

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

## The Heat Capacity of Ethane from 15°K. to the Boiling Point. The Heat of Fusion and the Heat of Vaporization

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Calorimetric measurements on ethane extending to low temperatures are of interest in the general program of obtaining entropies with the aid of the third law of thermodynamics. The value of the entropy of ethane obtained in this research is also important in demonstrating the correctness of the entropies of other simple hydrocarbons obtained by the application of the third law. This has been discussed briefly by Kemp and Pitzer.<sup>2</sup> A fuller discussion appears concurrently with this paper.

**Preparation.**—Ethane was prepared by the electrolysis of a potassium acetate solution as suggested by Moser.<sup>3</sup> For purification, the gas was passed successively through a 30% solution of sodium hydroxide, fuming sulfuric acid, concentrated sulfuric acid, an alkaline solution of sodium hydrosulfite, sodium hydroxide sticks and phosphorus pentoxide. Previous to the purification, the line was evacuated with a mercury diffusion pump. About 160 cc. of liquid ethane was prepared and then, for a final purification, fractionated. The middle fraction of 80 cc. was used in the measurements.

The purified ethane contained about 5 parts in a thousand of liquid-soluble, solid-insoluble impurity. This was calculated from the premelting heat effect evident in the heat capacity measurements preceding the melting point.

**Apparatus and Measurement of Amount.**—The measurements were made with a vacuum calorimeter assembly similar to that described by Giauque and Wiebe.<sup>4</sup> The copper calorimeter used in this research had a volume of 70 cc. A copper-constantan thermocouple, of laboratory designation W-23, was soldered in a well on the bottom of the calorimeter with Wood's metal. W-23 had previously been compared with thermocouple W-22, the present laboratory standard, which had been calibrated directly against a helium thermometer.

The amount of ethane was measured volumetrically in the calibrated bulb described in detail by Giauque and Johnston.<sup>5</sup> The following data from the "I. C. T." were

TABLE I

## THE HEAT CAPACITY OF ETHANE

Molecular weight = 30.0462. 1.1391 moles in calorimeter. 0° C. = 273.10° K.

T, °K.	$\Delta T$	$C_p$ , cal./deg./mole	Series
15.53	2.469	0.730	I
21.59	1.928	1.807	I

(1) National Research Fellow, academic years 1931-1933.

(2) Kemp and Pitzer, *J. Chem. Phys.*, **4**, 749 (1936).

(3) Moser, "Die Reindarstellung von Gasen," F. Enke, Stuttgart, 1920.

(4) Giauque and Wiebe, *THIS JOURNAL*, **50**, 101 (1928).(5) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

23.44	1.311	2.139	II
23.59	1.570	2.193	I
26.24	2.216	2.756	I
27.89	2.356	3.096	II
28.78	2.335	3.318	I
30.41	2.119	3.632	II
31.20	2.317	3.915	I
33.00	2.685	4.296	II
33.36	1.901	4.403	I
36.83	4.781	5.239	II
43.15	3.610	6.635	II
46.74	3.024	7.245	II
50.11	2.901	7.828	II
53.29	2.907	8.317	II
56.32	2.543	8.841	II
58.97	2.299	9.28	II
63.03	2.486	9.95	II
66.59	3.891	10.60*	II
70.87	3.975	11.33*	II
75.00	3.491	12.43*	II
78.55	3.090	13.45*	II
81.66	2.710	14.77*	II
84.37	2.365	16.68*	II
86.73	1.901	20.81*	II
89.87	Melting point		
91.59	0.756	16.31	III
92.97	1.645	16.35	III
94.94	1.594	16.33	III
96.60	1.566	16.30	III
98.23	1.498	16.45	III
98.89	1.477	16.33	III
100.49	1.500	16.32	III
104.05	2.504	16.38	III
106.67	2.434	16.45	III
109.24	2.361	16.46	III
111.67	2.308	16.51	III
114.20	2.250	16.48	III
116.24	2.565	16.52	III
119.33	3.308	16.55	III
122.72	3.185	16.58	III
125.96	3.089	16.62	III
129.47	3.587	16.61	III
134.49	4.123	16.63	III
138.72	3.976	16.66	III
142.83	3.845	16.69	III
145.97	3.714	16.73	III
149.80	3.631	16.79	III
153.58	3.519	16.90	III
157.95	4.638	16.90	III
162.82	4.280	16.96	III
167.43	4.430	17.08	III
172.02	4.144	17.09	III
176.54	3.994	17.21	III
180.88	3.891	17.22	III
184.1	Boiling point		

