sent these data in tabular form, rather than by equations.

TABLE III

DIELECTRIC CONSTANTS OF THE METHANOL-WATER SYSTEM

Weight % methanol	Temperature, °C. 5.00	15.00	25.00	35.00	45.00	55.00
0.00	86.10	82.19	78.48	74.94	71.50	68.13
10.00	81.68	77.88	74.18	70.68	67.32	64.08
20.00	77.38	73.59	69.99	66.52	63.24	60.06
30.00	72.80	69.05	65.55	62.20	58.97	55.92
40.00	67.91	64.31	60.94	57.72	54.62	51.69
50.00	62.96	59.54	56.28	53.21	50.29	47.53
60.00	57.92	54.71	51.67	48.76	46.02	43.42
70.00	52.96	49.97	47.11	44.42	41.83	39.38
80.00	48.01	45.24	42.60	40.08	37.70	35.46
90.00	42.90	40.33	37.91	35.65	33.53	31.53
95.00	39.98	37.61	35.38	33.28	31.29	29.43
100.00	36.88	34.70	32.66	30.74	28.92	27.21

These values at 25.00° differ from the values of Jones and Davies[4] by less than one part in 500.

Summary

The dielectric constants of the methanol-water system have been measured for the temperatures of 5 to 55° by using an a.c. bridge circuit. It is believed that values given are accurate to within one part in 1000, or better, assuming that the dielectric constant of water at 25.00° is 78.48.[7]

MADISON, WISCONSIN RECEIVED NOVEMBER 19, 1945

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

The Heat Capacity, Vapor Pressure, Heats of Fusion and Vaporization of Cyclopropane. Entropy and Density of the Gas[1]

BY R. A. RUEHRWEIN[2] AND T. M. POWELL[3]

This paper is a report on the low temperature calorimetric investigations of cyclopropane. By means of these data and the third law of thermodynamics a value of the entropy of the gas has been obtained and this value compared with that calculated from spectroscopic and molecular data. The two values agree within their limits of error.

The measurements were made in a calorimeter with the laboratory designation Gold Calorimeter II. The apparatus and method of measurement have been described previously.[4]

Preparation and Purity of Cyclopropane.—The cyclopropane was obtained from the Ohio Chemical Company. It was purified by distilling through a vacuum-jacketed fractionating column packed with single-turn glass helices. From calorimetric measurements of the premelting effect the impurity was estimated to be 0.03 mole per cent.

The Melting Point of Cyclopropane.—A summary of the observations on the melting point is given in Table I.

The Vapor Pressure of Cyclopropane.—The vapor pressure was measured with a Société Génévoise cathetometer with a precision of 0.002 cm. It was used as a comparison instrument for a standard meter suspended between the arms of a mercury manometer. The manometer was in a case in which the air was circulated to ensure a uniform temperature. The acceleration of gravity was taken as 979.973 cm. sec.$^{-2}$ for this location and the standard acceleration as 980.665 cm. sec.$^{-2}$. The meniscus corrections were taken from the work of Cawood and Patterson[5] and data given in the "I.C.T."[6] were used to correct the observations to international cm. of Hg.

TABLE I

MELTING POINT OF CYCLOPROPANE

0° C. = 273.10° K.

Time	% Melted	T, °K., resistance thermometer	T, °K., thermocouple
4/27			
10:18 p. m.	Heated into melting point		
11:05 p. m.	10	145.413	145.42
12:00 m.	10	145.397	145.40
4/28			
12:35 a. m.	10	145.392	145.40
1:03 a. m.	10	145.390	145.40
1:35 a. m.	Supplied heat		
10:50 a. m.	30	145.491	145.50
11:20 a. m.	30	145.490	145.49
2:16 p. m.	Supplied heat		
5/1			
12:01 a. m.	56	145.515	145.54
12:39 a. m.	Supplied heat		
11:00 a. m.	80	145.515	145.54
		Accepted value	145.54

The data have been represented by the equation, 183.1 to 241.1° K.

$$\log_{10}P \text{ (inter. cm. Hg)} = 9.03877 - \frac{1348.2}{T} - 0.00823\ T + 7.45 \times 10^{-6}T^2 \quad (1)$$

The vapor pressure observations are compared

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(1) Presented to the American Association for the Advancement of Science, Pasadena Meeting, June, 1941.

