Our method might also be used in investigating the conditions of water in soils.

Work on the freezing of hydrogels is being continued in this laboratory.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

THE MEASUREMENT OF CRYOSCOPIC CONSTANTS AT ELEVATED TEMPERATURES.

BY J. HOWARD MATHEWS.

Received March 27, 1917.

All of the really accurate work on freezing-point constants to be found described in the literature has been limited to measurements made on substances having rather low melting points, where temperature control of the surroundings is easy. Obviously it is highly desirable that we have at our disposal a method capable of giving the same degree of accuracy in measurement for solvents which have comparatively high melting points.

While it is true that a considerable amount of cryoscopic work has been done with solvents having higher melting points, a critical examination of the methods used reveals the fact that no very high degree of accuracy can be claimed. In most cases the methods have been very crude indeed, while even in those where more care was taken it is evident that the methods used leave much to be desired in the way of precision. Brief mention will be made of some of the methods previously used.

Tolloczko[1] worked with antimony trichloride, whose melting point is 73.2°, using the ordinary form of Beckmann freezing-point apparatus the outside of the water mantle being wrapped with asbestos to keep the temperature constant. This is a fair example of the methods that have been used by a number of investigators. A considerable inprovement in experimentation was made by Auwers,[2] who reported a number of determinations in which the highest freezing point studied was that of benzil, which is 94°. He used the ordinary Beckmann apparatus, but surrounded it by a constant temperature bath, which was of course a great advance over the arrangement used by Tolloczko. Eykmann[3] made a large number of measurements with his depression bottle. This bottle, or "depressimeter," is not surrounded by a bath at constant temperature and has no device for stirrring the contents (except shaking by hand), yet its sponsor considered it to be accurate to 0.01°.

A considerable amount of cryoscopic work with organic solvents has

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[1] *Z. phys. Chem.*, 30, 705 (1899).

[2] *Ibid.*, 18, 595 (1895); 30, 300 (1899); 32, 55 (1900).

[3] *Z. phys. Chem.*, 2, 964 (1888); 3, 113 and 203 (1889); 4, 497 (1889).

been done by a number of Italian investigators, in particular by Garelli and his co-workers;[1] and also by Bruni,[2] Padoa,[3] Mascarelli and Babini,[4] Olivari,[5] Poma,[6] and Jona.[7] The exact experimental details involved in the attainment of the results reported by these investigators unfortunately have not been stated.

The best apparatus that has been used heretofore for measuring cryoscopic constants at elevated temperatures is undoubtedly that used by Beckmann[8] in his measurements made on the halogen salts of mercury. Since these salts melt at temperatures between 200 and 300° his usual form of apparatus required considerable modification. The apparatus he devised for this particular work consisted of the usual form of freezing-point tube, holding the thermometer and a hand stirrer, contained in a larger tube which served as an air jacket. This, in turn, was surrounded by a cylindrical glass vessel having two openings at the top, one for a thermometer and one for a calcium chloride tube; and was filled with concentrated sulfuric acid which served as the heating bath. The whole apparatus was covered with a thick asbestos jacket to reduce loss of heat by radiation. The freezing points determined with this apparatus were considered to be accurate to 0.01°.

An electrically heated mantle ("electrische ofen"), consisting essentially of a tube wound with resistance wire, was used by Beckmann and Hanslian[9] in their work on mercuric iodide. By means of this mantle the temperature of the surroundings was kept constant to a few tenths of a degree. The apparatus has the disadvantage that the experimenter cannot see through the various walls and observe conditions inside the freezing-point tube. Judging from the published diagram and description of the apparatus, it seems rather improbable that the temperature was anywhere near uniform throughout the mantle.

Beckmann and Maxim[10] have mentioned the use of a vapor mantle in their cryoscopic work on the iodides of mercury. The temperature of this vapor mantle was controlled by boiling α-bromonaphthalene under a pressure which was regulated by a manostat. No further details are given as to the assembly of apparatus. The writer assumes that the

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[1] Garelli, *Gazz. chim. ital.*, **24b**, 263 (1894); Garelli and Ferratini, *Ibid.*, **23a**, 442 (1893); Garelli and Montanari, *Ibid.*, **24b**, 229 (1894).

[2] *Ibid.*, **28b**, 322 (1898).

[3] *Ibid.*, **41a**, 203 (1911).

[4] *Ibid.*, **41a**, 89 (1911).

[5] *Rend. Lincei*, **18b**, 287 (1909); *Atti accad. Lincei*, **22**, II, 697; *Ibid.*, **23**, I, 45.

