minke is two calories. This is good agreement considering all the difficulties encountered in this determination. Our results indicate a slight curvature.

Summary

Measurements of the electromotive forces of the cell $H_2 \mid KOH(m) \mid K_xHg \mid KOH(0.05) \mid H_2$ have been made from 0 to 35° inclusive at 5° intervals and *m* was varied from 0.1 to 4 *M*.

2. From these data, the activity coefficient, relative partial molal heat content, and the relative partial molal heat capacity have been computed. Satisfactory agreement with similar results derived from calorimetric data has been obtained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Carbon Disulfide from 15 to 300°K. The Entropy and Heat of Fusion of Carbon Disulfide

BY OLIVER L. I. BROWN[1] AND GEORGE G. MANOV

The heat capacity of solid and liquid carbon disulfide, and the heat of fusion have been determined in order to complete the data necessary for the calculation of the entropy of carbon disulfide.

Material.—The carbon disulfide was fractionally distilled several times after drying with calcium chloride. About two liters of material obtained in this way was fractionally distilled using a special column about 60 cm. high, packed with brass shoe eyelets. The distilling flask contained phosphorus pentoxide to remove the last traces of water, and the distillation was carried out in an atmosphere of helium gas to avoid possible oxidation of the carbon disulfide. About half the distillate was collected as a middle fraction, which served as the starting material for a new fractionation. This procedure was repeated a third time before the product was placed in the calorimeter. The calorimeter, which was copper, was filled in such a manner that the carbon disulfide came in contact with only helium, copper, glass and the solder used for sealing the top. A small amount of helium was admitted to ensure heat conduction in the sample before the calorimeter was sealed. From the change in melting point with percentage

TABLE I

HEAT CAPACITY OF CARBON DISULFIDE; 0°C. = 273.1°K.

Run	T, °K.	C_p cal./mole/deg.	ΔT
37	15.05	1.65	2.771
38	17.50	2.22	2.239
39	20.15	2.87	3.113
40	23.06	3.48	2.754
41	26.19	4.18	3.237
42	29.76	4.96	3.953
43	33.68	5.64	3.970
44	37.67	6.32	4.054
45	42.22	6.97	4.676
46	47.39	7.53	5.670
47	52.25	7.91	4.646
48	57.52	8.50	5.884
49	63.47	8.92	6.289
50	69.96	9.36	6.856
51	75.54	9.57	4.579
52	81.19	9.86	6.543
53	87.21	10.31	6.496
5	89.37	10.31	4.584
6	94.17	10.61	4.733
54	94.21	10.76	6.441
7	99.00	10.98	4.950
8	104.00	11.31	4.708
1	108.17	11.48	3.937
9	108.93	11.59	5.114
10	114.03	11.82	5.854
2	119.36	12.04	4.013
11	119.91	12.07	5.913
12	126.03	12.39	5.397
13	131.54	12.58	5.578
14	137.38	12.81	6.112
15	144.31	13.05	6.521
16	150.47	13.26	5.747
3	152.23	13.34	4.720
17	155.63	13.50	4.548
4	156.83	13.53	4.488
18	158.74	14.46	1.621
	161.11	Melting point	
19	163.93	18.10	4.895
20	169.51	17.97	6.314
21	176.17	17.91	6.968
22	183.04	17.94	6.672
23	189.64	17.99	6.418
24	192.30	17.91	5.926
25	198.44	17.90	6.446
26	205.28	18.00	7.007
27	211.83	18.02	5.884
28	219.31	17.95	7.620
29	227.34	17.93	8.347
30	235.80	18.00	7.764
31	244.25	18.00	8.712
32	253.06	17.88	8.430
33	261.66	18.10	8.034
34	269.69	18.08	7.478
35	278.22	18.06	8.932
36	297.43	18.17	9.440

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melted and the absence of appreciable premelting, it was estimated that the solid-insoluble liquid-soluble impurity was less than 0.001 mole per cent. Measurements were made on a sample of 145.987 g. (weight *in vacuo*).

