Freezing-Point Depression in Electrolytic Solutions. By
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The following research was undertaken for the purpose of determining the freezing points of solutions under conditions which would involve a different systematic error from that encountered when the ordinary method of procedure is followed; and, secondly, for the purpose of obtaining ionisation values for electrolytic solutions by the cryoscopic method which should be made by compensation as far as possible independent of any systematic error in determining the freezing points.

The freezing point of a solution is the temperature at which the solution is in equilibrium with ice, and can only be strictly ascertained when the system of ice and solution is entirely isolated, so that the heat is neither gained nor lost by communication with the exterior. Such a condition is impossible to realise in practice, but the effects of heat transference may be so minimised as not to exceed the experimental errors due to other causes.

The first theoretical discussion of the subject was given in a paper by Nernst and Abegg (*Zeitschrift f. physik. Chem.*, xv. 681), and further contributions have since appeared in the following papers in the same journal:—Abegg, xx. 207; Raoult, xxvii. 617; Wildermann, xix. 63; xxx. 577; Loomis, xxxii. 578. Briefly, the account of the matter given by Nernst and Abegg is as follows. If the system is not isolated from the exterior, and if only liquid is present, the thermometer will settle at a temperature determined by the environment, which is called the *convergence temperature*. Ice being now added, the temperature would, if there were no heat communication with the exterior, reach the equilibrium temperature of the ice and solution—that is, the thermometer would register the true freezing point. But the actual temperature registered is neither of these temperatures, but a compromise between them. On the one hand there is heat exchange with the

exterior tending to the attainment of the convergence temperature, and on the other hand a compensation for this by the formation or fusion of ice, heat being thereby produced or absorbed, and the system tending in consequence to its true freezing point. The thermometer after a time becomes stationary at an apparent freezing point, which lies between the true freezing point and the convergence temperature, and may differ from the former by a very considerable amount. The divergence between the true and apparent freezing points depends on two factors. First, it depends on the difference between the true freezing point and the convergence temperature, and, second, on the rate at which ice is formed and dissolved. If the convergence and true equilibrium temperatures are identical, the thermometer will evidently give the true freezing point. The true freezing point will also be registered if the rate of formation or fusion of ice is infinitely great, for then the compensation for heat exchange will be instantaneous and complete.

In most of the accurate work hitherto done, attention has been paid to the first mode of securing the exact freezing point—that is, by suitably tempering the bath in which the apparatus is immersed, the convergence temperature has been nearly adjusted to the freezing point which it is desired to determine. The external bath is in such a case at a temperature a little below the true freezing point, so that the heat gained from the room through the thermometer, stirrer, etc., is lost to the external bath, and so the influence of the exterior is on the whole reduced to zero. It must be remembered, however, that this mode of external compensation is only theoretically perfect if the *whole* environment is at the same temperature, *i.e.*, the freezing point. In actual practice, the external bath is below the convergence temperature, whilst the upper parts of the thermometer, along which conduction takes place, are above that temperature. When the freezing point experiment takes place, therefore, although ice on the whole may neither be formed nor dissolved, local formation of ice near the external bath, and fusion of ice near the thermometer, stirring apparatus, etc., must occur, so that constant stirring must be resorted to in order to eliminate to some extent this error. The stirring in itself, of course, generates heat, and has an appreciable effect on the apparent freezing point,

but this is allowed for in fixing the temperature of the external bath, which is adapted to a certain uniform rate of stirring.

If we consider the other factor which determines the difference between the true and apparent freezing points—namely, the rate of formation or fusion of ice—it is evident that this rate depends, first, on the quantity or proportion of ice present; second, on the fineness of its state of division—together, on the surface of contact between the ice and solution. For a given quantity of solution, the more ice we take and the more finely we divide it, the more rapidly will the equilibrium temperature be restored after any disturbance, and the more closely will the apparent and true freezing points coincide. In the present research it has been specially our effort to reduce the error arising from the finite time required for this restoration to a minimum by employing an amount of ice as great as circumstances would permit.