(2) Present address: Monsanto Chemical Company, Dayton, Ohio.

(3) Present address: Standard Oil Co., Richmond, Calif.

(4) (a) Blue and Giauque, THIS JOURNAL, **57**, 991 (1935); (b) Giauque and Wiebe, *ibid.*, **50**, 101 (1928); (c) Giauque and Johnston, *ibid.*, **51**, 2300 (1929); (d) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(5) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. I.

with Equation 1 in Table II. The temperatures are given to 0.001° only because of the high relative accuracy.

From Equation 1 the boiling point of cyclopropane was found to be 240.30° K.

TABLE II

VAPOR PRESSURE OF CYCLOPROPANE

Boiling point 240.30° K. (0° C. = 273.10° K.)

T, °K.	$P_{\text{obsd.}}$, int. cm. Hg	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$T_{\text{obsd.}} - T_{\text{calcd.}}$
183.131	2.626	−0.001	+0.006
191.350	4.895	− .014	+ .044
195.695	6.673	+ .002	− .003
199.856	8.824	− .000	+ .001
204.943	12.202	− .004	+ .006
209.926	16.491	+ .003	− .003
215.046	22.085	.000	.000
220.053	28.959	+ .001	− .000
225.131	37.588	+ .001	− .000
229.877	47.390	.000	.000
235.177	60.618	.000	.000
238.351	69.839	+ .013	− .004
241.077	78.559	− .017	+ .005

In Table III the melting and boiling points are compared with those obtained by previous observers. The boiling points of the previous investigators have been corrected to 76 cm. by means of Equation 1.

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF CYCLOPROPANE

M. p., °K.	B. p., °K.	Observer
146.5	239.1	Ladenburg and Krugel[7] (1900)
146.1	238.91	Trautz and Winkler[8] (1922)
....	240.34	Ashdown, Harris and Armstrong[9] (1936)
145.54	240.30	This research

The Calorimetric Observations.—The amount of cyclopropane used for the heat capacity measurements was found by condensing and weighing the material in a steel bomb equipped with a steel valve and ground glass joint through which it could be filled. The bomb weighed 450 g. and had a capacity of 150 cc. A weight of 69.583 g., equivalent to 1.6537 moles of cyclopropane, was used for the measurements.

The heat capacity observations on solid and liquid cyclopropane are given in Table IV. The value marked with an asterisk is high due to premelting. The results on the liquid were corrected for vaporization into the small gas space of the calorimeter and connecting line. In making this correction the measurements of Grosse and Linn[10] on the density of cyclopropane were used. A small pressure of helium gas was introduced into the calorimeter during the measurements on the solid to ensure the attainment of thermal equilibrium. One international joule was taken as 4.1832 calories in calculating energy.

TABLE IV

MOLAL HEAT CAPACITY OF CYCLOPROPANE

(0°C. = 273.10°K.) Molecular weight, 42.078; 1.6537 moles in calorimeter.