Heat Capacity Measurements.—The method used for the heat capacity measurements has been described previously.[2] One calorie was taken equal to 4.1833 international joules, and the molecular weight of carbon disulfide was taken as 76.12. The heat capacities are tabulated in Table I, and plotted as a function of temperature in Fig. 1. The values of the heat capacities are listed in the order of increasing temperature, but are numbered in the order in which they were determined. No previous values for the heat capacity of solid carbon disulfide have been reported in the literature. Previous measurements on the liquid have been made by Koref,[3] Hartung[4] and Battelli.[5] Koref made seven determinations, all of which agree with our results to within 0.2%. Hartung reported only one value, which agrees with our results to within 0.16%. Our results are not in agreement with those of Battelli, whose values differ in some cases by as much as 17% from those reported here.

Melting Point and Heat of Fusion.—The melting point and heat of fusion were obtained by the method described by Johnston and Giauque.[6] The melting point determination is summarized in Table II. The resistance thermometer had a temperature coefficient of one ohm per degree in this range. The values of the resistance are included in the table because of the greater accuracy of the resistance thermometer for small temperature changes, although the actual temperatures were obtained from the thermocouple readings. The thermocouple was calibrated in terms of the laboratory standard No. 17, and is believed to be accurate to 0.05°K. After the completion of these measurements the thermocouple was compared directly with the boiling point of hydrogen and found to correspond to within 0.02°K.

Previous values for the melting point have been reported by Henning[7] (−112.00°C.), Timmermans, van der Horst and Onnes[8] (−111.6°C.), Timmermans[9] (−111.8°C.), Keyes, Townshend and Young[10] (−112.97°C.), and Skau[11] (−111.88°C.).

The heat of fusion of carbon disulfide was found to be 1049.0 cal. per mole. We were able to make only one heat of fusion measurement, as the calorimeter unfortunately split open after the completion of run No. 54, and while the calorimeter was being heated up to the melting point in order to make a second determina-

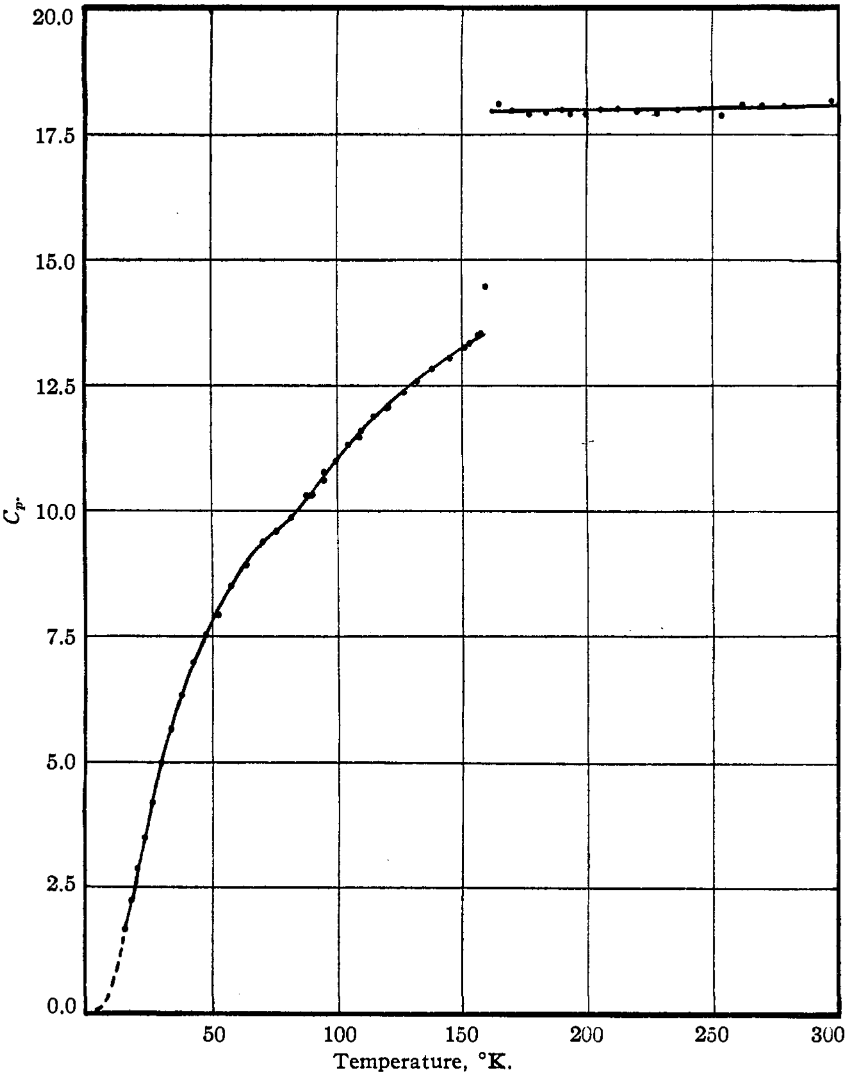

Fig. 1.—Molal heat capacity of carbon disulfide.