[6] *Gazz. chim. ital.*, **41b**, 518 (1911).

[7] *Ibid.*, **39b**, 289 (1909).

[8] *Z. anorg. Chem.*, **55**, 175 (1907).

[9] *Ibid.*, **89**, 167 (1914).

[10] *Ibid.*, **89**, 169 (1914).

vapor mantle referred to is similar to the ordinary vapor mantle used by Beckmann in his ebullioscopic work, which arrangement is different from the one to be described in this paper. It may be well, however, to mention at this point the fact that the apparatus described in this paper was first built and used in the winter of 1912–13, considerably over a year before the work of Beckmann and Maxim appeared.

The writer has failed to find any account of a method which is capable of giving data accurate to 0.001° for cryoscopic measurements at elevated temperatures, and feels that with a number of the methods previously used the claimed accuracy of 0.01° is improbable.

Experimental.[1]

The apparatus devised for cryoscopic measurements at elevated temperatures is shown in Fig. 1. The freezing-point tube proper which is about 20 cm. long and 4 cm. in diameter, is placed in a larger tube, which serves as an air jacket, the purpose of which is to prevent sudden changes in temperature should the surroundings temporarily become slightly too warm or too cold. These two tubes, freezing-point tube and air-jacket, are suspended in the neck of a specially designed heating chamber, B, which constitutes the unique feature of the ensemble. This heating chamber,

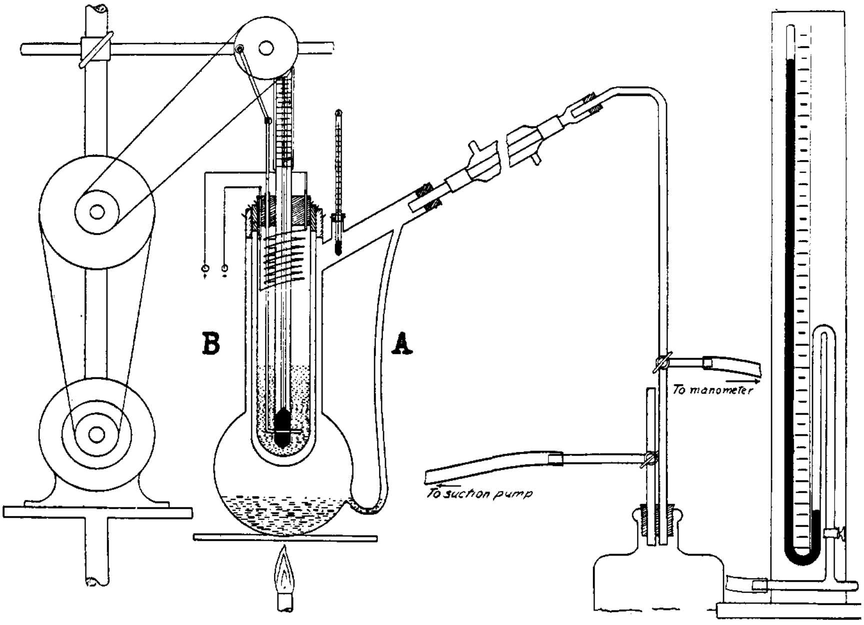

Fig. 1.

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[1] I am deeply indebted to three of my former students, Miss Katharine E. Faville, Miss Elizabeth F. Fox, and Mr. Clarence G. Sutton, for competent and painstaking assistance in making the measurements recorded in this paper.

or vapor mantle, constitutes a very efficient thermostat, whose temperature can be controlled easily. A suitable liquid, usually some hydrocarbon or mixture of hydrocarbons, having a boiling point a few degrees above the freezing point of the solvent to be studied, is placed in the bulb of this heating mantle and is made to boil by placing a small burner beneath. The vapor rises and completely envelopes the freezing-point tube, the uncondensed vapor passing on up the side arm to the condenser, through which cold water is flowing. From the condenser, the cool, condensed liquid is returned to the boiling chamber by way of the by-pass A, thus preventing the chilling of the liquid in the freezing-point tube, which would otherwise be experienced. It will be seen that there is a continual circulation of vapor through the apparatus, insuring a constant temperature throughout.