T, °K.	ΔT	C_p, cal./deg. mole	T, °K.	ΔT	C_p, cal./deg. mole
14.45	1.594	0.631	114.39	5.469	13.20
16.86	3.217	0.871	120.00	5.814	13.60
19.80	2.812	1.307	125.89	6.097	14.09
22.78	3.319	1.858	131.82	5.769	14.54
26.09	3.249	2.496	137.36	5.427	15.20[a]
29.82	4.193	3.245	145.54	Melting point	
33.96	4.015	4.192	153.65	6.449	18.06
37.60	3.319	4.980	160.44	6.842	17.96
41.12	3.493	5.592	167.33	6.604	17.96
47.84	4.019	6.744	174.17	6.648	17.97
52.06	4.429	7.443	182.26	7.056	18.02
56.97	5.359	8.179	188.44	6.811	18.10
62.00	4.756	8.860	195.55	6.568	18.17
67.18	5.615	9.393	202.80	6.909	18.31
72.54	5.113	9.952	210.00	6.671	18.45
77.42	4.690	10.37	217.17	6.709	18.61
82.32	4.971	10.84	224.27	6.471	18.81
87.49	5.203	11.26	230.86	5.682	19.05
92.57	4.867	11.70	237.04	5.434	19.35
97.55	5.068	12.14	242.83	5.313	19.39
103.44	5.784	12.47	240.30	Boiling point	
109.03	5.447	12.89			

[a] High due to premelting.

Heat capacity values taken from a smooth curve through the observations are given in Table V. The curve should give the heat capacity to within 0.2% above 35° K.; at 20° K. the error may be about 1% and at 15° K. as much as 5%.

TABLE V

MOLAL HEAT CAPACITY OF CYCLOPROPANE

Molecular weight, 42.078. Values taken from a smooth curve through the observations.

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
15	0.68	130	14.39
20	1.34	140	15.18
25	2.27	145.54	Melting point
30	3.31	150	18.12
35	4.42	160	17.97
40	5.41	170	17.95
45	6.28	180	18.00
50	7.11	190	18.11
60	8.59	200	18.26
70	9.71	210	18.45
80	10.62	220	18.69
90	11.49	230	19.01
100	12.27	240	19.44
110	12.94	240.30	Boiling point
120	13.62		

The observations on the heat of fusion are given in Table VI. The measurements were started a

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(7) Ladenburg and Krugel, *Ber.*, **33**, 638 (1900).

(8) Trautz and Winkler, *J. prakt. Chem.*, **104**, 37 (1922).

(9) Ashdown, Harris and Armstrong, THIS JOURNAL, **58**, 850 (1936).

(10) Grosse and Linn, *ibid.*, **61**, 751 (1939).

little below the melting point and ended somewhat above. A correction was applied for the $\int C_p dT$ and for the small amount of premelting that had occurred at the starting temperature due to the impurity.

TABLE VI

MOLAL HEAT OF FUSION OF CYCLOPROPANE

Melting point 145.54° K. (0° C. = 273.10° K.)

Temperature interval	Cor. heat input, cal. mole^{-1}	$\int C_p dT$ cal. mole^{-1}	Pre-melting cal. mole^{-1}	ΔH, cal. mole^{-1}
141.570–150.176	1444.61	145.61	2.6	1301.6
140.691–148.843	1434.57	134.87	1.8	1301.5
140.178–147.203	1412.63	112.83	1.4	1301.2
			Mean value	1301

For measurements of the heat of vaporization the amount evaporated was measured by means of a 5-liter thermostated bulb, initially filled with mercury which was removed automatically as the gas was accepted at constant pressure. This apparatus has been described previously.[4c] The cyclopropane from two sets of three of these fillings was collected and weighed in the steel bomb mentioned above. From these data a value of the gas density was calculated. The data are shown in Table VII.

TABLE VII

GAS DENSITY OF CYCLOPROPANE

$T = 25°$ C.

Bulb volume, cc.	Pressure, inter. cm. Hg	Total amt., g.	λ
5432.2	72.302		
5321.6	75.569	27.536	−0.0138
5333.3	75.978		
5325.8	76.159		
5322.5	77.156	28.114	−0.0155
5320.7	76.388		
$PV = RT(1 + \lambda P)$		Accepted value	−0.0150

The accepted value, $\lambda = -0.0150$, is a weighted mean because of a rather large line volume correction in the first bulb filling. The density calculated to 1 atmosphere was 1.7463 ± 0.0009 g./liter at 25.00°. Corrections were applied to the measurements of the heat of vaporization for the small amount of gas in the line connecting to the calorimeter and for the fact that the temperature at the start and end of the measurement was not exactly the vaporization temperature. The measurements of the heat of vaporization are given in Table VIII.

