; the question can only be decided by experiments made when the barometric pressure happens to change by several millimetres in the course of a few hours. We might expect the correction to be smaller, as the contraction of the glass vessel due to increase of pressure probably takes place very slowly, just as the apparent rise of temperature in a thermometer placed in a cold mixture of constant temperature takes place very slowly and only reaches a maximum after two or three days.

The best plan of obviating this possible source of error is doubtless to rely only on experiments made under favourable atmospheric conditions. The variation of the barometer pressure in the course of 8 or 10 hours is often under 1 mm. and seldom amounts to more than 2 mm. The exceptional days on which the variations are as much as

3 or 4 mm. are unsuitable for delicate freezing-point determinations, however accurately the corrections required may be examined and studied. The only possible remedy in such a case is to make two or three control determinations of the freezing point of pure water in the course of the day; or only to make determinations of freezing points of the more concentrated solutions.

As to the degree of accuracy attained in these experiments, it may be stated that the variations of the thermometer readings amount to one or two, seldom to three ten-thousandths of a degree. In the case of the small thermometer, the differences amount to one or two thousandths of a degree under similar circumstances. It is thus obvious that under ordinary circumstances, when the barometric variation is not excessive, it is possible to make much more accurate and delicate readings with the $1/1000^{\circ}$ thermometer than with the $1/100^{\circ}$ thermometer.

Manipulation.

A flask with 1250 c.c. of water is left standing during the night in the zinc vessel which is surrounded by ice, so that on the following morning water at about 0° may be obtained for the experiment. The stirrer should be left all night in the beaker filled with distilled water so as to cleanse it; as the experiment is carried on with dilute solutions, this is quite sufficient unless the beaker is a new one, in which case it should be washed first with sulphuric acid, then with water, and finally steamed.

The first step is to make the ice bath of the right temperature (-1.8° to -2°). The beaker and stirrer are then dried with good filtering paper, 1250 c.c. of water of about 0° is poured into the beaker, and the stirrer placed in the beaker together with a thermometer divided to tenths of a degree. The beaker is then placed in the ice bath and the liquid stirred thoroughly now and then with the stirrer; as soon as the liquid acquires a temperature of $+0.2^{\circ}$, the greatest care must be observed in further cooling; the beaker must remain at rest and the liquid be stirred now and then very gently. In this operation the stirrer must never be taken out of the liquid neither must it be allowed to rub against the sides of the beaker, or freezing occurs before the temperature reaches -1.2° or -1.3° . When the temperature of -1.2° is reached, the $1/10^{\circ}$ thermometer is laid aside and placed in a beaker with distilled water. The outside of the beaker is now dried with a cloth as quickly and gently as possible, and it is placed on a dry mat of felt in the air chamber, taking care that it is in the right position so that the thermometers may be in their proper places with regard to the stirrer. The zinc vessel must then be closed with its asbestos cover, and the stirrer taken out of the liquid for 30 or 40 seconds, so that

no ice flakes may form on it; this precaution is especially necessary if the solutions are very dilute. The thick cork with the delicate thermometer is then fixed in its place in the zinc lid.

The stirrer must be so placed as to move freely up and down without touching the thermometers, and the thermometers must be vertical; after some practice, these adjustments take but little time. Now the stirring should go on very quietly, without interruption, and after a very short interval a reading of the $1/100^{\circ}$ thermometer should be taken to ascertain the amount of super-cooling. A little fragment of ice is then brought in by laying it against the stem of the stirrer, and the freezing of the liquid, already cooled below its freezing point, is thus determined. As a rule, freezing begins very soon; it must not be too long delayed or ice will be formed on the thermometer and stirrer, as also in solutions which give a depression of about 0.02° . During the rise of temperature, the stirrer must be quietly and uninterruptedly moved by one hand, while with the other, the thick cork is tapped very gently, so gently that there is no rattling of the opal-glass scale of the thermometer, and that only a slight movement of the mercury in the reservoir is perceptible. This must be done in order that the mercury thread may attain its maximum height as quickly as possible. If this continual tapping be omitted, the thread may remain at rest far below its proper position, and then rise suddenly owing to some accidental shake as the stirrer is moved. Any stronger tapping, for example, with a knife on the head of the thermometer, or with the stirrer on the bulb, must be avoided, as this not infrequently causes a break in the thread of mercury at the neck of the bulb. The chief difficulty is to bring about and observe the rise of the mercury through the last thousandth and ten thousandth of a degree. The maximum has been attained when the mercury thread remains in a fixed position for more than a minute in spite of tapping; this usually occurs about five minutes after the time when the rise of temperature was first observed. The temperature must remain constant for 8 to 10 minutes after the maximum has been reached; during this period, about ten readings may be made, and it is sufficient if the stirrer be used several times without tapping, and the cork tapped several times without stirring, before a reading is taken. In the case of the smaller thermometer, the upper end can be gently tapped with a small knife, without danger of the formation of a vacuum space at the neck of the bulb, or of the separation of the thread of mercury. In reading the thermometer a good ordinary lens may be used; this is more convenient than, and, for a practised eye, quite as serviceable as a microscope with a micrometer scale. Individual readings are of course subject to small variations, amounting to one or two or sometimes three ten-thousandths of a degree (see Tables, pp. 13, 14).