The reflux condenser is attached to a large reservoir (preferably a five-gallon carboy or bottle) which, in turn, is attached to a suction pump and to a manometer. The temperature of the vapor in the mantle surrounding the freezing-point tube and air jacket is regulated to any desired point by changing the pressure in the system, and is subject to both easy and accurate control. This temperature is read from a thermometer (capable of being read to 0.01°) introduced through the tubulure just below the reflux condenser. Once the pressure necessary to give any desired temperature is established, that temperature can be maintained indefinitely by controlling the pressure so that the manometer reading is constant.[1] As has been intimated, it was found desirable to have the air reservoir of several gallons' capacity to minimize pressure (and consequently temperature) fluctuations. While the apparatus is in use the suction pump (an ordinary water pump) is kept going continuously, the pressure in the system being regulated by the stopcock in the T tube leading to the pump. The maintenance of a constant temperature is, as can readily be seen, remarkably easy.

The liquid in the freezing-point tube is kept agitated by means of a stirrer consisting of a slight glass rod with a ring at the bottom encircling the thermometer bulb. The rod passes through a close fitting glass sleeve about two inches long, and is attached to an eccentric and pulley operated by a small motor, whose speed is controlled by a rheostat. The sleeve, which acts as a guide for the stirrer, fits closely to prevent loss of solvent by circulation of the vapor of the solvent through it.

The thermometer used in the work here recorded was a Beckmann having a large, long bulb and correspondingly large bore. By the use of a reading telescope (which eliminated parallax) readings to 0.001°,

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[1] While a manostat arranged to keep the pressure constant automatically would be desirable, it was not found to be really necessary. In future work, in which we hope to get a still greater accuracy, such a device will probably be used.

could be made with certainty. The thermometer was always tapped gently before being read, although the vibration due to the mechanical stirrer was sufficient to prevent "sticktion" of the thread.

While working with solvents which sublime easily, such as naphthalene, an error due to sublimation is likely to be made. This is a source of error, the importance of which has apparently been previously overlooked or underestimated. While working with naphthalene (the first solvent to be studied) we noticed that crystals formed in the upper part of the freezing-point tube, above the level of the side arm leading to the condenser, and also on the upper part of the stirring rod. The amount of solvent so sublimed was sufficient to cause serious error in our calculations. To avoid this condensation we placed a coil of fine platinum wire in the upper part of the tube, as shown in the diagram, and passed a feeble electric current through it. The quantity of current passing through the coil was regulated by means of an external resistance placed in series with it. This simple device prevented sublimation entirely.

In carrying out a determination, a weighed amount of the solid solvent to be studied was placed in the freezing-point tube and was melted by placing the tube in the vapor of some substance having a boiling point considerably above the melting point of the solvent, using the accessory apparatus shown in Fig. 2. While the solvent was melting, the liquid in the boiling chamber was brought to boiling and the temperature of the vapor adjusted to the freezing point of the solvent, by reducing the pressure to the proper point. After the freezing-point tube containing the molten solvent had been placed in the vapor mantle and the stirrer and thermometer had been adjusted, the temperature of the vapor was gradually lowered, by reducing the pressure, until crystals began to appear, at which point the pressure was again increased until the temperature of the vapor was at that point where a few crystals were in equilibrium with the liquid. The temperature necessary to insure equilibrium between the liquid and a very few crystals can be maintained indefinitely.

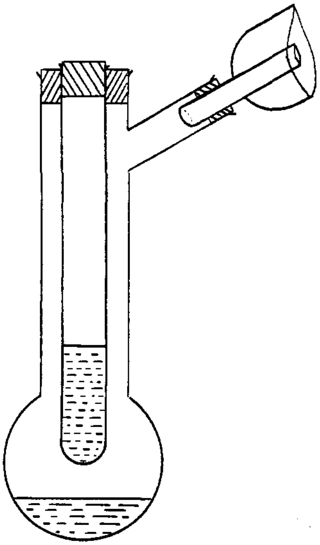

Fig. 2.

Once the desired experimental conditions had apparently been established, readings were taken on both thermometers at intervals of one minute, care being taken to keep the pressure constant. Having taken a sufficiently large number of readings, weighed amounts of the solute were added and a new series of readings were taken as before.

