

## AN EXAMINATION OF THE ABEGG METHOD OF MEASURING FREEZING-POINT DEPRESSIONS

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BY E. H. LOOMIS

Under the title, «Depression of the Freezing Point in very Dilute Solutions,»<sup>1</sup> Abegg has recently described various modifications of his former method<sup>2</sup> which have greatly increased its accuracy. Besides repeating the measurements made with the earlier method on NaCl, cane sugar and alcohol, he has determined, in addition, the freezing points of the following solutions :—KCl, K<sub>2</sub>SO<sub>4</sub>, tartaric acid, grape sugar and urea. It is to be regretted that he did not subject MgSO<sub>4</sub> and KNO<sub>3</sub> to the same careful examination, since it will be remembered that these salts according to the measurements of Loomis exhibit a marked departure from the theory which Arrhenius proposed and which Abegg accepts. The mere fact that NaCl, KCl, K<sub>2</sub>SO<sub>4</sub> and the great majority of the compounds examined by me seem to support this theory strongly, makes it, I think, the more important that those, at least, who accept the theory, should in their work of repeating the investigations of other observers, give careful attention to the solutions which present exceptions. Any broadening of the present theories must come by a critical examination of the exceptional cases, and these need first of all to be established upon a sure experimental basis before any modification or extension of present theories may be safely undertaken. In regard to all hasty efforts in this direction the words of caution which Abegg himself expresses (page 232) are most timely :—«Neither the extent nor certainty of the present experimental data is sufficient to furnish a sure foundation for speculation.» These words, specifically uttered with sole reference to his own work, the great accuracy of

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<sup>1</sup>Abegg. *Zeit. phys. Chem.* **20**, 207 (1896).

<sup>2</sup>Nernst and Abegg. *Ibid.* **15**, 681 (1894).

which appears to the most hasty as well as to the most critical reader, could, I think, be wisely appropriated by all workers in this field of research.

The present work commends itself for the manifest purpose of the observer to secure exact results whatever may be their bearing on any accepted theory; and it is hoped for this reason that the work will be extended over a large range of characteristic compounds. The great need at present is a broader basis of well established experimental facts.

In regard to the present method of Abegg, one observes that it differs from the earlier method (Nernst and Abegg) in the following particulars:—

1. The substitution of a mixture of salt water and fine ice in place of the former «cryohydrate» in the production of the cold bath of constant temperature outside the air mantle in which the «freezing vessel» is placed. This cold bath is kept at a constant temperature a few tenths of a degree below  $0^{\circ}\text{C}$ . (Loomis)
2. The substitution of an automatically regulated mechanical stirrer for the former hand stirrer. (Abegg)
3. The increase of the dimensions of the apparatus so that 1000 cc. of the solution are used instead 100 cc. (Jones)
4. The use of a mechanical vibrator for jarring the thermometer while in use. (Pickering<sup>1</sup>)
5. The initial overcooling, which the solutions undergo before freezing begins, was not allowed to exceed  $0.8^{\circ}\text{C}$ , in general it was  $0.5^{\circ}\text{C}$ . (L.) In the former method this overcooling was left to take care of itself and usually reached  $1.30^{\circ}\text{C}$ .

These modifications in the method together with the fact that the work is now done at a room-temperature usually below  $6^{\circ}\text{C}$  enable Abegg to dispense with the corrections which had to be applied to the results obtained with the earlier method as follows:—

First, the adoption of the ice and salt water mantle, the temperature of which is kept a few tenths of a degree below  $0^{\circ}\text{C}$  (L.),

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<sup>1</sup>This jarring of all finely divided thermometers, now generally known to be indispensable to their accurate performance, while universally credited to Loomis, was introduced by S. U. Pickering in his calorimetric work in 1886. See *Phil. Mag.* (5) **21**, 330 (1886) and *Jour. Chem. Soc.* **51**, 294 (1887).

together with the fact that the room temperature was lowered to a point as near  $0^{\circ}\text{C}$  as the method would permit (L.) has brought the «convergence temperature» to such close coincidence with the true freezing point of the solution that the correction for the different values of the Nernst and Abegg constant  $K$  in different solutions vanishes.