In practically all previous researches ice has been introduced into a solution of known concentration by slightly overcooling the solution, and then inducing crystallisation by inoculation with a minute fragment of ice on the end of a wire or capillary. A certain quantity of ice then separates in correspondence with the degree of overcooling, but this quantity is of necessity small if the equilibrium concentration of the solution is to be accurately known, for as ice separates from the solution the concentration increases, and it is the equilibrium concentration alone with which we are concerned. In Raoult's experiments, the ice which separated was only about one-half per cent. of the weight of the solution. In many other cases the amount of ice did not exceed 0.2 per cent. In our own experiments the minimum proportion of ice was 12 per cent., the average being about 15 per cent.

Of course, when such large proportions of ice are present, it is impossible to ascertain the equilibrium concentration of the solution from the initial concentration. We therefore adopted the expedient previously employed by Roloff (*Zeitschrift f. physikal. Chem.*, xviii. 572) for concentrated solutions, and filtered off the solution from the ice after equilibrium had been attained, the concentration being then determined by analysis.

The ice which we used was prepared by freezing distilled water,

and thereafter reduced to a fine state of division by planing with an ordinary hand plane, which was, of course, kept scrupulously clean. As the setting of the plane was never altered, and the amount of dry ice in the wet mass obtained was found to be subject to little variation under our experimental conditions, we were confident that the surface of contact between the ice and the solution varied little in the various experiments. This point is of some importance, as it is well known that the ice which separates from many solutions on overcooling is by no means in the same state of division as the ice which separates from pure water under the same conditions, so that the error due to the lag in attainment of equilibrium may vary considerably owing to this circumstance.

The external bath by which our apparatus was surrounded was invariably an ice bath. It was impossible, therefore, for ice to form within our apparatus, whether it contained ice or solution. By this means a possible source of error was avoided, the formation, namely, of a skin of ice round the bulb of the thermometer, which, according to the experiments of Wildermann, greatly affects the apparent temperature of equilibrium (*ibid.*, xv. 358).

Apparatus.

The general arrangement of our apparatus is shown on p. 367. The vessel used to contain the experimental liquid was a Dewar vacuum tube, which was closed by a rubber stopper perforated by three holes. Into these holes were fitted three tubes, which served as collars. The central tube C was of copper and was wide enough to admit the thermometer T. The other two tubes were of glass, and through them passed the filter F and stirrer S respectively.

The stirrer was made of light glass tubing bent horizontally to a circular form at its lower extremity. On the inner surface of the circular portion was a number of small holes, through which, by means of a hand blower attached to the upper portion of the stem, fine jets of air could be blown, thereby supplementing the mixing brought about by the vertical motion of the stirrer as a whole. The filter tube was made of narrow glass tubing widened to a conical shape at its lower end. The filter, which consisted of a small disc of filter paper supported between two discs of muslin,

was tied by means of cotton thread over the widened end of the filter tube.

The thermometer was attached above C to the stage of a microscope used for accurately reading the position of the mercury on the scale. The microscope with the thermometer was movable vertically on a stand, fine adjustments for reading being made with the screws of the microscope stage. The hammer of an electric bell, covered with chamois leather, was fitted for tapping the thermometer (compare Barnes, *Trans. Roy. Soc., Canada*, vol. vi. p. 37).

In order to obtain ionisation values for a strong electrolyte, our intention was to make on the same day two experiments, one with a non-electrolyte, the other with a strong electrolyte, the freezing-point depression being made as nearly as possible the same in the two cases. From the concentration of the two solutions it would then be possible to calculate the ionisation value of the strong electrolyte, due allowance being made for the small difference in the freezing-point depression according to Blagden's law. Since, however, the accurate analytical estimation of a suitable non-electrolyte was found to be a matter of considerable difficulty, we chose instead acetic acid, which is very feebly ionised, and whose small ionisation values are accurately known. Our day's work finally resolved itself into determining the freezing-point depression and equilibrium concentration of an approximately decinormal solution of acetic acid, and immediately thereafter the same magnitudes for a solution of a good electrolyte of approximately the same freezing point.

