

II.—ON THE DETERMINATION OF THE FREEZING-POINT DEPRESSIONS OF DILUTE SOLUTIONS OF ELECTROLYTES—BY THOS. C. HEBB, M. A., *Dalhousie College, Halifax, N. S.*

(Read March 10th, 1902.)

Dr. MacGregor has shown,\* that, if for any electrolyte curves be plotted using ionization coefficients as ordinates and the equivalent depressions of different observers as abscissae, the curves so drawn diverge, as dilution increases, some to the right and some to the left of what their general course is at moderate dilution. He has also shown, that this tendency to diverge is less for the results of Archibald and Barnes, both of whom worked in the Dalhousie Physical Laboratory. This indicates that the method they adopted was free from some source or sources of error which affected the methods of other observers. As they had not carried their observations to solutions of great dilution, he suggested that I should go over the ground with one or two electrolytes and see if, for higher dilutions, their results were borne out. This I have done for potassium chloride with the results given below.

I chose this electrolyte for the following reasons:—(1) It is one of the salts for which Whetham† has made determinations of the ionization coefficients for dilute solutions at 0°C.; (2) The rightward or leftward tendency, above mentioned, is most marked for this electrolyte; and (3) solutions of known concentrations are quite easily made up.

*Salt.*

The salt was obtained as chemically pure from Merck. On testing it, however, I detected free acid. This disappeared on once re-crystallizing and heating to constant weight. Solutions

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\* Proc. and Trans. N. S. Inst. Sci., Vol. X., p. 211, 1899-00.

† Phil. Trans., A, Vol. 194, 1900, pp. 321-360.

of it gave values of conductivity agreeing very well with those given by Kohlrausch.\*

#### *Water.*

The water used, both in making up the solutions and in determining the freezing-point of water, was purified by boiling distilled water, containing a few grammes of barium hydroxide in a copper boiler and condensing it in a block-tin worm. It was kept in glass bottles, which had been used several years for that purpose. The conductivity of the water, obtained by once distilling, was never more than  $1.25 \times 10^{-6}$  at  $18^{\circ}\text{C}$ . expressed in Kohlrausch's new unit ( $\text{ohm}^{-1} \text{cm.}^{-1}$ ).† The determination of the conductivity was made by means of Kohlrausch's method with the alternating current and telephone. The constant of the electrolytic cell used was determined by comparing the conductivities of known solutions at  $18^{\circ}$  with those given by Kohlrausch.‡ I did not try to obtain water of a greater degree of purity, for the amount of any electrolyte present to give it this conductivity is so small that the freezing-point would not be affected in the fourth place of decimals. This I have determined by using Kohlrausch's§ table of conductivities, together with observations made on the freezing-point depressions of electrolytes of different observers. Of course there is the possibility of a non-electrolyte being present, but we may safely assume that the amount of it present is, at least, not greater than that of the electrolyte, and even twice the amount of salt present, which would be necessary to give the above conductivity, will not affect the freezing-point of water in the fourth place of decimals.

#### *Solutions.*

All solutions were made up at  $0^{\circ}\text{C}$ . The greater number of them were made by putting a known amount of the water-free salt in a 1000 c. c. flask, and filling it up with water at  $0^{\circ}\text{C}$ . A few of the diluter solutions were made from these by means

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\* Kohlrausch u. Holborn : Leitvermögen der Elektrolyte, 1898, p. 159, tab. 2.

† Kohlrausch u. Holborn : Leitvermögen der Elektrolyte, 1898, p. 1.

‡ *Loc. cit.*

§ *Loc. cit.*

of another flask of 200 c. c. capacity. Both flasks were calibrated at  $0^{\circ}\text{C}$ . The concentrations, in gramme-equivalents per litre of solutions at  $0^{\circ}\text{C}$ ., were hence easily calculated. But in some of the cases I was not sure of the dryness of my salt, and hence determined their concentrations gravimetrically by precipitating the  $\text{KCl}$  of a known quantity of the solution with  $\text{Ag NO}_3$ .

#### *Measurement of Freezing-Points.*

The method used in determining the freezing-points was a modification of that used by Loomis.\* The principal changes were: (1) the stirring was done mechanically and at a constant rate; (2) the stirrer was not simply of the ring form but had vanes attached to it; (3) the temperature surrounding the whole apparatus was kept within .5 degree of  $0^{\circ}\text{C}$ . The work was done in a basement room of the college in which there was no source of heat, and experiments were only made when the temperature of the air could be kept at  $0^{\circ}\text{C}$ . by raising the windows.

The freezing-apparatus consisted of three parts as follows: (1) an outer bath containing ice and water; (2) a bath which stood in this called the protection-bath, and which contained a mixture of salt water and snow, at a temperature of .005 degree centigrade below the freezing-point of the solution, whose freezing-point was being determined; (3) the freezing-tubes immersed in this, which contained the solution under experiment.