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TABLE II

MELTING POINT OF CARBON DISULFIDE

Date	Time	Resistance thermometer, ohms	T, °K.	% melted
7/20/35	3:00 p.m.	(Heated into melting point)		
	5:50 p.m.	151.3615	161.113	10
	7:10 p.m.	151.3610	161.118	10
7/21/35	12:45 a.m.	151.3611	161.114	30
	11:00 a.m.	151.3596	161.122	55
	2:00 p.m.	151.3606	161.101	70
	3:30 p.m.	151.3623	161.099	70

Average melting point 161.11 ± 0.05°K. (−111.99°C.).

tion of the heat of fusion. Since circumstances have arisen which make it unlikely that we will repeat these measurements, we have considered it best to offer our results even though the lack of a second heat of fusion makes it difficult to estimate the total probable error. We have no reason to suspect the accuracy of our single measurement, and in similar measurements made in this Laboratory by other workers the error has not usually exceeded 0.3% or about 3 cal. per mole. We have assigned the total probable error in the entropy as 0.5 E. U., which we believe to be a very conservative figure.

The heat of fusion of carbon disulfide has been determined indirectly by Timmermans,[12] and Mitsukuri and Aoki,[13] who measured the change in freezing point when organic solutes were dissolved in carbon disulfide. The former gives 1350 cal. per mole with an uncertainty of 10 to 20%, and the latter give 660 cal. per mole for the heat of fusion.

Entropy of Carbon Disulfide.—The entropy calculations are summarized in Table III. The graphical portion of the entropy was obtained from an integration of C_p *vs.* log T, and also as an arithmetical check, from an integration of C_p/T *vs.* T. The entropy of vaporization was taken from the work of Mathews,[14] who found by direct vaporization using electrical energy that the heat of vaporization of carbon disulfide at 45.29° was 84.07 ± 0.03 cal. per gram. The vapor pressure, heat capacity of the vapor, critical temperature and critical pressure used in calculating the last three items in Table III were taken from the "International Critical Tables."[15]

TABLE III

CALORIMETRIC ENTROPY OF CARBON DISULFIDE

0–15.05°K., Debye extrapolation	0.629 E. U.
15.05–161.11°K., solid, graphical	17.881
Fusion, 1049.0/161.11	6.511
161.11–298.1°K., liquid, graphical	11.080
298.1–318.39°K., liquid, extrapolated	1.192
Vaporization, 84.07 × 76.12/318.39	20.099
Compression, $R \ln (736.5/760)$	−0.063
318.39–319.35°K., vapor	.036
Berthelot ideal gas correction	.110

Entropy of ideal gas at 319.35°K., 57.48 ± 0.5

The entropy of gaseous carbon disulfide may be calculated from spectroscopic data using the moment of inertia of Cross,[16] which was checked by Sanderson,[17] the vibration frequencies of Dennison and Wright[18] and the methods of Giauque.[19] The result of this calculation at the temperature of the normal boiling point, 319.35°K., is summarized in Table IV.

TABLE IV

ENTROPY OF CARBON DISULFIDE FROM SPECTROSCOPIC DATA

$S°$ Rotation		15.725 E. U.
$S°$ Translation		39.255
$S°$ Vibration	$v_1 = 655.5$ cm.$^{-1}$	0.441
	$v_2 = 396.8$ (double wt.)	2.167
	$v_3 = 1532$	0.016
$S_{319.35}$; CS_2 (gas)		57.60

The calorimetric value (57.48 E. U.) agrees with the spectroscopic value (57.60 E. U.) well within the estimated experimental error.

Summary

The heat capacity and heat of fusion of carbon disulfide have been measured. The entropy calculated from calorimetric data agrees with the spectroscopic value within the experimental error. The entropy of liquid carbon disulfide at 298.1°K. was found to be 36.10 E. U.

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