Second, the restriction of the overcooling of the solution to the small average amount of  $0.5^{\circ}\text{C}$  makes it no longer necessary to apply the correction for changes in the concentration of the solution due to the separation from the solution of a considerable part of the solvent in the form of «ice».

The former correction was first theoretically calculated by Nernst and Abegg, as well as experimentally verified by them, and is undoubtedly valid.

The latter correction has only a rough theoretical foundation and, so far as is known to me, has had no experimental verification. It was undoubtedly Abegg's effort to eliminate this uncertain correction that led to the modifications of his former method. These modifications at the same time necessarily eliminated the other correction, since any attempt to confine the overcooling to a small amount, with the purpose of having a very small quantity of ice present in the solution, at once requires that the solution be completely isolated from the disturbing outside temperatures. *This was the fundamental idea in the Loomis method* (1893). It may not be out of place here to refer to the original publication of this method in Wiedemann's *Annalen*, **51**, 504 (1894) where the following words are found: «*Es liegt somit die Nothwendigkeit vor die Flüssigkeit deren Gefrierpunkt bestimmt werden soll, vor den störenden Einflüssen der Aussentemperaturen zu schützen.*» Accordingly the overcooling was confined to the limits  $0.15^{\circ}\text{C}$ — $0.25^{\circ}\text{C}$  and the freezing vessel was surrounded with an air bath protected, *except at the top*, with an auxiliary cold bath of constant temperature  $0.3^{\circ}\text{C}$  below that of the freezing point of the solution. To guard against the disturbing influence of the air, the freezing tube was made very long and the solution was confined to its lower extremity, so that it was deeply submerged in the «protection bath». To provide still farther against any disturbance due to the room-temperature, the room-temperature was

lowered until it was as near  $0^{\circ}\text{C}$  as the season of the year would permit. All subsequent measurements have been made at about  $3^{\circ}\text{C}$ . I have taken several occasions to emphasize my belief that a last degree of exactness in freezing point work is to be looked for only when the room temperature is kept constant at  $0^{\circ}\text{C}$ . This has thus far been impossible with the facilities which have been at my command. That these experimental precautions, developed after many thousand observations of the freezing-point of pure water, resulted in the complete elimination or perhaps better *balancing* of all the disturbing influences, was established, I think, by the long series of experiments which showed that the thermometer gave sensibly the same readings when only mere *traces* of ice were present as when there were large quantities in the water<sup>1</sup>. It seems fair to assume that this would have been impossible if the «convergence temperature» had not been practically identical with the *true* freezing point of the solution, and my original conclusion seems to be abundantly justified, namely, that «The disturbing influences of the freezing bath and the air were so far eliminated that the *actual* freezing point of water as well as that of a dilute solution may be determined with the greatest certainty.»<sup>2</sup> The word «actual» was here employed to distinguish the true freezing point from what Nernst and Abegg call the «apparent» freezing point. This reference is sufficient explanation of the fact that I have never thought it necessary to examine my method «with reference to the sources of error which Nernst and Abegg discovered» and will leave, I think, little reason for them «to wonder».

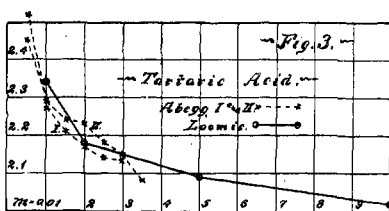
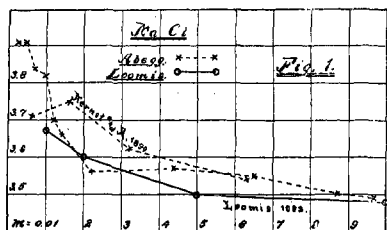
It may be safely accepted that the convergence temperature plays no rôle in the results obtained by the Loomis method. The almost complete identity of these later results of Abegg (1896) with those obtained by me (1893) is additional ground for believing that this conclusion is valid. See for example Fig. 8, where the results of these observers for alcohol are graphically represented. While it thus appears that, in main features, the present method of Abegg is essentially that introduced by Loomis, it must not be overlooked that Abegg has very ingeniously protected his freezing vessel

<sup>1</sup>Wied. Ann. **51**, 511 (1894).

