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

Methyl Bromide. The Heat Capacity, Vapor Pressure, Heats of Transition, Fusion and Vaporization. Entropy and Density of the Gas

BY CLARK J. EGAN AND J. D. KEMP[1]

Entropies obtained from low temperature calorimetric data with the aid of the third law of thermodynamics recently have been employed to estimate the magnitudes of the potential barriers hindering the free rotation of methyl groups in hydrocarbon molecules.[2-4] In these calculations the height of the barrier has been determined as that necessary to bring the spectroscopic entropy value into agreement with the experimental entropy value. This procedure assumes that the entropies of these molecules containing methyl groups can be obtained correctly from low temperature experimental measurements.

Because the presence of similar barriers in the methyl halides is quite unlikely, the entropies of these compounds may be obtained readily from spectroscopic and molecular structure data. Calorimetric investigations of these halides offer then an opportunity to compare the experimental and spectroscopic entropies in order to confirm further the above assumption.

Purification of Methyl Bromide.—Methyl bromide from a cylinder was condensed in the calorimeter without purification. From the change of the melting point with percentage melted, the amount of impurity was estimated to be 0.1 mole per cent. Another portion of material from the cylinder was distilled twice in a vacuum-jacketed fractionating column, the middle one-third being collected each time. This procedure did not appreciably decrease the amount of impurity. The end portions of the first distillation were then bubbled through 36 *N* sulfuric acid and passed through a tube containing phosphorus pentoxide. This treatment removed practically all of the impurities and this portion was used for the heat capacity measurements. Additional material purified in the same manner was used in the measurements of the heats of vaporization. From the constancy of the melting point and the course of the premelting heat capacity curve, the amount of liquid-soluble solid-insoluble impurity was estimated to be 0.001 mole per cent.

Apparatus and Measurement of Amount. The Density of Methyl Bromide Gas at 1 Atmosphere and 298.10°K.—The calorimetric apparatus and procedure have been described previously.[5,6] Gold Calorimeter IV was used for the investigation.

After the heat capacity measurements the amount of material in the calorimeter, 2.0610 moles, was condensed and weighed in a previously evacuated bulb. The methyl bromide used for the heats of vaporization was measured volumetrically by means of the 5-liter measuring bulb described by Giauque and Johnston.[7] The gas was then condensed and weighed in order to determine its density under these conditions. At P near 1 atm. and T near 298°K. the molal volume V was found to be

$$V = 82.06T/P - (569 \pm 5)\text{ cc.} \qquad (1)$$

This, combined with the molecular weight of CH_3Br, 94.950,[8] gives 3.9739 ± 0.0009 grams/liter for the density of methyl bromide gas at $P = 1$ atm. and $T = 298.10$°K.

Vapor Pressure.—The procedure used in the measurements of vapor pressure has been described previously.[5] The observations have been represented by the equation

liquid methyl bromide, 203 to 278°K.

$$(0\text{°C.} = 273.10\text{°K.})\ \log_{10} P(\text{Int. cm. Hg}) = -(1541.437/T) + 8.49274 - 0.00424740T + 1.7599 \times 10^{-6}T^2 \qquad (2)$$

A summary of the measurements is presented in Table I. The calculated and observed values are compared in columns 3 and 4. The temperatures have been given to 0.001° because of the high relative accuracy. The absolute temperatures may be in error by several hundredths of a degree. Column 5 contains values of the rate of change of pressure with temperature calculated from equation (2).

The boiling point calculated from equation (2)

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(1) Present address: Standard Oil Company of California, Richmond, Calif.

(2) Kemp and Pitzer, *J. Chem. Phys.*, **4**, 749 (1936); THIS JOURNAL, **59**, 276 (1937).

(3) Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

(4) Kemp and Egan, THIS JOURNAL, **60**, 1521 (1938).

(5) Kemp and Giauque, *ibid.*, **59**, 79 (1937).

(6) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(7) Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

(8) Int. At. Wt. Committee, *ibid.*, **60**, 737 (1938).

TABLE I

VAPOR PRESSURE OF LIQUID METHYL BROMIDE

0°C. = 273.10°K.