We first charged the Dewar vessel with 80 c.c. of distilled water cooled to 0° , and thereafter added 45 grams of freshly-planed ice made from distilled water. This ice was, of course, a wet mass, but the quantity of dry ice it contained could be estimated from the final concentration of the solution in the manner to be afterwards described. The stopper, with stirrer and filter attached,

was then placed in position, and the vessel immersed in crushed ice contained in a large glass jar protected by thick felt. The ice was heaped up above the level of the stopper so as to surround the tubes which acted as collars. The thermometer was now removed from the ice and water in which the bulb was constantly kept when it was not in use, and introduced through the tube C, being at the same time attached to the stage of the observing microscope. A thick felt cover was now placed on the top of the ice, and the stirrer was moved up and down a few times for the purpose of thoroughly mixing the ice and water, the process being assisted by the hand-blower, which also served to saturate the water with air. The position of the thermometer relatively to the vessel was always the same as measured on a millimeter scale.

The reading on the thermometer was generally constant as soon as the stirring was over. Observations were made from time to time during at least fifteen minutes with intermittent stirring. If the reading changed appreciably the thermometer was so far raised out of the solution as to alter slightly the position of the mercury on the scale, and then replaced in the liquid. In every case, with one exception, the reading was then constant for at least fifteen minutes.

The rubber tube of the hand-blower was now removed from the top of the stirrer, down which was delivered, by means of a graduated pipette, a sufficient quantity of cooled normal acetic acid solution to give approximately the required freezing-point depression. The stirring tube was then washed down with a little cooled distilled water. The blower was now reattached and the solution thoroughly mixed by means of a rapid stream of air bubbles and the vertical motion of the stirrer. The thermometer at once adjusted itself to a new position of equilibrium. Stirring and reading were then continued intermittently as before, and after the lapse of at least half an hour the liquid was filtered off. During the stirring the filter was kept at the top of the liquid, but before filtration it was lowered so as to be on a level with the bulb of the thermometer. The upper end of the filtering tube was connected to a tube passing through the stopper of a filter flask, which was in its turn connected with a 100 c.c. pipette filled with water and used as an aspirator. Two separate portions, of about 30 c.c. each, were then filtered off and analysed separately.

As a check on the readings, a thermometric reading was made after the filtration had been completed. Notwithstanding the changed conditions owing to the filtration, this reading did not differ from the equilibrium reading when the vessel was fully charged by 0.0005°. The apparatus was now removed from the ice bath, thoroughly cleaned, and used for a second precisely similar experiment, hydrochloric acid or some similar substance being used instead of acetic acid.

The following numbers will serve as an example of our experimental data:—

I.—Barometer 762.7 mm. Room temperature 15.7°.

80 c.c. water and 45 grams wet ice.

Time. h. m.	Thermometer.	Micrometer.	
11.0	5.06°	8.0	
11.15	...	9.0	
11.35	...	8.9	Added 11.5 c.c. normal acetic acid.
11.45	5.24°	25.0	
11.55	...	22.0	
12.0	...	22.0	
12.5	...	22.0	
12.19	...	22.0	Filtered off two portions.

II.—Barometer 763.0 mm. Room temperature 15.3°.

80 c.c. water and 45 grams wet ice.

Time.	Thermometer.	Micrometer.	
12.58	5.06°	8.0	
1.2	...	8.7	
1.47	...	8.9	Added 5.7 c.c. normal hydrochloric acid.
1.55	5.25°	2.0	
1.59	...	2.0	
2.31	...	2.0	Filtered off two portions.

The readings on the thermometer are the divisions on its scale to which the zero of the micrometer scale was adjusted, so as to measure back to the meniscus. Since the two scales read in opposite directions, the freezing-point depression may be obtained by adding each thermometric reading to its appropriate micrometer reading, and then subtracting the one temperature from the other. Thus in the first example, the lowering of the freezing point is $(5.24^\circ - 5.06^\circ) + (22.0 - 8.9)$ divisions. From the calibration table it is then found that this corresponds to a depression in terms of the thermometer scale of 0.1844°. Each division on

the scale of the micrometer in the eyepiece of the microscope corresponds on the average to $0\cdot000384^{\circ}$.

Sources of Error.

To estimate the degree of ionisation with the accuracy we desired, it was necessary for us, with depressions of about $0\cdot2^{\circ}$, to secure an error not exceeding $0\cdot0005^{\circ}$. With regard to the accuracy attainable in cryoscopic measurements, we cannot do better than quote the words of the originator of the method, as given in his last paper on the subject (Raoult, *loc. cit.*). "The final result of this investigation is, that with the apparatus above described, and with due observance of all precautions, it is fairly easy to determine the freezing-point depressions of dilute solutions with an accuracy of $0\cdot001^{\circ}$.