<sup>2</sup>See Phys. Rev. **1**, 213 (1893).

above so that there is the most complete isolation of his solutions from the room temperature and he is thus able to secure good results even at ordinary room temperatures. He has also introduced successfully a mechanical stirrer, and thus justly claims to have barred out the last possibility of the observer's bias affecting the results. This is an advance by no means insignificant. In connection with my work I have found, however, after proper precautions are taken to eliminate the observer's bias, and when his only concern is to stir the solution uniformly, that hand stirring is entirely permissible and is so sensibly uniform that no appreciable errors are introduced from this cause. In regard to the value of increasing the quantity of the solution as Abegg has done, in accordance with the suggestion of Jones, from 100 cc. to 1000 cc., I think there is some doubt. Following the same suggestion I increased the quantity from 70 cc. to 250 cc. but failed to observe any reduction in the experimental errors. Abegg does not call attention to any facts that would lead us to believe that this change has contributed anything to the accuracy of his new method.

We are now ready to pass to an examination of the new results themselves. Without giving the data in tabular form they are graphically represented Figs. 1-8, where the x—x—x lines represent Abegg's values of the molecular depression. Ordinates



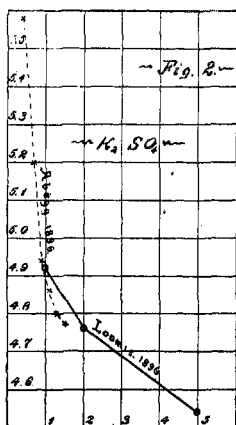
are molecular depressions and abscissæ are gram-molecular strength of the solutions (gram. mol. per liter of the solution). The o—o—o lines in the figures are the corresponding values found by Loomis.

1. By an examination of these "curves" it appears, that, barring zigzags, they present in general a most gratifying agreement with those obtained by me. This agreement is so close in all cases except cane sugar and urea in extreme dilution ( $m = 0.01-0.02$ )

as to amount to little less than an identity. Thus, taking the measurements for the 1/100 normal solutions and "smoothing" out the various curves as far as experimental errors will justify we find the following differences between the measurements of Abegg and Loomis :—

NaCl	+0.0010°	Cane Sugar	+0.0016°
K <sub>2</sub> SO <sub>4</sub>	0.0000°	Grape Sugar <sup>1</sup>	—0.0007°(?)
Tartaric Acid <sup>1</sup>	—0.0005°	Urea	+0.0013°
KCl	+0.0003°	Alcohol	+0.0006°

These differences can hardly be looked upon as large even in the extreme cases of cane sugar and urea ; and they practically disappear altogether in the regions of greater concentration. It is not to be overlooked that these differences between Abegg's results and those found by me are *less* than the differences exhibited by the two parallel series of observations made by Abegg himself on the respective solutions. For a tabular exhibit of these differences the reader is referred to Abegg's paper.<sup>2</sup> The full significance of these facts appears very strongly in the results for tartaric acid, KCl, and alcohol. (See Figs. 2, 4, 8.) I may be allowed the privilege of expressing here my deep satisfaction at this splendid verification of my early work by such careful and conscientious investigators as Nernst and Abegg, especially in the case of the alcohol results, which have so long stood alone, and which the former work of Nernst and Abegg certainly did not confirm. That the greater accuracy of Abegg's new method should result in such close duplication of my values is most gratifying. I am however unable to agree with Abegg in his explanation of the *low* values for alcohol, namely, that they arise

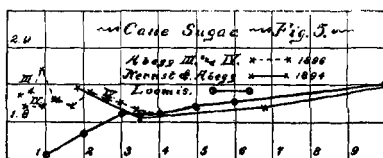
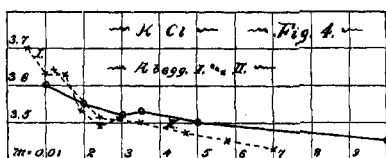


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<sup>1</sup>Princeton Bulletin, 1896, Oct. page 56.