After the readings have been made, the condition of the solution must be carefully examined. The cork with the thermometers must be taken off and the beaker removed to make sure that no cap of ice has formed upon the bulb of the thermometer, or any coating of ice upon the stirrer or beaker, but that the ice consists of fine flakes* and is present in the liquid in sufficient quantity. The greater part of the ice is then melted by placing the beaker in a vessel of water of the temperature of the room, and a certain number of c.c. of the solution is drawn off and the same volume of a solution of known strength is added. The more concentrated solution thus obtained must be warmed at first to $+0.7^{\circ}$ to $+1^{\circ}$, and the beaker containing it is then again brought into the ice bath.

From this point a fresh experiment begins, and must be made with the same precautions as the preceding one. In every experiment, the temperature of the bath and of the room, the height of the barometer, and the condition of the ice round the thermometer must be noted.

Corrections.

After the freezing point of pure water or of the solution under examination has been determined, a definite number of c.c. are removed by means of a pipette, and replaced by the same number of c.c. of a solution of known strength; the strength of the resulting solution is then calculated before the freezing point is determined. In calculating the molecular lowering of the freezing point, we have to consider not the degree of concentration thus calculated, but that which actually exists at the freezing temperature after some of the solvent has separated in the form of ice. It is assumed throughout that the dissolved substance does not separate in the solid form along with the solvent. The calculation of the actual strength at the freezing point is very simple; if the solution be cooled to a temperature n° below the freezing point, then it must rise again through n° , and, in doing this, 1 kilo. of the solution will absorb heat equivalent to n calories; now this heat must be obtained at the expense of that which is developed in the formation of ice, and the amount of ice formed will therefore depend on it. The latent heat of fusion of 1 kilo. of ice is 80 cal., hence $n/80$ kilos. of ice must separate, or, in other words, $n \times 100/80$ per cent. of the solvent must solidify. The strength corresponding to an observed lowering of the freezing point must therefore be greater by $100 \div (100 - 100n/80)$ than before solidification took place. As we have only to deal with a correction applicable to very dilute solutions, we can make the approximation that the specific

* For formation of ice on the thermometer and stirrer, especially in determining the freezing points of water and of very dilute aqueous solutions, see footnote, p. 6.

THE FREEZING POINTS OF VERY DILUTE SOLUTIONS. 13

Potassium Chloride Solutions, 1.214 normal.

Condition of experiments.	Readings of 1/1000° ther- mometer.	Time. Hours. mins.	Readings of 1/100° ther- mometer.
1. Distilled water. Bath -1.8° . Barometer 757 mm. § Temp. of the room 13.5° .	0.4873° 0.4874 0.4873 0.4873(4)	12 18 12 23 12 28 10 minutes	*5.50 6.147 6.147 6.147
1. Distilled water. Bath -1.8° . Barometer 757 mm. § Temp. of the room 13.7° .	0.4872 0.4873 0.4872 0.4872(3)	1 3 1 18 15 minutes	*5.32 6.147(6) 6.147(6)
2. { -10 c.c., +10 c.c. KCl sol. (sol. = 0.009711 mol. norm.) Bath -1.8° . Barometer 756.8 mm. § Temp. of the room 13.8° . ‡	0.4520 0.4521 0.4522 0.4520 0.4521	1 56 2 1 2 7 2 10 14 minutes	*5.245
2. Bath -1.8° to -2° . Barometer 757 mm. Temp. of the room 14° . § ‡	0.4525 0.4524 0.4523 0.4524 0.4524	5 18 5 27 9 minutes	*5.20
3. { -10 c.c., +10 c.c. KCl sol. (sol. = 0.01934 mol. norm.) Bath -1.8° to -2° . † Barometer 757 mm. ‡ Temp. of the room 14° .	0.4197 0.4196 0.4196 0.4196 0.4196	6 10 6 14 6 16 6 20 10 minutes	*5.19
3'. Bath -1.8 to -2° . Barometer 757 mm. Temp. of the room 14° . † ‡	0.4197 0.4196 0.4197 0.4198 0.4197 0.4197 0.4197	7 0 7 5 7 10 7 15 15 minutes	*5.257

For *, †, ‡, §, see footnotes on next page.

Potassium Chloride Solutions, 1.214 normal—(continued).