"It is a matter of great difficulty, however, to carry accuracy any further, chiefly on account of chance variations in the zero point; but if one is so fortunate as to possess a thermometer in which these variations are small and regular, one may indulge the hope of reaching an accuracy of $0\cdot0002^{\circ}$. In my experiments on the molecular depression of dissolved oxygen I actually attained this degree of accuracy."

In the following paragraphs we discuss the various sources of error to which our experiments were liable, and the degree of uncertainty to be expected in each case.

The Thermometer.—We experienced some trouble in obtaining a thermometer suited to our experiments. The Beckmann thermometers belonging to the Chemistry Department of this College were found to be unreliable when readings were pushed beyond the thousandth part of a degree, owing to the tendency of the mercury to stick at certain places of the scale, no amount of tapping or other mechanical agitation of the thermometer being sufficient to ensure consistent readings. A thermometer, however, belonging to the Physiological Department proved on investigation to be entirely satisfactory, and we have here to express our thanks to Professor Waymouth Reid for kindly placing this instrument at our disposal during the experiments. The thermometer, made by Goetze of Leipzig, was a fixed zero instrument, but as there was a small bulb at the top of the stem, it was possible with care

to detach a small amount of mercury, so that the zero point was only a few tenths of a degree from the bottom of the scale, which was just visible above the copper tube C. Very little of the mercury column was thus exposed to the room temperature.

The scale divisions of the thermometer corresponded to 0.01° , and each of them was divided by the micrometer scale of the microscope into 26 parts on the average. Since it was easily possible to estimate the quarter of a division by the eye, the merely optical accuracy of the thermometric reading corresponded to 0.0001° . In the interval of 0.3° in which all our observations lay, we carefully determined the value of each thermometer division in terms of micrometer divisions. The values varied from 25 to 27 micrometer divisions for each scale division. The difference between two observations of the value of the same thermometer division did not in any case exceed 0.3 micrometer divisions. The relation of the above part of the tube to the whole scale was then determined by the ordinary calibration with mercury threads. The tube was found to be of remarkably uniform bore, with the exception of the extreme upper part, which we never used in our experiments. Finally, the value of a degree of the thermometer was determined for us by Professor Kuenen and Mr Robson by comparison with a platinum resistance thermometer. The value of the degree of our thermometer was found to be identical with that of the air thermometer within the error of experiment, which was estimated at 0.4 per cent.

As has already been mentioned, very little of the stem of the thermometer which contained mercury was exposed to the room temperature. Special experiments showed that at 0° , *i.e.*, at the point where the greatest column of mercury was exposed, a variation of 2° in the room temperature was barely perceptible on the freezing points as read off on the thermometer, *i.e.*, probably did not amount to 0.0002° . The temperature of the basement room in which we worked varied very slowly, never more than 1° during a complete depression experiment, so that the effect of variation of room temperature on the exposed stem may be neglected.

Since at the freezing point of water, 0.2° more of stem was exposed than at the freezing point of the solutions we mostly

examined, the apparent lowering of the freezing point will be too great by 0.0003° if the room temperature is taken at 15° . This value was obtained from direct experiment with an exposed stem of 4° . The above error is only of importance however where *absolute* values of the freezing-point depressions are desired. For *relative* values even on different days it is only the variation of this error caused by change of the room temperature that concerns us. Since the extreme variation of the room temperature during the whole course of our experiments was only 3° , this source of error falls out of account.

The effect of pressure on the reading of our thermometer was unusually small, being considerably less than 0.0001° for 1 mm. of mercury.

Since in each case the thermometer was in the same position with regard to the vessel, the pressure under which the freezing point of the solution was measured was somewhat higher than the pressure under which the freezing point of water was observed, the vessel in the former case containing more liquid. The maximum error from this source, however, was only 0.00015° , by which the depression would be too small. On only one day was the change in the atmospheric pressure sufficiently great to affect the freezing-point depression perceptibly.