The constancy of the readings of the freezing point is all that can be desired. Once the proper temperature for the mantling vapor is determined, it can be kept at that point indefinitely, and the solution and a few crystals will remain in equilibrium as long as the adiabatic conditions are maintained. The first readings taken are of course not to be depended upon, as it takes from 20 to 40 minutes for the Beckmann thermometer to adjust itself to its new temperature environment; but after the thermometer has so adjusted itself the readings remain constant within the error of reading of a Beckmann thermometer. We have taken as many as forty-nine consecutive readings at intervals of one minute without finding a change of as much as 0.001°. Furthermore, if equilibrium is disturbed it can easily be restored and the temperature readings can be duplicated to 0.001°, as we have demonstrated repeatedly. A higher degree of accuracy than we have attained is impossible with the mercury thermometer. Our experience with the method has convinced us that it is sufficiently accurate to justify the use of a platinum resistance thermometer capable of giving readings to 0.0001°. This thermometer would have other decided advantages as well, such as freedom from hysteresis and "sticktion," and a quicker response to any slight changes in temperature, to say nothing of the elimination of the many corrections required in accurate mercurial thermometry.

To test the apparatus and method, determinations were made on the freezing point of several concentrations of anthracene in naphthalene, of anthracene in acetanilide, of anthracene in benzoic acid, and of anthracene in cinnamic acid. Each solvent was carefully purified, the test for purity being the requirement that all of the substance should solidify at a constant temperature.

Anthracene in Naphthalene.—The naphthalene was purified by sublimation. Its melting point was taken with a thermometer, the corrections for which had been furnished by the Bureau of Standards, and was found to be 79.25°. The anthracene was recrystallized three times from pure alcohol, washed with alcohol and dried. The liquid placed in the boiling-chamber was a mixture of benzene and toluene boiling at about 85° under atmospheric pressure.

In the table following the symbols have the following significance:

W = weight of solvent taken.

s = weight of solute.

Δ = the depression of the freezing point produced.

t = the number of successive readings, taken at intervals of one minute, during which the freezing point of the solution remained constant to ±0.001°.

K = the freezing-point constant, calculated from the equation

$$K = \frac{M \times \Delta \times W}{100\ s},$$

where

M = the molecular weight of the solute, and

L = the latent heat of fusion of the solvent, calculated from the van't Hoff relation

$$L = \frac{0.01985\ T^2}{K}.$$

TABLE I.[1]

No.	W (in g.).	s (in g.).	Δ.	t.	K.	L.
1.....	21.951	0.4056	0.715°	23 min.	68.91	35.74 cals.
2.....	21.951	0.7062	1.245	17	68.91	35.74
3.....	31.358	0.5009	0.620	11	69.12	35.63
4.....	28.029	0.7820	1.080	16	68.93	35.73
5.....	30.400	1.0060	1.283	13	69.04	35.68
6.....	31.289	1.0128	1.255	17	69.04	35.68
				Mean,	68.99	35.70 cals.

Eykmann's[2] data for naphthalene, as recalculated correctly by Auwers,[3] gave 67.7 as the mean value for K, and 36.40 cals. for its heat of fusion. Auwers' own work gave the values 69.4 and 35.87 for K and L, respectively.

The latent heat of fusion of naphthalene has been determined experimentally by Batelli,[4] who found the value 35.50 cals. at 79.2°; by Pickering,[5] who found the value 35.62 cals. at 79.86°; by Allouard,[6] who obtained the value 35.68 cals. at 79.97°; and by Bogojawlenski,[7] who obtained the value 34.69 cals. at 80.05°. The mean of the first three values is 34.60 cals., with which value our result is in excellent agreement. Barker[8] calculated the heat of fusion of naphthalene from accurate measurements of its vapor pressure, obtaining the value 34.65 cals. at 80°, which is somewhat lower than the values obtained by the direct methods, with the exception of that of Bogojawlenski.

Anthracene in Acetanilide.—The acetanilide was purified by two recrystallizations from alcohol. Its melting point as determined by means of a thermometer standardized at the Physikalisch-Technisch Reichsanstalt was found to be 113.94°. The anthracene was purified as already

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[1] Determinations 1 and 2 were made by Miss Faville; 3, 4, 5 and 6 by Miss Fox.

[2] *Z. phys. Chem.*, 3, 113 and 203 (1889); 4, 497 (1889).

[3] *Ibid.*, 18, 595 (1895).

[4] *Atti ist. Venice*, [6] 3, 1781 (1884–5); *Rend. Lincei*, 1, 621 (1885).

[5] *Proc. Roy. Soc.* (*London*), **49**, 18 (1890–1).

[6] *Ann. chim. phys.*, [3] **57**, 476 (1859); *Ann.*, 113, 150 (1860).

[7] *Chem. Zentr.*, **1905**, II, 945.

[8] *Z. phys. Chem.*, 71, 248 (1910).

described. The liquid in the boiling chamber was in this case a mixture of toluene and xylene boiling at 120° under atmospheric pressure. The data and the results of the calculations made therefrom appear in Table II.