<sup>2</sup>Zeit. phys. Chem. 20, 224 (1896).

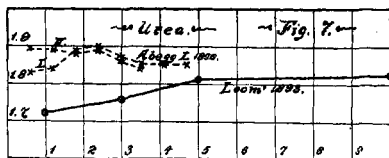
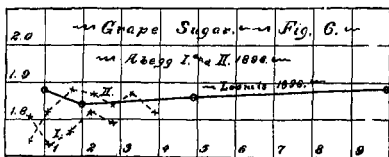
from inaccuracies in the generally accepted specific gravity tables,<sup>1</sup> particularly since such explanation would require that these tables are about five per cent wrong. I am not aware that the extensive and widely varied work on the properties of alcohol solutions has ever before raised any such suspicion. Quite recently Wildermann has similarly sought to explain the low values which I found for urea by supposing that I incorrectly determined the strength of the



original solution. Such an explanation is not at all improbable, and makes it desirable that the observers who repeat this work should start out from a normal solution of the compound prepared by direct weighing, and that they should then carefully determine its specific gravity after making sure that the urea is pure. The urea which I employed was the ordinary *c. p.* compound prepared by Henn and Kittler, Strasburg, and was used without recrystallization. The

sp. gr.  $\left(\frac{18^\circ}{4^\circ}\right)$  of the «normal» solution (normal at  $6^\circ\text{C}$ ) was 1.0148.

These data would enable any chemist to decide how much in error my «normal» solution must have been.



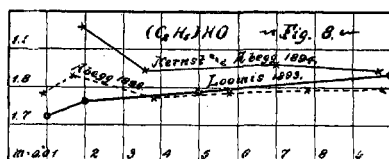
2. An examination of the experimental results affords the means for a trustworthy estimation of the method's accuracy.

It is to be observed in the first place that the careful isolation of the solution from disturbing influences together with the great uniformity of the stirring and extremely constant temperature of the

<sup>1</sup>Those of Mendelejeff were used in my work on alcohol. Abegg does not indicate whose tables he employed.

«protection bath» enable Abegg to attain an absolutely stationary mercury column, which according to his direct experiments could be maintained continuously for *three hours*, during which time no variation amounting to  $1/10000$  of a degree was observed.

May it not be asked if this surprising constancy may not be misleading? It certainly has proved so in the  $1/100^\circ$  thermometer used by me, and I have elsewhere ventured to suggest that this stationary position of the mercury should not be taken as a decisive indication that the temperature of the solution has become constant; since I have found that the mercury, having once become stationary, remains so for any length of time during which the bulb experiences only slight changes of temperature, say a few ten-thousandths of a degree. Alas, this is the most troublesome way in which, what Abegg calls the «inertia» of these fine thermometers comes to



light. It is for this reason that I have always been obliged to operate with a rising mercury column and that too with constant jarring, of great uniformity. In this way the errors arising from this

source always lie on the same side and in measuring depressions of the freezing point would largely drop out. I have repeatedly observed this absolute constancy of the *mercury column* during a period of ten minutes, but the observation has never produced any feeling but that of despair, since it is reasonably sure that an absolutely constant *temperature* cannot be maintained for a period of ten minutes, to say nothing about three hours.

That the constancy of Abegg's *thermometer* is no certain test of the constancy of the *solution's* temperature but is due to «inertia», I think appears from an examination of a series of observations which he made on the freezing point of water (page 216). Eight such observations are published by him together with the barometric pressure at the time of each. Correcting these observations to a constant pressure by using the data which were obtained directly by experiment, we find that these eight determinations vary among themselves  $0.005^\circ\text{C}$ . This is more than ten times greater than the estimated error of the method. Abegg, however, is led to



refer these great variations to *accidental impurities of the distilled water*. A moment's reflection shows that such supposed impurities would need to be so enormous that they would raise the water to the order of a 1/1000 normal solution at least, which would correspond to about 0.06 grams of sodium chlorid per liter ! Since Abegg operated on salt solutions containing only a trifle more than twice this amount (0.00241-normal), we are forced to believe that he must have given some due attention to the preparation of suitable water for his work as well as taken the usual precautions for its protection against accidental contamination. One is the more safe in making this assumption since he gives the molecular strength of his dilute solutions to the fifth decimal or to a degree of accuracy a hundred-fold greater than his supposition in regard to the impurities of the water itself would permit.