The zero of our thermometer when in use varied very regularly. In no case did the zero change by as much as 0.001° in twenty-four hours. The maximum difference observed between the zero taken in the morning experiment and that taken in the afternoon was 0.0003° , except on one occasion, when the thermometer accidentally received a sharp blow on the bulb, when the zero was found to have suddenly changed by 0.002° .

Convergence temperature.—The convergence temperature in our apparatus was found to be about $+0.04^{\circ}$, the temperature of the external bath being 0° . The maximum freezing-point depression which we observed was 0.19° , so that in the most unfavourable case the equilibrium temperature was 0.23° below the convergence temperature. By direct experiment we found that at -0.25° the liquid in the Dewar vessel gained 0.16 gram-calories per minute, *i.e.*, enough heat to melt 2 milligrams of ice per minute or 0.12 grams per hour. Since the quantity of solution employed was 120

grams, the ice melted in one hour would in the most unfavourable case only reduce the concentration by 0.1 per cent. and the freezing-point depression by a like amount. Most of the heat was apparently conducted by the thermometer, etc., the Dewar vessel forming a very efficient protection.

Dissolved air.—Raoult showed that water saturated with air had a freezing point 0.002° lower than water which was air-free. It is therefore of some importance to have the water and solution always saturated with air before the freezing point is observed. Owing to the method of air-stirring which we employed, the liquids whose freezing point we observed were always fully charged with air.

Analysis.—The solutions investigated were either acids or chlorides. The acids were estimated by means of N/20 baryta solution with phenol phthaleine as indicator, and the chlorides by Volhard's method with N/50 solutions of silver nitrate and ammonium thiocyanate. A decinormal solution of hydrochloric acid was taken as ultimate standard both for the baryta and for the silver nitrate. The baryta solution, however, was also checked with pure succinic acid, and the silver nitrate solution with pure potassium chloride.

As an example of the constancy of composition of the different portions filtered off from the experimental solutions, and of the magnitude of the analytical error, we here give the analysis of the solutions for which the thermometric readings were detailed on p. 369. The concentrations of the solutions are given in terms of normal solutions.

	Acetic acid.	Hydrochloric acid.
First filtrate . . .	0.09697	0.05225
Second filtrate . . .	0.09709	0.05213
	Mean, 0.09703	Mean, 0.05219

Here the divergence of any result from the mean does not greatly exceed 0.1 per cent. At the outside we may take 0.2 per cent. as the limit of error from sampling and analysis.

Quantity of ice.—From the results of analysis the quantity of ice in contact with the solution at equilibrium could be roughly calculated in the following manner. In the above experiment with acetic acid, 11.5 c.c. of normal acetic acid solution were

added to the original water (p. 369). But the concentration of the solution at equilibrium was 0.097 normal. There was therefore present at equilibrium $11.5 / 0.097 = 119$ c.c. of acetic acid solution. Now the total weight in the vessel was made up as follows:—

Water	.	.	.	.	.	80 g.
Wet ice	.	.	.	.	.	45
Acetic acid	.	.	.	.	.	11.5
Wash water	.	.	.	.	.	1
Total,						137.5 g.

If from this total we subtract 119 g. as the weight of the final solution, we obtain 18.5 g. as the quantity of ice present at equilibrium.

Experiments with Malonic Acid.

In order to test the validity of the method for determining ionisation values, we made several experiments with malonic acid, which obeys Ostwald's dilution law, that is, gives an ionisation constant when the values are determined from the electrical conductivity. The following numbers were obtained in determining this constant at 0°:—

Malonic acid, $C^2H^4(COOH)^2$, at 0°.
 $\mu_{\infty} = 228.$

v	μ	m	k
10	25.5	0.112	0.00141
20	36.0	0.158	0.00148
33.3	43.0	0.189	0.00147
50	52.8	0.232	0.00140
			Mean, 0.00144

In the above table, v represents the dilution, μ the molecular conductivity in reciprocal Siemens units, m the degree of ionisation, and k the ionisation constant calculated by Ostwald's formula

$$k = \frac{m^2}{(1-m)v}.$$

Freezing-point experiments with approximately decinormal solutions resulted as follows:—

I.

	Depression.	Concentration.
Acetic acid	0.1775	0.09337
Malonic acid	0.1779	0.08445

II.