T, °K.	P	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$T_{\text{obsd.}} - T_{\text{calcd.}}$	dP/dT, cm./deg.
203.186	1.298	−0.008	+0.083	0.101
211.245	2.383	.000	.000	.170
220.247	4.418	+ .013	− .045	.288
228.834	7.534	+ .002	− .005	.451
236.484	11.709	− .002	+ .002	.651
243.098	16.739	+ .012	− .014	.875
250.633	24.467	+ .001	.000	1.193
258.008	34.644	− .002	.000	1.581
258.016	34.664	+ .006	− .004	1.582
265.020	47.250	.000	.000	2.027
270.801	60.178	− .003	+ .001	2.456
274.232	69.097	+ .009	− .003	2.739
277.682	79.056	.000	.000	3.044

is 276.66 ± 0.05°K. (3.56 ± 0.05°C.). This is higher than the value 276.33°K. from the vapor pressure equation of Hsia.[9]

Melting Point.—The melting point was observed with various percentages of the methyl bromide melted. The results are summarized in Table II.

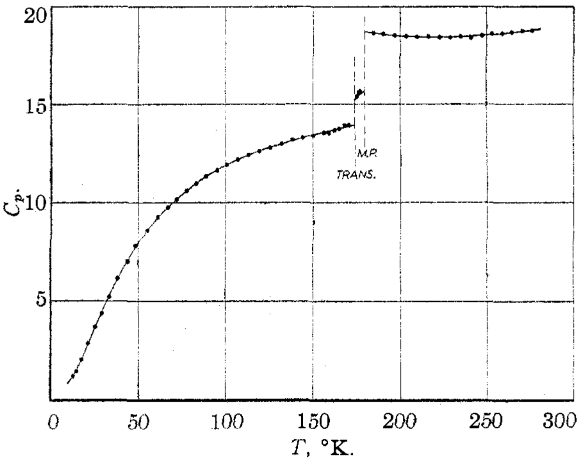

Fig. 1.—Heat capacity of methyl bromide in cal./deg. per mole.

Transition Point.—Methyl bromide undergoes a transition in the solid about 5.7° below the melting point. Determinations of the transition temperature are summarized in Table III. During these observations equilibrium was established very slowly. A region of indifference exists in which the methyl bromide may be superheated or supercooled 0.1–0.2° above or below 173.75°K.

Heat Capacity of Methyl Bromide.—No previous measurements of the heat capacity were found in the literature. The present observations are tabulated in Table IV. One calorie was taken equal to 4.1833 International joules. A graphical representation of the data is shown in Fig. 1. Table V contains values of the heat capacity taken from a smooth curve through the data.

Heat of Transition.—The transition in solid methyl bromide has not been reported previously. Six determinations of the heat of transition were made. The results are summarized in Table VI.

The spread of the measured values for the heat of transition is outside of the limits of accuracy of the measurements. However, in determinations 4, 5 and 6 there was evidence that, due to supercooling, some of the high temperature form

TABLE II

MELTING POINT OF METHYL BROMIDE

0°C. = 273.10°K.

Time	% melted	T, °K. resistance thermometer	T, °K. thermocouple
0:00		Stopped supply of heat	
1:30	10	179.439	179.43
2:00	10	179.440	179.44
2:30	10	179.437	179.44
2:50		Stopped supply of heat	
4:10	20	179.440	179.44
4:50	20	179.447	179.43
5:30	20	179.443	179.43
6:00		Stopped supply of heat	
7:10	40	179.440	179.44
7:45	40	179.439	179.44
8:10		Stopped supply of heat	
10:00	65	179.439	179.44
10:40	65	179.438	179.44

Accepted value 179.44 ± 0.05°K.

TABLE III

TEMPERATURE OF TRANSITION IN SOLID METHYL BROMIDE

Date	Method of approach	Amount of high temp. form present, %	T, °K., from thermocouple	Time in hours after heating or cooling	Drift in degrees per hour
4/30/37	Heating	30	173.84	4	0.011 cooling
	Heating	57	173.86	5	.010 cooling
5/1/37	Cooling	89	173.46	7	.039 warming
6/4/37	Cooling	30	173.67	15	.002 warming
	Heating	40	174.07	1.5	.027 cooling
	Heating	48	174.11	1	
6/5/37	Cooling	36	173.65	18	
	Heating	49	174.10	1	
6/7/37	Heating	15	173.81	4	.010 cooling
	Heating	35	174.01	2	.012 cooling
	Cooling	22	173.71	19	
	Heating	62	174.07	2.75	.010 cooling
	Heating	76	174.10	1.5	

Accepted value 173.75 ± 0.15°K.