It seems most reasonable to suppose, on the contrary, that these variations in the observations, great as they are, are to be referred jointly to the «inertia» of the thermometer, and the inability of the method to reproduce and maintain exactly the true freezing temperature of the water.

It may not be without value to call attention to the variations in the similar observations made with my thermometer (1893-1896).

The first series, extending over a period of five weeks, and comprising *sixteen* determinations, showed a maximum variation of  $0.0015^{\circ}\text{C}$ .<sup>1</sup> The second series, made during a period of twelve weeks, and comprising *twenty-five* determinations, show a maximum variation of  $0.0038^{\circ}\text{C}$ .<sup>2</sup> While a third series, not yet published, made during twelve weeks of the past winter and comprising *nineteen* determinations show a variation of  $0.0030^{\circ}\text{C}$ . It needs to be added that in this latest series the variation is of the nature of an almost uniform rise during the entire period. While the variations in my determinations of the freezing point of water appear thus to be about fourfold less than those of Abegg, I have never been able to believe that any measurable part of the variation could be referred to «accidental impurities» in the water itself. In fact, it is so desira-

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<sup>1</sup>Wied. Ann. **51**, 512 (1894).

<sup>2</sup>Ibid. **57**, 515 (1896).

ble to *know* that the water which I employed remained free from such accidental impurities that I have always measured periodically its *electrical conductivity* with this in view. Fortunately, I have thus far found no evidence of any accidental contamination of my stock of distilled water.

We should now seek a final answer in regard to the accuracy of the method by a direct examination of the results themselves. At the outset it is apparent that this accuracy is considerably greater in the new than in the old method. Inspection, however, of the results as exhibited by the curves in Figs. 1-8, for example in Fig. 1, where the results for NaCl are plotted, shows that much is still to be desired. If we suppose, as Abegg undoubtedly does, that the irregularities of this NaCl curve have no significance with reference to the solution itself at these points, but are to be referred to experimental errors, then we are obliged to admit that in the region  $m = 0.022$  there is an experimental error of about *two hundredths* of a degree. Such errors must be assumed quite generally throughout the NaCl series as well as elsewhere in other solutions, in order to reduce the results to the required regularity. These errors are not to be explained by referring them to inaccuracy in the preparation of the solutions, though Abegg says this may amount to two per cent, since the total depression at  $m = 0.022$  in the case of NaCl is only  $0.0784^\circ$  and an error of two per cent would still be less than  $0.002^\circ\text{C}$ , while the actual error here is something like ten times this amount. A study of these NaCl results together with those for grape sugar, Fig. 6, will require Abegg to agree with me in believing that his method has not yet reached a degree of accuracy which will justify its application to «very dilute solutions», and that the region of dilution beyond the 1/100 normal, while the most important of all, has as yet furnished few if any trustworthy results.

3. A careful study of the present method, independent of the results obtained by its use, leads one to regard it as entirely free from objections in principle; and convinces one that it marks a positive advance in freezing-point methods. The fact that Abegg's results do not justify this conclusion is not decisive against it. It seems certain if he will subject each solution to a number of entirely independent observations, that the average values will show little trace

of irregularity. I have always made five or more such independent determinations of each solution, and while the average *variation* in these series is not far from a full thousandth of a degree, the *mean values* thus obtained have never shown the slightest irregularity except in the region of extreme dilution. The work involved is great, but the method so carefully developed by Abegg warrants the belief that if this course is followed great increase in accuracy will result and important theoretical conclusions be established.

For the present the questions remain :—

Is the molecular depression in the case of non-electrolytes *constant*?

Or does it increase uniformly with increase of concentration?

Or does it exhibit a minimum value?

A decisive experimental answer to these important questions is most desirable. The persistent effort to perfect experimental methods of which the present one of Abegg marks a positive advance, warrants the hope that in the near future the difficult problems which this region of experimental Physics presents may be solved.

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