	Depression.	Concentration.
Acetic acid	0.1853	0.0974
Malonic acid	0.1825	0.08665

The first experiment may be used to exemplify the mode of calculating the ionisation value from the cryoscopic data. An acetic acid solution of the concentration 0.09337 normal gives a depression of 0.1775°. Now we know from conductivity measurements that such a solution is ionised to the extent of 0.012. A solution of a non-ionised substance which would give the same depression would therefore have the concentration $0.09337 \times 1.012 = 0.0945$ normal. But the depression given by the malonic acid solution is 0.1779°. According to Blagden's law, that the depression is proportional to the concentration, a solution of a non-ionised substance which would give this depression would have the concentration 0.0947 normal. We may therefore say that a 0.08445 normal solution of malonic acid has the same freezing-point depression as a 0.0947 normal solution of a non-electrolyte, *i.e.*, that these solutions contain the same number of molecules. The degree to which the malonic acid solution is ionised is therefore $\frac{0.0945 - 0.08445}{0.08445} = 0.121$. In this calculation the change of

the degree of ionisation of the acetic acid with concentration has been neglected, since it is so small that the final result is not thereby appreciably affected. A change on the concentration of the acetic acid solutions which is less than 20 per cent. will have no noticeable effect on the calculation.

The second experiment with malonic acid yields the ionisation value 0.120. Calculating now the ionisation value m from Ostwald's dilution formula, we obtain the numbers 0.121 and 0.120 respectively for the two experiments. Here the concordance is absolute, but this absolute agreement is accidental, as these ionisation values are affected with an uncertainty of approximately 5 units in the third decimal place. In any event the accordance of the numbers gives ample evidence of the validity of our method.

Further to test the matter, we made experiments with approximately 0.05 normal solutions of the same substances. Here the relative error of our method is greater owing to the smaller depressions observed.

I.		
	Depression.	Concentration.
Acetic acid	0·0950	0·04965
Malonic acid	0·0977	0·04483
II.		
Acetic acid	0·0986	0·0517
Malonic acid	0·0935	0·0431

Calculated from these numbers we obtain the ionisation values 0·158 and 0·156 respectively. From the conductivities we obtain the values 0·162 and 0·164. Although these numbers are somewhat more divergent than in the previous instance, still they do not lie beyond the estimated error of the experiments.

Experiments with Strong Electrolytes.

Having thus shown that in the case of malonic acid our method gave results sufficiently in accordance with the electrical method, we now proceed to give the freezing-point experiments for strong electrolytes for which previous observers had obtained results which were not accordant with the ionisation values obtained from the conductivities.

Hydrochloric Acid, HCl.

Concentration.	Depression.	Conc. of Acetic Acid.	Depression.	Ionisation.
0·05141	0·1847	0·0970	0·1848	0·909
0·05219	0·1870	0·0970	0·1844	0·908

Potassium Chloride, KCl.

0·0527	0·1841	0·09757	0·1856	0·858
0·05275	0·1839	0·1000	0·1907	0·850

Sodium Chloride, NaCl.

0·0519	0·1829	0·09668	0·1840	0·874
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If now we compare these ionisations with the values deduced from the conductivity method, we obtain the following table for 0·05 normal solutions:—

	HCl.	KCl.	NaCl.
From conductivity at 18° *	0·937	0·895	0·874
" " 0° †	0·956	0·892	0·877
From freezing point	0·908	0·854	0·874

* Kohlrausch und Holborn, *Leitvermögen der Electrolyte*, pp. 159, 160, 200.

† J. G. MacGregor, *Trans. Roy. Soc. Canada*, 1960-1, pp. 6, 7.