The freezing-tubes consisted of two glass tubes one inside the other, the outer being about 3.2 cm. in diameter. The space, of about 1 mm., between the two was kept uniform throughout by winding silk thread about the inner one at two distinct places. This air-space, together with one at the bottom of the tubes, caused by the bottom of the inner tube being re-entrant, kept an ice sheath from being formed on the wall of the tube. The two tubes were sealed together at the top, in order to keep moisture from getting in between them, and in order to have their relative positions always the same. These

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\*Phys. Review, 1, 199, 1893, and 9, 237, 1899.

tubes fitted tightly into the cover of the protection bath, and, as the outer tube was 30 cm. in length, they extended to a considerable distance into this bath. A cork made of vulcanite and pierced by three holes fitted into the inner tube. Through the hole in the centre of the cork a thermometer passed. It was fastened tightly, and in such a manner, that its bulb came within 2 cm. of the bottom of the inner tube. A stirrer passed through one of the other holes, while the third was kept for the introduction of an ice crystal. The last two mentioned holes were lined with platinum foil.

The stirrer which was made in the usual form with a ring at the bottom, was of platinum wire. This ring, which was smaller than the internal diameter of the inner tube, had fastened to it vanes of platinum foil. These were fastened on by platinum wire and extended in towards the centre. This form of stirrer I found to be much more effective in stirring than the ring commonly used.

In order to guide this stirrer, and in order to keep the thermometer in the centre of the freezing-tube, another cork, of rubber, was fastened on to the thermometer, some distance above the highest point reached by the solution when the thermometer was in position in the freezing-tube. Through this cork there were two holes—one for the stirrer and one for the introduction of an ice crystal. These holes were lined with glass tubing.

The above arrangement kept the stirrer from scraping against the sides of the freezing-tubes. And, in order to keep it as much as possible from rubbing against the sides of the holes in the corks, a link was introduced in the part of the wire outside of the tubes. This allowed it to hang in a perfectly vertical position.

The protection bath was 38 cm. in height and 13 cm. in diameter. Its cover consisted of a brass plate through which passed the freezing-tubes, a thermometer and a stirrer. This stirrer consisted of a wire shaft, which had two rings fastened to it—one for the upper and one for the lower portions of the mixture. The rings held vanes of tin. This kept the mixture

well stirred, and any change in temperature was quickly recorded by the thermometer.

It was so arranged that both these stirrers—viz., the one in the protection bath and the one in the freezing-tubes—should have the same stroke. Hence they were both fastened to a slider on a vertical guide-post. This slider was worked by a crank vertically above it. The axis carrying the crank was turned by a hot-air motor. The stroke of the crank was equal to the stroke required by the stirrers.

The two thermometers—viz., the one in the protection bath and the one in the freezing-tubes—were both of the Beckmann form, and were graduated to .01 degree. The one used in the freezing-tubes had been calibrated at the Physikalisch-Technische Reichsanstalt, Berlin. The value of its degree—its length being about 5.4 cm.—was given to the third place of decimals. As, however, it had been tested with its bulb at 0°C. and its scale at 15°C., I had to make a correction due to the fact that I used it with its scale also at 0°C. In the corrected form the value of the degree was correct. For some time before it was used, and while it was being used, it was kept hanging in a vertical position with its bulb and scale approximately at zero. This precaution is indispensable, as the constancy of the thermometer depends on it. This thermometer was read by means of a microscope, which was firmly mounted on an adjustable stand. The eye-piece of the microscope contained a micrometer scale, thirty-seven divisions of which corresponded to .01 degree. As half divisions were easily estimated I could read to .0001 degree. To get a clear image of scale and mercury, a small incandescent lamp, driven by a current from several Samson cells, was placed, when a reading was being taken, directly behind the thermometer. As, however, the mercury and scale are at different distances from the microscope, one cannot focus the both at once. Hence I always made a reading with the mercury focussed, for it was quite easy to estimate the centre of the blurred image of the scale line. In the course of my experiments, I found out how important it was to have the microscope always inclined at the

same angle to the thermometer. This one sees when he takes into consideration, that the distance between the mercury column and the scale, which is back of it, is at least 120 times as great as the smallest distance read on the scale. In order to keep the microscope always at the same inclination to the thermometer, I had two arms rigidly attached to the microscope—one above and one below it. Before a reading was taken, the stand of the microscope was so adjusted that the arms touched the thermometer.

Directly over the top of the thermometer was placed an electric hammer, driven by a current from a Samson battery. It gave quick, sharp taps and, hence, prevented the mercury from sticking at one place.