The value of the heat of vaporization obtained from the vapor pressure observations and given in Table VIII includes a gas imperfection correction of −148 cal. mole.$^{-1}$ In obtaining the gas imperfection, Berthelot's equation was used with reasonable assumptions for the values of the critical constants, $T_c = 375$ °K., $P_c = 50$ atm., which fit the value of the gas density at 25° found above. Rather large variations of the values of the assumed critical constants do not appreciably change the calculated value of λ at the boiling point.

TABLE VIII

HEAT OF VAPORIZATION OF CYCLOPROPANE

Boiling point, 240.30° K.

Run	Moles evaporated	Time of energy input, min.	ΔH vap., cal. mole^{-1}
1	0.21038	51	4789
2	.22030	52	4791
3	.22114	52	4796
4	.22178	52	4797
		Average value	4793 ± 3
From vapor pressure equation 1 assuming a Berthelot gas			4775

The value of the heat of vaporization obtained from the vapor pressure measurements is given no weight in comparison with the direct calorimetric result but the rather good agreement justifies the use of Berthelot's equation with the assumed critical constants in obtaining the gas imperfection correction to the value of the entropy.

The Entropy of Cyclopropane.—A summary of the calculation of the entropy from calorimetric data is given in Table IX.

TABLE IX

THE MOLAL ENTROPY OF CYCLOPROPANE FROM CALORIMETRIC DATA

0–15°K. Debye function, $h c \nu / k = 130$	0.243
15–145.54°K., graphical	15.733
Fusion 1301/145.54	8.939
145.54–240.30°K., graphical	9.176
Vaporization 4793/240.30	19.946
Entropy of actual gas at boiling point	54.04 ± 0.1
Correction for gas imperfection	0.13
Entropy of ideal gas at 1 atm. and 240.30°K.	54.17 cal. deg.$^{-1}$ mole^{-1}

The correction for gas imperfection was calculated from the Berthelot gas expression

$$S\text{ ideal} - S\text{ actual} = 27RT_c^3P/32T^3P_c$$

using the assumed critical constants as mentioned above.

The entropy of cyclopropane has been calculated by Linnett[11] and Kistiakowsky and Rice.[12] The fundamental frequency assignment of Linnett as modified by Kistiakowsky and Rice to give better agreement with the observed value of the heat capacity of gas is

3000(1), 1485(1), 1187(1), 1070(1), 3000(2), 1435(2), 1022(2), 860(2), 1000(1), 3050(1), 1041(1), 3080(2), 1125(2) and 740(2) cm.$^{-1}$

In calculating the moments of inertia the C–C distance of 1.53 Å. was taken from the election diffraction investigations of Pauling and Brock-

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(11) Linnett, *J. Chem. Phys.*, **6**, 692 (1938).

(12) Kistiakowsky and Rice, *ibid.*, **8**, 610 (1940).

way.[13] The value of 1.09 Å. was used for the C–H distance and the H–C–H angle was taken as 116°56′ as suggested by Linnett.[11] From the data the moments of inertia times 10^{40} g. cm.^{2} were found to be $I_1 = I_2 = 42.3$ and $I_3 = 67.4$. The symmetry number is 6.

In these calculations the nuclear spin entropy, $6R \ln 2 = 8.263$ cal./deg. per mole, has been neglected. The values are compared in Table X. Those calculated from the molecular data may be in error by several hundredths of a unit.[14]

TABLE X

T, °K.	Calorimetric data Actual gas	 Ideal gas	Molecular data less nuclear spin entropy
240.30	54.04	54.17	54.26
298.10	...	56.75	56.84

The agreement of the two entropy values is within their limits of error and shows that cyclopropane approaches zero entropy as the absolute zero is approached.