Except in the case of sodium chloride it will be seen that here there are great divergences between the ionisation values calculated from cryoscopic and electrical observations. The error of the freezing points can scarcely amount to a unit in the second decimal. The error in the conductivities is much smaller than this, so that we are obliged to conclude that the two methods lead to essentially different results in the case of hydrochloric acid and potassium chloride. It is true that, owing to the uncertainty in the maximum molecular conductivity of all acids, the electrical ionisation value for hydrochloric acid is affected by a greater error than the corresponding numbers for the neutral chlorides, but the divergence from the cryoscopic value is much too great to be accounted for in this way. It might be urged that, as we have taken acetic acid as our standard of reference, the differences might arise from some peculiarity in the behaviour of this substance. When we consider, however, that we obtain correct values for the ionisation of malonic acid by the use of the same method, it must be conceded that such an objection loses much of its force. Again, we find, in accordance with other observers, that by the cryoscopic method sodium chloride appears to be less highly ionised than potassium chloride, whereas by the conductivity method the reverse is apparently the case. Here, if the standard substance is merely uniform in its behaviour, whatever be its peculiarities in other respects, we have a well-marked divergence between the cryoscopic and electrical methods.

Equivalent Depression for Acetic Acid.

The following table shows the depressions actually observed for approximately decinormal solutions of acetic acid under the conditions prevailing on different days, and for the purpose of comparison a column has been added which gives the values for accurately decinormal solutions calculated by means of Blagden's law from the two columns immediately preceding it. This table, like all others in this paper, gives the depressions as they were obtained directly from the thermometer, no corrections of any kind, except calibration corrections, having been applied.

Acetic Acid.

Barometer.	Temp. of Room.	Ice present.	Concentration.	Depression.	Depression for decinormal solution.
763 mm.	13°	18.5 g.	0.0970	0.1848	0.1905
758	15	18	0.09668	0.1840	0.1903
763	15	18	0.09757	0.1856	0.1902
772	15	20	0.1000	0.1907	0.1907
771	15	15	0.09337	0.1775	0.1903
769	15.5	17.5	0.0974	0.1853	0.1903
763	15.5	18	0.0970	0.1844	0.1901
Mean					0.1903

The last column shows the extremely uniform character of the results obtained under a very considerable variety of conditions. The extreme difference of the depressions is only 0.0006° , and the greatest divergence from the mean is only 0.0004° , the divergence from the mean in six observations out of the seven being 0.0002° or less.

If we take the ionisation of decinormal acetic acid to be 0.012, we obtain the number 0.188 as the depression which would be shown by acetic acid if it were undissociated in decinormal solution. The equivalent depression for acetic acid, *i.e.*, the value of the depression divided by the concentration, would thus for the undissociated compound be 1.88. The mean value found by Loomis for nine non-electrolytes of small molecular weight is 1.85, the greatest value being 1.87 and the smallest 1.81.

Comparison with other Observers.

When we compare our depressions for strong electrolytes with those of other observers, we find that there is on the whole an excellent agreement. The comparison is best made by ascertaining the equivalent depressions for the various solutions, and then by interpolation reducing these values to the equivalent depression for exactly 0.05 normal solution.

Hydrochloric Acid.

Depression.	Concentration.	Equiv. Depression.	Equiv. Depr. for N/20.
0.1847	0.0514	3.593	3.594
0.1870	0.0522	3.583	3.585
Mean,			3.590

Potassium Chloride.

Depression.	Concentration.	Equiv. Depression.	Equiv. Depr. for N/20.
0·1841	0·0527	3·494	3·497
0·1839	0·05275	3·486	3·489
			Mean, 3·493

Sodium Chloride.

0·1829	0·0519	3·524	3·526
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Taking the results of Loomis and Barnes from the tables compiled by MacGregor (*Trans. Nova Scotia Institute of Science*, 1899-1900, pp. 218-220), we obtain the following comparison for equivalent depressions in 0·05 normal solution :—

	Hydrochloric Acid.	Potassium Chloride.	Sodium Chloride.
Loomis	3·59	3·50	3·531
Barnes	3·597	3·504	3·536
Walker and Robertson	3·590	3·493	3·526

The divergence of our results from the mean of those of Loomis and Barnes is for hydrochloric acid 0·1 per cent., for potassium chloride 0·25 per cent., and for sodium chloride 0·2 per cent. In each case our result is the smaller. This may be due to a difference in the degree value of the thermometers employed by the different observers—our own is uncertain to 0·4 per cent.—or it might be due to the difference of the systematic error of the methods employed by Barnes and Loomis on the one hand and ourselves on the other. Whatever be the cause of the slight difference, the agreement as it stands is of a very satisfactory nature, and tends to increase confidence in the results of exact cryoscopy.

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