THE HEATS OF FUSION OF SOME ORGANIC SOLVENTS WHOSE MELTING POINTS ARE RELATIVELY LOW.

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The heats of fusion of organic solvents, whose melting points are relatively low, have scarcely been measured up to the present. O. Maass and L. J. Waldbauer⁽¹⁾ measured the heat capacities of several organic solvents between various points at low temperatures and at room temperature, and thence calculated their heats of fusion. E. Beckmann and his co-workers⁽²⁾ measured the lowerings of freezing points of solutions in organic solvents and calculated the heats of fusion of those solvents by the van't Hoff's formula.

The present author also determined the lowerings of the freezing points of the solutions, and thence calculated the heats of fusion of several solvents by a thermodynamical formula. He, however, constructed an apparatus of new design, which was specially suitable for the determination of the melting points with a relatively small quantity of the samples.

I. The Apparatus and the Method of the Experiment.

The relation between the freezing point and the concentration of a solution is given by the following formula, which can be proved thermodynamically : that is,

$$\frac{d\ln N}{dT}=\frac{Q}{RT^2} \quad \cdots\cdots\cdots\cdots(1)$$

where N is the molar fraction of the solvent and Q is the heat of fusion of the solvent at the freezing point of the solution, T. Now, if the range of temperature is small and Q is taken as constant over this range, formula (1) can be integrated to the following :

$$\ln\frac{N}{N'}=\frac{Q}{R}\left\{\frac{1}{T'}-\frac{1}{T}\right\} \quad \cdots\cdots\cdots\cdots(2)$$

where T and T' are the freezing points of the solutions with the concentrations N and N' respectively. By this formula, the heat of fusion of the

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(1) Maass & Waldbauer, *J. Am. Chem. Soc.*, 47 (1925), 1.

(2) Beckmann & Waentig, *Z. anorg. allgem. Chem.*, 67 (1910), 17.
Beckmann & Faust, *Z. physik. Chem.*, 89 (1915), 249.

solvent can be calculated from the freezing points of two solutions at different concentrations.

It is general, however, that a pretty large quantity of the sample is necessary to determine the freezing points of organic solvents, because they are easy to supercool. The present author, therefore, cools the sample once down to the temperature where it perfectly solidifies, thence heats it up, and takes the point, where its melting finishes, as the temperature the same as the freezing point of the solution. Solid organic matters, however, are generally bad conductors of heat, and they can not be maintained at uniform temperature throughout all their parts during the heating, and consequently they can not melt at the same moment when they are heated. To overcome this difficulty, the present author designed the metal vessel shown in Fig. 1.

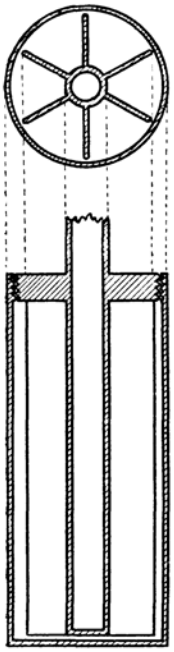

Fig. 1.