The value of the entropy calculated from the molecular data is probably the more accurate of the two and this value, 56.84 cal./deg. per mole at 298.10°K., is the one to be used in thermodynamic calculations.

Summary

The heat capacity of solid and liquid cyclopropane has been measured from 15°K. to the boiling point.

The melting and boiling point temperatures were found to be 145.54 and 240.30°K., respectively (0°C. = 273.10°K.).

The heats of fusion and vaporization were determined by calorimetric observation to be 1301 and 4793 cal. mole^{-1}, respectively.

The vapor pressure of liquid cyclopropane was measured and the data has been represented by the equation

$$183 \text{ to } 241°\text{K.} \quad \log_{10} P(\text{inter.cm.Hg.}) = 9.03877 - \frac{1348.2}{T} - 0.00823T + 7.45 \times 10^{-6}T^2$$

The density of cyclopropane gas at 298.10°K. and one atmosphere was found to be 1.7463 g./liter.

The calorimetric data have been used to calculate the entropy of cyclopropane gas and this value has been compared with one obtained from molecular data and it is found that the entropy of cyclopropane approaches zero near the absolute zero of temperature.

The most reliable value of the entropy is the one obtained from molecular data, 56.84 cal./deg. per mole at 298.1°K. and one atmosphere. This value does not include the nuclear spin entropy.

RECEIVED MARCH 7, 1946

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[13] Pauling and Brockway, THIS JOURNAL, **59**, 1223 (1937).

[14] Note added in proof.—The modified frequency assignment of Smith, *Phys. Rev.*, [2] **59**, 924 (1941), and an H–C–H angle of 136° as suggested by his measurements of the rotational structure of the C–H vibration give 54.20 for the entropy at 240.30°K. which is in better agreement with calorimetric entropy. The corresponding value at 298.10°K. is 56.81 cal./deg. per mole.

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

The Thermodynamics of 2,2-Dimethylbutane, Including the Heat Capacity, Heats of Transitions, Fusion and Vaporization and the Entropy

BY JOHN E. KILPATRICK AND KENNETH S. PITZER

These measurements were made primarily to test the reliability of the general formulas[1,2] for the entropies of paraffin hydrocarbons proposed by one of us in 1940. As can be seen from Table X the agreement is excellent. In addition an interesting sequence of transitions was found in this substance, this sequence being very similar to that of cyclopentane.

Apparatus.—Three different calorimeters were used in this investigation. Hereafter they will be referred to as calorimeters I, II and III. The same numerals will be used to designate the three series of measurements performed, respectively, in the three calorimeters.

The basic apparatus, excluding the calorimeter, was essentially the same in all three series of measurements. This apparatus and calorimeter I have been described previously.[3]

In series I, measurements were made from 14° K. to above the triple point. At this time, it became obvious that a small leak had developed in the calorimeter. This series was terminated. Since it proved to be impractical to repair the leak a new calorimeter was constructed.

It was intended that calorimeter II should duplicate calorimeter I; however, certain changes were made inadvertently which caused it to be slow to reach equilibrium. Therefore, no heat capacity measurements with calorimeter II are reported. Calorimeter III was generally similar, but its platinum resistance thermometer was constructed with wire helices on a mica cross and extended to the top of the calorimeter.

The thermometers of calorimeters II and III were annealed in the usual manner and calibrated at the hydrogen triple point and at several vapor pressures of hydrogen, at the 43.76° K. transition of oxygen, its triple point and several vapor pres-

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[1] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

[2] Pitzer, *Chem. Rev.*, **27**, 39 (1940).

[3] L. Guttman and K. S. Pitzer, THIS JOURNAL, **67**, 324 (1945).