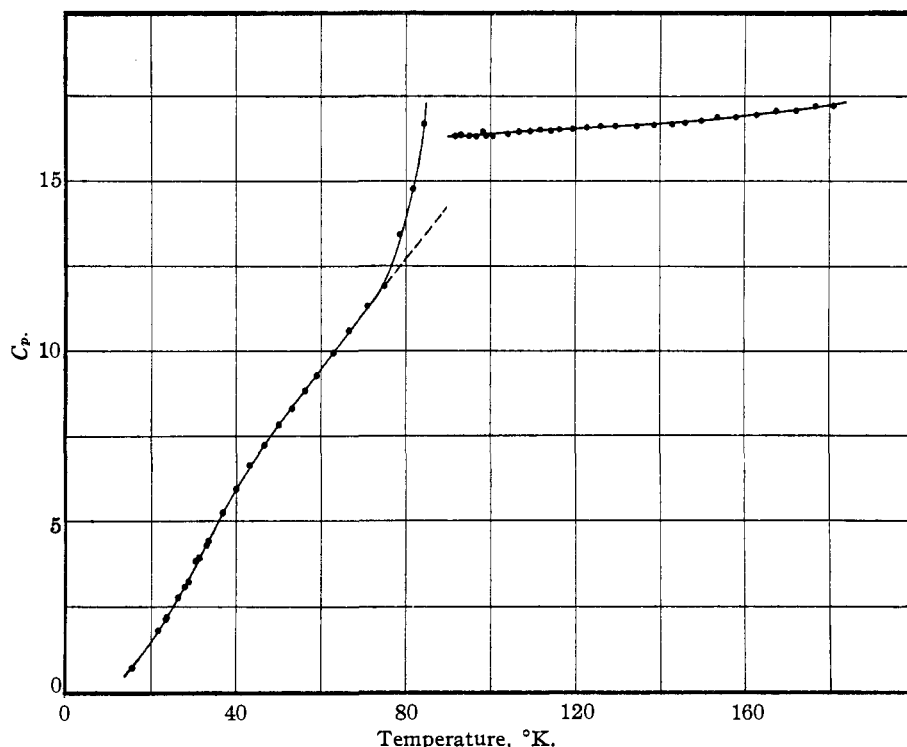


Fig. 1.—Heat capacity of ethane in calories per mole per degree.

used in the calculation: gas density at 0° and 760 mm. = 1.3566 g./l., molecular weight = 30.0462, coefficient of thermal expansion = 0.0036777 and the coefficient of deviation from Boyle's law = -0.00120. The pressure observations were converted to international atmospheres.

**The Heat Capacity of Ethane.**—The heat capacity measurements were calculated using the method described by Giaque and Johnston.<sup>5</sup> Corrections were made for the heat effects due to the evaporation into the dead space above the liquid in the calorimeter. The constants used for the energy calculation were: 1.0004 absolute joules = 1 international joule, 4.185 absolute joules = 1 calorie.

The heat capacity data are collected in Table I. Fig. 1 gives a graphical representation of the heat capacity measurements.

The heat capacity measurements in Table I which are marked with an asterisk are high due to the premelting effect caused by the presence of impurities in the ethane.

Values of the heat capacity of ethane taken from the smooth curve are given in Table II. Correction has been made in this table for the effect of premelting on the measured heat capacities. The percentage deviations of the results of other observers from those of this research are also given in Table II.

The measurements of Wiebe, Hubbard and Brevoort<sup>6</sup> on liquid ethane are in excellent agree-

(6) Wiebe, Hubbard and Brevoort, *THIS JOURNAL*, **52**, 611 (1930).

TABLE II  
HEAT CAPACITY OF ETHANE

Molecular weight, 30.0462. Values taken from smooth curve through observations.

T, °K.	$C_p$ , cal./deg./mole	% deviation W., H. and B. —W. and K.	% deviation E. and H. —W. and K.
15	0.655		
20	1.535		
25	2.470		
30	3.590		
35	4.785		
40	5.944		
50	7.810		
60	9.450		
70	11.09		
80	12.72		
90	16.30		
100	16.38	-0.1	9.9
110	16.47	- .6	9.6
120	16.55	- .7	14.2
130	16.61	- .4	16.2
140	16.69	- .1	17.9
150	16.79	+ .2	19.7
160	19.93	.4	21.7
170	17.08	.8	23.0
180	17.26	.7	24.0

ment with our results. The work of Eucken and Hauk,<sup>7</sup> however, shows extremely large deviations. Wiebe, Hubbard and Brevoort<sup>6</sup> have discussed these deviations adequately.