The following method was used to find the convergence temperature. The apparatus, as described, was set in order with a mixture at  $0^{\circ}\text{C}$ . in the protection bath, and water in the freezing-tubes, and then the stirring was begun and kept running until the apparatus arrived at a state of thermal equilibrium. With the apparatus working at 50 complete strokes per minute, I found it to be .005 degree above that of the protection bath. Hence in all of my determinations of freezing-points, the temperature of the protection bath was kept .005 degree below the freezing-point of the solution under experiment—it having been approximately determined beforehand. This convergence temperature is much smaller than that found by other experimenters. Its smallness may be due to two things: (1) the freezing-tubes may be too easily affected by the protection bath, or (2) the apparatus may be free from friction and other sources of heat. I am fully convinced that its smallness in my case was not due to the former, but due to the fact that the amount of friction was very small, and that the air temperature was  $0^{\circ}\text{C}$ .

The following was the method used in making a determination of the freezing-point. The approximate freezing-point of the solution having been found, the temperature of the protection bath was brought to be .005 degree below this. The portions of the apparatus in contact with the solution were then

thoroughly cleaned and rinsed with the solution. The inner freezing-tube was then filled up to a mark on its side—this mark being about 2mm. above the highest position reached by the stirrer. The cork bearing the thermometer was put in its place, the tubes were then placed in a mixture of snow and salt, and the solution kept continually stirred until its temperature fell to  $-3^{\circ}\text{C}$ . below its freezing-point. They were then placed in position in the protection bath, and the stirring was begun. When the mercury, which rose very slowly, arrived at .1 degree below the freezing-point, an ice-crystal was introduced through the holes in the corks. After the mercury became stationary, the tapping of the electric hammer was begun and lasted for half a minute. The stirring was then stopped, the light put into position, and a reading made with the microscope. The stirring was then begun again and after a few minutes a second reading made. With my apparatus, I found no difficulty whatever in getting the mercury to remain stationary for at least five minutes. In cases where more than one observation was made on the same solution, the mean value was taken. As it was only the depressions that I wanted, I found the freezing-point of water immediately before or immediately after the above determination. The water used was of the same degree of purity as that used in making up the solutions. Other conditions, such as the introduction of the ice-crystal, were kept the same in both cases. If the barometer was varying rapidly, the freezing-point of water was taken immediately before and after that of the solution, and the mean taken.

The depression is the difference between the freezing-point of water and that of the solution under consideration. I found by experiments performed on different days, that of a series of depressions, a single value varied from the mean value by not more than .0005 degree. As this would be large for dilute solutions, I was unable to deal with solutions of greater dilution than I have used.

To correct for the change in concentration, due to the introduction of an ice-crystal .1 degree below the freezing-point, I made use of Raoult's method\* for determining the depression

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\* Ztschr. f. phys. chem., 27 613, 1899.

when the over-cooling is zero. For this purpose I took a solution and found its depressions for different over-coolings. These depressions I plotted as ordinates against the over-coolings as abscissae. This gives practically a straight line which, if produced to cut the depression axis, cuts off a portion from it representing the depression when the over-cooling is zero. Raoult has shewn that the following relation holds for solutions of different concentrations

$$C^1 = C(1 + KS)$$

where  $C^1$  is the observed depression for over-cooling  $S$ ,  $C$  is the depression for over-cooling zero, and  $K$  is a constant. Hence, determining  $C$  and  $S$  for different solutions, and knowing  $K$  to hold for all solutions, we can find  $C$  in each case. I determined  $K$  to have the value .02. Hence it can easily be seen that for an over-cooling of .1 degree the values of the depressions will be .02% too great.

The ionization coefficients are taken from a paper by Whetham.\* Since he only carried his concentrations to .03 gramme-equivalents per 1000 grammes of solution, I have extended the curve under guidance of extrapolated values given by Dr. MacGregor.† He obtained his extrapolated values by plotting, alongside of one another, the ionization coefficient-concentration curves for 0° and 18°—the latter being obtained from data given by Kohlrausch.

In the following table the concentrations are given in gramme-equivalents per litre of solution at 0°C. The depressions, which have been corrected for over-cooling, as pointed out, are given in degrees Centigrade. The ionization coefficients are for 0°C., and the equivalent depressions are the depressions in degrees Centigrade divided by the concentration in gramme-equivalents per litre of solution at 0°C. The letters *i* and *e* after the coefficients shew whether they were obtained by interpolation or extrapolation.

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\* *Loc. cit.*

† Proc. and Trans. N. S. Inst. Sci., Vol. X. p. 218, 1899-90.



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The table also contains the values of the depression constant, *i. e.*, the lowering produced by each gramme-molecule or gramme-ion of the electrolyte in solution. It has been calculated by aid of the expression:  $\delta = i(1 + a)$  where  $\delta$  is the equivalent depression, *i* is the constant and *a* is the ionization coefficient. This formula only holds for electrolytes such as KCl where the gramme-molecule is equal to the gramme-equivalent and the molecule breaks up into two ions.