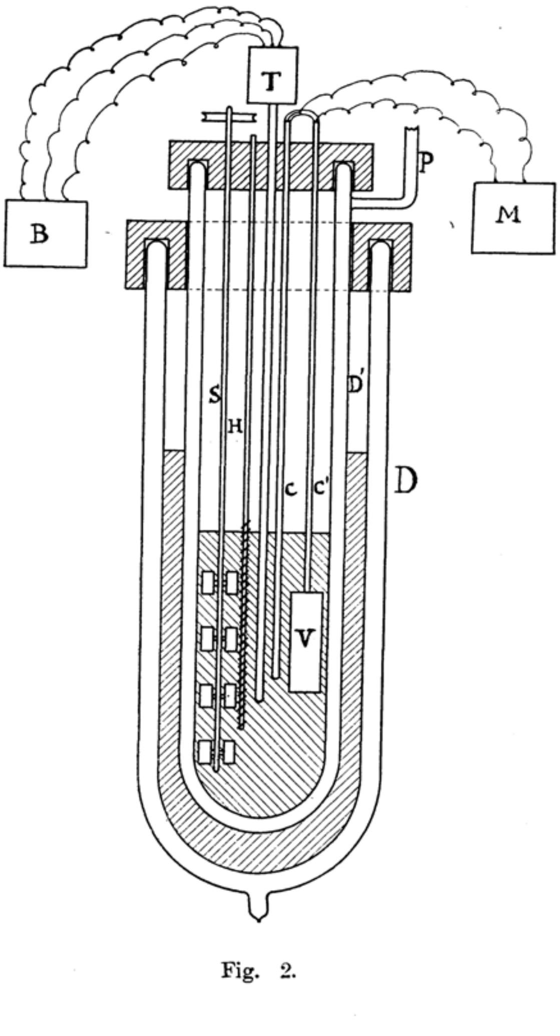

Fig. 2.

It consists of a cylindrical outer part and radial partition inside, whose function is to make heat conduction good so that the whole sample is maintained at the uniform temperature as far as possible. All the part of the vessel are made of brass, and the inner side is electrically coated with silver.

The whole apparatus is shown in Fig. 2. D is a large Dewar vessel, inside of which a double walled glass vessel D′ is placed ; the space between the double walls of this vessel is connected to a vacuum pump by the pipe P. V is the vessel for the sample shown in Fig. 1, in the middle hole of which one end of the thermocouple, C′, is inserted, the other end of it, C, is placed quite near to V. CC′ is an 8 series copper-constantan thermocouples, whose potential difference between C and C′ is measured by a millivoltmeter with 1/10 millivolt scale, M, and whose E.M.F. is 0.24 m.v. per degree centigrade. T is a platinum-resistance thermometer of about 2.5 ohms at 0°C., the resistance of which is measured by the bridge B, made by Leeds & Northrup Co, specially for the use with a resistance thermometer. By uniting these two the temperature can be measured with the precision of 1/100 degree centigrade. Inside the vessel D′, ether or pentane is put in, and this is stirred with the stirrer S to maintain a uniform temperature. H is a heater made of a coil of resistance wire, which is used for heating the liquid electrically.

The sample is put in the vessel V, the cover screwed in, sealed with water-glass, and then the vessel is placed in the liquid in D′. The space between the double walls of D′ is then filled with air to make heat conduction from the outside to the inside of the vessel good, and then liquid air is poured into D to cool the inside of D′. When the temperature of the liquid is about 20° below the point where the sample perfectly solidifies,—this is indicated by the cooling curve,—the vessel D is lowered so that D′ is out of the liquid air. Adjusting the electric current in the heater H and the degree of vacuum within the double walls, the heating rate inside D′ is regulated optionally. In this experiment the rate of 1.0—1.3 degree/minute is used. The temperature of the liquid in D′, which is measured by the thermometer T, is taken on abscissa and the E.M.F. of the thermocouple CC′, which corresponds to the temperature difference between the outside and the inside of V, is taken on ordinate, a curve is obtained. As the heat is absorbed at the region where fusion takes place, the temperature difference indicated by ordinate increases, and the curve ascending in this part, and when the heat absorption ends, the temperature difference again decreases and the curve descends ; thus it shows a maximum. The temperature where the extensions of the curve before and after the maximum intersect, minus the temperature difference corresponds to the maximum of the curve, is taken as temperature where fusion ends, that is the freezing point. Of course, this temperature may not indicate the true freezing point, but as the quantity which is needed is not the absolute values of the temperature, but the difference of the temperatures, no correction on this deviation is necessary.

II. The Results of the Experiment.

The materials used were all specially purified in this laboratory from the pure chemicals of Kahlbaum.

The results are tabulated in the following tables.