TABLE II.[1]

No.	W (in g.).	s (in g.).	Δ.	t.	K.	L.
1.....	22.146	0.1520	0.267°	42 min.	69.27	42.90 cals.
2.....	21.663	0.4180	0.751	30	69.31	42.88
3.....	21.663	0.8528	1.533	28	69.34	42.86
4.....	21.663	1.2627	2.270	23	69.35	42.85
				Mean,	69.32	42.87 cals.

No work appears to have been done previously with acetanilide as solvent, nor have determinations of the heat of fusion of the substance been made.

Anthracene in Benzoic Acid.—The benzoic acid was recrystallized twice from absolute alcohol and then sublimed. The sample so obtained froze completely at 119.53°. Resublimed anthracene was used as solute. The liquid in the boiling chamber was a mixture of toluene and xylene having a boiling point at 124.5° under atmospheric pressure. The data obtained, with values of K and L calculated therefrom, appear in Table III.

TABLE III.[2]

No.	W (in g.).	s (in g.).	Δ.	t.	K.	L.
1.....	33.992	0.5102	0.741°	13 min.	87.92	34.79 cals.
2.....	33.992	1.0135	1.471	7	87.86	34.81
3.....	33.992	1.5097	2.191	6	87.85	34.81
				Mean,	87.88	34.80 cals.

The only cryoscopic work with benzoic acid as solvent to be found described in the literature is that of Garelli and Montanari,[3] in which the values 78.5 and 39.65 cals. were found for K and L, respectively. No determinations of the heat of fusion seem to have been made.

Anthracene in Cinnamic Acid.—The cinnamic acid used was recrystallized from pure alcohol until it had a constant freezing point, which was found to be 132.50°. The anthracene was prepared by recrystallization, as already described. The data obtained for the three concentrations used appear in Table IV.

TABLE IV.[4]

No.	W (in g.).	s (in g.).	Δ.	t.	K.
1........	33.06	0.8068	1.322°	17 min.	96.46
2........	33.06	1.0213	1.610	32	92.81
3........	33.06	1.6475	2.545	14	90.94

[1] Data taken by Miss Faville.

[2] Data taken by Miss Fox.

[3] *Gazz. chim. ital.*, 24*b*, 229 (1894).

[4] Data taken by Mr. Sutton.

Since the values of K decrease with increasing concentration, it is evident that the anthracene associates in cinnamic acid, and for this reason a calculation of the latent heat of fusion is impossible. No record of previous work with cinnamic acid as solvent has been found.

Conclusions.

From the work here recorded it is evident that:

(1) The apparatus described has given much more accurate cryoscopic data for substances having considerably elevated melting points than any which has been used heretofore.

(2) The method is one which can be used for a large number of substances covering a wide range of melting points, since it is possible to secure the necessary adiabatic conditions by simply choosing a liquid having an appropriate boiling point for the mantling vapor.

(3) It can safely be concluded that the more serious sources of error usually found in such cryoscopic measurements, in particular the errors due to imperfect adiabatic conditions and to the sublimation of the solvent, have now been removed.

(4) The limit of accuracy of the method seems now to be limited to the accuracy with which temperatures can be read by the thermometer.

Further work along this same line, but with a platinum resistance thermometer capable of reading temperatures to 0.0001°, is contemplated.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY.]

THE APPLICABILITY OF THE ISOHYDRIC PRINCIPLE TO TENTH-NORMAL MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE.[1]

BY N. EDWARD LOOMIS, J. L. ESSEX, AND MERLE R. MEACHAM.

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In a previous paper[2] Loomis and Meacham showed that within the limits of our knowledge of the contact potential of the system

$$0.1\ N\ \mathrm{HCl}\text{–}0.1\ N\ \mathrm{KCl}$$

the potential of the 0.1 *N* hydrochloric acid calomel electrode is identical with that of the 0.1 *N* potassium chloride calomel electrode, thereby indicating that at 0.1 *N* concentration hydrochloric acid and potassium chloride have approximately equal degrees of dissociation.

In accordance with the isohydric principle, it follows that if 0.1 *N* potassium chloride and hydrochloric acid are equally dissociated, these solutions may be mixed in any proportion without changing their de-

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[1] Reports on sections of this work were submitted to Purdue University by J. L. Essex and Merle R. Meacham in partial fulfilment of the requirements for the degrees of Master of Science and Chemical Engineer, respectively.

[2] THIS JOURNAL, 38, 2310 (1916).