(7) Eucken and Hauk, *Z. physik. Chem.*, **134**, 161 (1928).

The accuracy of our measurements is estimated to be about 0.4% from 35°K. to the boiling point of ethane. At 25°K., the accuracy may be about 1% decreasing to about 2 or 3% at 20°K. and to about 5% at 15°K.

**The Melting Point and Boiling Point of Ethane.**—The melting point was observed for various percentages of the ethane melted. 89.87 ± 0.1° K. was obtained as the melting point of ethane, after appropriate correction was made for the amount of impurity present.

Only a rough measurement was made of the boiling point. The value obtained was 184.1 ± 0.1°K. Table III summarizes measurements of the melting and boiling points of ethane.

TABLE III  
MELTING POINT AND BOILING POINT TEMPERATURES OF ETHANE

(0°C. = 273.10°K.)		
M. p., °K.	B. p., °K.	Observer
...	180.1	Olszewski <sup>8</sup> (1894)
100.9	187.7	Ladenburg and Krügel <sup>9</sup> (1900)
...	184.6	Maass and McIntosh <sup>10</sup> (1914)
...	183.8	Burrell and Robertson <sup>11</sup> (1915)
...	184.47	Loomis and Walters <sup>12</sup> (1926)
89.45	...	Wiebe, Hubbard and Brevoort <sup>6</sup> (1930)
89.87 ± 0.1	184.1 ± 0.1	This research

**The Heat of Fusion.**—The heat of fusion was measured by starting the energy input at a temperature somewhat below the melting point and continuing until a temperature a few degrees above the melting point was reached. Correction was made for the  $\int C_p dT$  and the premelting effect. Table IV summarizes the data on the heat of fusion.

TABLE IV  
THE HEAT OF FUSION OF ETHANE

Temperature interval	Corrected total heat input per mole	$\int C_p dT$ and premelting effect	$\Delta H$ , cal./mole
86.729–91.038	739.6	57.0	682.6
86.776–90.447	727.1	44.1	683.0
86.395–91.696	756.7	73.6	683.1
	Accepted value		682.9 ± 0.7

(8) Olszewski, *Berl. Ber.*, **27**, 3305 (1894).

(9) Ladenburg and Krügel, *Ber.*, **33**, 637 (1900).

(10) Maass and McIntosh, *THIS JOURNAL*, **36**, 737 (1914).

(11) Burrell and Robertson, *ibid.*, **37**, 1893 (1915).

(12) Loomis and Walters, *ibid.*, **43**, 2051 (1926).

Wiebe, Hubbard and Brevoort<sup>6</sup> have obtained 667.5 cal./mole for the heat of fusion of ethane. This value is probably low due to their inability to apply an accurate premelting correction. They had a larger amount of impurity and could not extend their measurements to a low enough temperature in order to obtain a reasonably good idea of the course of the true heat capacity of ethane near the melting point.

**The Heat of Vaporization.**—The heat of vaporization of ethane was measured directly using the five-liter measuring bulb and a constant pressure regulating device described by Giauque and Johnston.<sup>5</sup> Table V gives a summary of the heat of vaporization measurements.

TABLE V  
THE HEAT OF VAPORIZATION OF ETHANE  
Boiling point 184.1°K. Molecular weight 30.0462

Amount evaporated, mole	Time of energy input, min.	$\Delta H$ at 760 mm., cal./mole
0.16816	75	3514
.18853	75	3520
.18443	75	3507
.16350	75	3513
.16382	75	3517
	Mean value	3514 ± 3.5

No other direct measurements of the heat of vaporization have been made. Values of the heat of vaporization obtained from vapor pressure equations cannot be given any weight in comparison to the direct observations.