Condition of experiments.	Readings of 1/1000° ther- mometer.	Time. Hours. mins.	Readings of 1/100° ther- mometer.
4. { -20 c.c., +20 c.c. KCl sol. (sol. = 0.03845 mol. norm.) Bath -1.8 to -2°. Barometer 756.8 mm. † Temp. of the room 14°. ‡	0.3517 0.3516 0.3517 0.3516 0.3517 0.3516(7)	8 3 8 5 8 6 8 9 8 10 7 minutes	*5.20
1''' Distilled water. Bath -1.8°. § Barometer 757 mm. Temp. of the room 14°.	0.4876 0.4877 0.4877 0.4876 0.4877 0.4876(7)	5 20 5 23 5 25 5 28 5 30 10 minutes	*5.34
4'. { -10 c.c., +10 c.c.; -10 c.c. +10 c.c.; -20 c.c. { +20 c.c. KCl sol. (sol. 0.03845 mol. norm.) † Bath -1.8°. ‡ Barometer 757 (756.8) mm. Temp. of the room 14°.	0.3527 0.3527 0.3526 0.3527 0.3526 0.3526 0.3526(7)	6 13 6 14 6 15 6 18 6 20 7 minutes	*5.22
5. { -40 c.c., +40 c.c. KCl. (sol. 0.076064 mol. norm.) Bath -1.8°. Barometer 757 mm. Temp. of the room 14°. † ‡	0.2223 0.2222 0.2221 0.2221 0.2220 0.2220 0.2221 0.2221	7 0 7 2 7 5 7 8 8 minutes	*5.40
5'. Bath -1.8°. Barometer 757 mm. Temp. of the room 14.3°. † ‡	0.2218 0.2217 0.2219 0.2218 0.2217 0.2217	8 0 8 2 8 4 8 7 8 10 10 minutes	*5.23

* Reading of small thermometer before the freezing of the solution.

† No formation of ice on thermometer or stirrer.

‡ Sufficient formation of ice. § Ice formed on the thermometer and stirrer.

heat and the latent heat of fusion of the dilute solution are the same as those of pure water. This mode of correcting is doubtless the safest and the most convenient; certainly it is to be preferred to the correction obtained by removing the ice and determining the density of the residual solution. In the experiments made by Loomis, who used a liquid bath and small quantities of solution, it is possible that the rapid cooling caused more ice to be formed than the theory indicates; but this cannot be the case in the above-mentioned experiments, where an air bath was used, and large quantities of solution were employed. As the total correction is small, the error introduced in making the correction as described can only be very minute.

For the corrections of reading for variations of atmospheric pressure, see p. 9.

For the corrections of the freezing point of water and of aqueous solutions in experiments in which the thermometer bulb was surrounded by a film of ice, see footnote, p. 6.

Before giving some of the results obtained, to serve as an illustration of the method, the mode of *calibrating* the more delicate thermometer may be described.

The operation was performed by reading the positions l and r of the two ends of a detached thread of mercury on the scale. A thread suitable for this purpose was obtained by heating the thermometer to some degrees above the temperature of the room, so that a sufficient quantity of mercury passed over into the lower part of the upper reservoir; on allowing the thermometer to cool, the mercury retreated into the bulb; a small quantity of mercury was then made to pass from the upper reservoir into the capillary in the same way as that commonly used in adjusting a Beckmann thermometer.

The small thermometer was an unusually fine instrument, tested in the Berlin Observatory, and found to be quite correct; it was used by Götze as a standard of comparison for his other thermometers.

In the following table

α = concentration of the solution taken in gram molecule per litre.

a = depression of the freezing point.

b = cooling of the liquid below the freezing point.

c = percentage weight of solvent (water), which crystallises out when the solution is super-cooled = b .

d = concentration actually subsisting after the separation of the quantity of solvent stated under c .

α_1 = corrected value of α .

β = molecular depression = $\frac{a}{\alpha_1}$.

$\frac{i-1}{2} \times 100$ = percentage of substance dissociated.

E = number of experiments from which the data for water and solution are obtained.

Van't Hoff's constant for water is 1.89.

Depression of the Freezing Point in very Dilute Solutions of Potassium Chloride.

E.	α . Mol. norm.	α . Depress. obs.	b.	c.	$\frac{d.}{\text{factor} \times a 10^5}$.	$a_1 10^5$.	$\beta = \frac{a}{a_1}$.	$i = \frac{\beta}{1.89}$.	$\frac{i-1}{2} \cdot 100$.
1 n. 2	0.009711	0.0352	0.867	1.084	$\frac{100}{98.92} \times \alpha =$	981.8	3.585	1.897	89.7
1' n. 2'	0.009711	0.0349	0.912	1.14	$\frac{100}{98.86} \times \alpha =$	982.2	3.553	1.88	88.0
1 n. 3	0.01934	0.0677	0.889	1.111	$\frac{100}{98.89} \times \alpha =$	195.6	3.472	1.837	83.7
1' n. 3'	0.01934	0.0676	0.822	1.027	$\frac{100}{98.97} \times \alpha =$	195.4	3.459	1.83	83.0
1 n. 4	0.03845	0.13565	0.811	1.014	$\frac{100}{98.99} \times \alpha =$	388.4	3.4925	1.848	84.8
1' n. 4'	0.03845	0.13495	0.792	0.990	$\frac{100}{99.01} \times \alpha =$	388.3	3.476	1.839	83.9
1 n. 5	0.076064	0.26555	0.481	0.6012	$\frac{100}{99.40} \times \alpha =$	765.2	3.470	1.836	83.6
1' n. 5'	0.076064	0.26585	0.651	0.8138	$\frac{100}{99.19} \times \alpha =$	766.8	3.467	1.835	83.5

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