Solvent	Solute	Mol. % 100 *N*.	Melt. pt. *T*.	$\frac{1}{T}$	log *N*
Chloroform	—	100.00	211.59	0.004726	0.0000
	Toluene	97.73	211.09	0.004739	− 0.0100
	Acetone	96.78	210.50	0.004750	− 0.0142
	Toluene	95.13	210.00	0.004762	− 0.0217
	Ether	94.08	209.31	0.004777	− 0.0265
	Acetone	90.80	207.91	0.004810	− 0.0419
Acetone	—	100.00	179.37	0.005575	0.0000
	Toluene	98.28	178.67	0.005597	− 0.0075
	Toluene	97.66	178.19	0.005612	− 0.0103
	Toluene	94.18	176.51	0.005665	− 0.0260
	Ether	92.88	175.73	0.005691	− 0.0321
Carbon-bisulphide	—	100.00	162.30	0.003161	0.0000
	Toluene	98.35	161.02	0.006211	− 0.0072
	Toluene	97.43	160.33	0.006237	− 0.0113
	Toluene	93.93	157.30	0.006357	− 0.0272
Ethyl-ether	—	100.00	150.61	0.006640	0.0000
	Acetone	98.78	150.41	0.006650	− 0.0053
	Acetone	97.37	149.53	0.006688	− 0.0116
	CS_2	96.15	149.53	0.006688	− 0.0170
	Methyl-alc.	95.86	149.34	0.006696	− 0.0184
	Acetone	95.12	148.85	0.006718	− 0.0217
Methyl-alcohol	—	100.00	177.40	0.005637	0.0000
	Ether	98.92	176.17	0.005676	− 0.0047
	Toluene	96.84	173.81	0.005753	− 0.0139
	Acetone	96.62	173.52	0.005763	− 0.0148
	Toluene	95.96	173.13	0.005776	− 0.0179
Ethyl-alcohol	—	100.00	157.93	0.006332	0.0000
	CS_2	99.11	157.25	0.006359	− 0.0039
	Methyl-alc.	97.83	156.37	0.006395	− 0.0094
	Methyl-alc.	97.04	155.59	0.006427	− 0.0131

If the formula (2) holds in the solutions investigated, the points on the diagrams in which $\log N$ and $\frac{1}{T}$ are taken as co-ordinates are to be on straight lines for each solvent. As the values in the above table nearly satisfy this condition, the heats of fusion of the solvents can be calculated by the formula from the values of two points on these straight lines. The results of the calculations are as follows :

Solvent.	Heat of fusion.
Chloroform	2080 calories.
Acetone	1300
Carbon-bisulphide	660
Ethyl-ether	1400
Methyl-alcohol	600
Ethyl-alcohol	650

The heat of fusion of chloroform was given by Beckmann and Faust as 2100 cal., which coincides with that of ours.

The heats of fusion of acetone and methyl-alcohol were given by Maass and Waldbauer as 1140 cal. and 520 cal., respectively, which are smaller than those of ours, but perhaps it is better to say that they concide with each other within experimental errors.

The heat of fusion of ethyl-ether was given by Beckmann and Waentig as 2030 cal. which is much larger than that of ours.

Summary.

An apparatus which is suited to determine the lowering of freezing point of organic solvents was described.

The lowerings of the freezing points of the solutions of chloroform, acetone, carbon-bisulphide, ethyl-ether, methyl-alcohol and ethyl-alcohol were determined, and their heats of fusion were calculated.

This paper is a brief abstract of the following papers :

The heats of fusion of chloroform, acetone and carbon-bisulphide.
by S. Mitsukuri and S. Aoki.

The heats of fusion of ethyl-ether, methyl-alcohol and ethyl-alcohol.
by S. Mitsukuri and K. Hara.

which are going to be published in the Science Reports of the Tohoku Imperial University. The full description of the experiments and some discussions on the results are to be found in the above papers.

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