**The Entropy of Ethane.**—An itemized account of the entropy of ethane is presented in Table VI. In obtaining the entropy of the solid, the extrapolated heat capacity curve in the neighborhood

TABLE VI  
THE ENTROPY OF ETHANE  
Molecular weight 30.0462

0–15° K. Debye function $h\nu/k = 131$	0.24
15–89.87°K., graphical	10.50
Fusion 682.9/89.87	7.60
89.87–184.1°K., graphical	11.95
Vaporization 3514/184.1	19.09
Entropy of actual gas at the boiling point	49.38 ± 0.15 e.u.
Correction for gas imperfection	0.16
Entropy of ideal gas at the boiling point	49.54 e.u.
$\int_{184.1}^{298.1} C_{p(gas)} d \ln T$ , graphical <sup>13</sup>	5.31
Entropy of ideal gas at 298.1° K.	54.85 ± 0.2 e.u.

(13) This is obtained from the data of Bucken and Parts, *Z. physik. Chem.*, **B20**, 184 (1933).

of the melting point was used, as the heat of fusion has been corrected for the effect of premelting. Thus very little uncertainty is introduced in the calculation of the entropy by the premelting effect.

The expression,  $\Delta S = R(27T_c^3P/32T^3P_c)$ , obtained by using Berthelot's equation in connection with the thermodynamic equation  $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ , was used to correct the entropy for gas imperfection at the boiling point. The critical pressure and temperature were taken as  $P_c = 48.8$  atm and  $T_c = 305.2^\circ\text{K}$ .<sup>14</sup>

The discussion of Kemp and Pitzer in the following paper shows that it is correct to use the third

(14) Pickering, *J. Phys. Chem.*, **28**, 97 (1924).

law value of the entropy of ethane in thermodynamic calculations.

### Summary

The heat capacity of solid and liquid ethane has been measured from  $15^\circ\text{K}$ . to the boiling point.

The melting point of ethane has been determined to be  $89.87 \pm 0.1^\circ\text{K}$ . The heat of fusion of ethane has been found to be 682.9 cal./mole.

The heat of vaporization of ethane at the boiling point has been found to be 3514 cal./mole.

The entropy of ethane gas at the boiling point calculated from the above data is 49.54 e.u. The entropy at  $298.1^\circ\text{K}$ . is 54.85 e.u.

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## The Entropy of Ethane and the Third Law of Thermodynamics. Hindered Rotation of Methyl Groups

By J. D. KEMP AND KENNETH S. PITZER<sup>1</sup>

Since the development of methods of calculating entropy from spectroscopic and molecular structure data, it has become possible to investigate the practical applicability of the third law of thermodynamics in a larger number of cases than previously. For many molecules, there is no question about the correctness of directly applying the third law to low temperature heat capacity measurements in obtaining entropies to be used in thermodynamic calculations. However, in certain cases, false equilibrium, encountered in obtaining low temperature calorimetric measurements, has complicated the use of the third law. The reasons for the complications in the several known cases are understood, and the immediate problem is to gather more information as to which molecules will be affected in order to increase the general usefulness of the third law.

The discrepancy found in hydrogen was first explained correctly by Giauque and Johnston,<sup>2</sup> who suggested the possibility of similar discrepancies in other molecules containing symmetrically placed hydrogens. Later investigations of the entropies of ammonia,<sup>3</sup> hydrogen sulfide<sup>4</sup> and

methane<sup>5</sup> have shown that there is no persistence of rotation in the crystal lattices of these molecules which contain symmetrically placed hydrogens. A discrepancy has been found to exist in the case of water, but it has been explained by Pauling<sup>6</sup> as due to the formation of hydrogen bonds in the crystal. In all of these cases, there is no reason to doubt that the calculation of the entropies from molecular structure data is correct.

As attempts are made to deal with larger and more complicated molecules, it becomes more difficult to obtain sufficient molecular data to make even approximately correct calculations of thermodynamic quantities. An increased knowledge as to which molecules the third law may be applied unambiguously will thus be very valuable.

It is of interest therefore to consider the correlation between the third law value of the entropy of ethane obtained by Witt and Kemp<sup>7</sup> and the various possible values of the entropy which may be calculated assuming different molecular models.

In this paper, a comparison of the third law value for the entropy of ethane with one derived

(1) Shell Research Fellow, academic year 1936-1937.

(2) Giauque and Johnston, *THIS JOURNAL*, **50**, 3221 (1928). See also Giauque, *ibid.*, **52**, 4816 (1930).

(3) Overstreet and Giauque, *ibid.*, **59**, 254 (1937).

(4) Giauque and Blue, *ibid.*, **58**, 831 (1936).

(5) Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

(6) Pauling, *THIS JOURNAL*, **57**, 2680 (1935).

(7) Witt and Kemp, *ibid.*, **59**, 273 (1937).