TABLE I.—KCl. (74.59).

Concentration. (gr. eq. /l.)	Depression of Freezing- Point.	Equivalent Depression.	Ionization Coefficients at 0° C.	Depression Constant ( <i>i</i> ).
.004124	.0151	3.66	.979 i.	1.850
.006207	.0228	3.67	.972 "	1.863
.006363	.0233	3.66	.972 "	1.857
.009310	.0341	3.66	.964 "	1.867
.009544	.0344	3.60	.963 "	1.836
.01009	.0362	3.59	.962 "	1.829
.01060	.0381	3.60	.961 "	1.833
.01085	.0395	3.64	.960 "	1.858
.01473	.0531	3.61	.952 "	1.847
.01514	.0549	3.63	.952 "	1.857
.01862	.0673	3.614	.946 "	1.857
.01909	.0688	3.60	.946 "	1.852
.020596	.0738	3.583	.943 "	1.844
.02402	.0860	3.580	.938 "	1.847
.03031	.1086	3.583	.932 "	1.854
.03161	.1131	3.578	.930 e.	1.854
.05541	.1950	3.519	.906 "	1.846
.05583	.1958	3.507	.906 "	1.840
.05673	.2001	3.527	.905 "	1.851
.05770	.2033	3.523	.905 "	1.849
.07383	.2578	3.492	.894 "	1.844
.07408	.2597	3.505	.894 "	1.851

In these results I have not continued my determinations to as concentrated solutions as I would have liked, but I was unable to do so on account of lack of cold weather. On the other hand, it would be useless for me to attempt to deal with diluter solutions than I have used, for my possible error is too great.

The values of the depression constant seem to oscillate about the value 1.85 and if the mean be taken we get 1.849. This is the value arrived at by two methods suggested by Dr. MacGregor. The one he applied\* and the other I applied† to a considerable number of data.

If from the above table we plot concentrations as ordinates against equivalent depressions as abscissae, we get points which, though they do not lie on a smooth curve, can be represented by drawing a smooth curve through them in such a manner that as many points fall on one side of it as on the other. If we draw in this curve we find that it is convex towards the concentration axis. Further, if we plot alongside of it similar concentration-equivalent depression curves for other observers, we find that in all cases their curves lie nearer the concentration axis than mine, although no two of them pursue exactly the same course. That the values of my depressions are greater than those of other observers might be expected, for I am not aware that any of them worked with their air temperature at zero. Also the fact, that the values of the depression constant, as obtained from my results, agree so well with what is expected, would lead one to suppose that my values of the equivalent depressions are not too great.

The following table will give some idea as to how Loomis',‡ Jones',‡ and my concentration-equivalent depression curves lie. I have roughly drawn smooth curves through each observer's results, and then read off the results for the different concentrations.

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\* Proc. and Trans. N. S. Inst. Sci., Vol. X., p. 211, 1899-00.

† Proc. and Trans. N. S. Inst. Sci., Vol. X., p. 409, 1901-02.

‡ Not having access to their papers, I have taken the data from a paper by Prof. MacGregor: Proc. and Trans. N. S. Inst. Sci., Vol. X., p. 211, 1899-00.

TABLE II.

Concentration. (gr. eq. /l.)	Equivalent Depression.		
	Loomis.	Jones.	Hebb.
.075	3.470	3.495	3.495
.05	3.50	3.518	3.528
.03	3.528	3.553	3.570
.02	3.550	3.575	3.598
.01	3.60	3.605	3.64
.005	....	3.665	3.67

If now we plot ionization coefficients as ordinates, against equivalent depressions as abscissae, it is generally assumed that at great dilution we should get a straight line. My results are too erratic to lie on a straight line, but the general course of them is no doubt a straight line, and does not tend to either the right or left, as do the curves of others—at least up to the concentration .01. Above this it seems to have a slight rightward tendency, but not nearly as great as Jones'. Of all the observer's results to which I have access, and this includes Loomis, Jones, Raoult, Abegg, Ponsot and Wildermann,\* there are none which give a curve as high or higher than mine. Jones' curve at the lower part seems to coincide with mine, but from the concentration of about .08 to .007 it goes to the left of mine, and from this on it passes away to the right. Loomis' curve is to the left of both Jones' and mine and has the leftward tendency, but looks as if it would pass off to the right, if dilution were carried far enough. Abegg's curve is to the left of Loomis'. It starts at a concentration of .07, runs parallel to mine for a space and then passes off to the right. Wildermann's curve has the leftward tendency, while Raoult's seems to be inclined towards the right. In plotting all the above curves I have used Whetham's coefficients.

Hence it appears to me that my results have borne out—at least to a large degree—what Archibald's and Barnes' results seem to imply.

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\*These data are all taken from MacGregor's paper cited above.