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[9] Hsia, *Z. ges. Kälte-Ind. Beihefte*, Series 1, No. 2, 1 (1931).

TABLE IV

HEAT CAPACITY OF METHYL BROMIDE

Molecular weight, 94.950; 2.0610 moles in calorimeter. 0°C. = 273.10°K.

T, °K.	C_p cal./deg. per mole	Approx. ΔT	Series
12.56	1.209	1.8	V
14.62	1.452	2.3	V
17.49	2.046	3.4	V
21.39	2.874	4.4	V
25.45	3.709	3.7	V
29.16	4.394	3.8	V
33.53	5.216	4.4	V
38.27	6.170	5.7	V
44.18	7.047	6.0	V
49.79	7.840	5.2	V
55.19	8.602	5.7	V
61.13	9.278	6.2	V
66.87	9.758	5.6	V
72.21	10.18	5.1	V
77.54	10.62	5.7	V
83.01	10.99	5.3	V
88.60	11.36	5.9	V
94.53	11.65	6.0	V
100.55	11.95	6.1	V
106.72	12.22	6.2	V
112.98	12.44	6.3	V
119.17	12.64	6.0	V
125.46	12.80	6.6	V
131.92	13.01	6.3	V
138.06	13.21	6.1	V
144.01	13.32	5.8	V
150.23	13.42	6.4	V
156.45	13.59	6.1	V
159.28	13.56	6.1	I
162.40	13.69	6.0	V
165.27	13.77	5.9	I
168.21	13.95	5.7	V
170.70	13.97	4.7	I
173.75	Transition temperature		
175.21	15.41	1.0	IV
176.41	15.56	1.3	IV
176.48	15.66	2.6	I
176.88	15.68	2.2	III
177.76	16.41	1.1	IV
179.44	Melting point		
184.46	18.63	3.9	II
190.08	18.62	6.4	II
196.54	18.52	5.9	II
202.92	18.49	6.4	II
209.63	18.45	6.3	II
216.05	18.48	6.1	II
222.40	18.43	6.0	II
228.61	18.42	5.9	II
234.74	18.46	5.7	II
240.60	18.41	5.6	II
247.07	18.53	5.5	II
252.86	18.61	5.4	II
258.47	18.64	5.3	II
264.25	18.69	5.7	II
270.21	18.77	5.5	II
275.59	18.78	4.5	II
276.66	Boiling point		

TABLE V

HEAT CAPACITY OF METHYL BROMIDE

Molecular weight, 94.950; 0°C. = 273.10°K. Values taken from a smooth curve through the observations.

T, °K.	C_p cal./deg. per mole	T, °K.	C_p cal./deg. per mole
15	1.540	140	13.21
20	2.560	150	13.44
25	3.600	160	13.66
30	4.554	170	13.88
35	5.488	173.75	Transition temp.
40	6.366	175	15.36
45	7.170	177	15.53
50	7.925	179	15.70
55	8.594	179.44	Melting point
60	9.155	180	18.70
65	9.600	190	18.59
70	10.02	200	18.51
75	10.42	210	18.45
80	10.79	220	18.43
85	11.12	230	18.44
90	11.42	240	18.48
95	11.68	250	18.56
100	11.92	260	18.65
110	12.34	270	18.74
120	12.67	276.66	Boiling point
130	12.96	280	18.84

TABLE VI

HEAT OF TRANSITION OF METHYL BROMIDE

No.	Temp. interval, °K.	Corrected heat input per mole	$\int C_p dT$	ΔH cal./mole	Series
1	173.010–175.060	155.8	42.5	113.3	I
2	173.333–175.786	166.6	53.8	112.8	III
3	173.247–175.535	164.1	50.0	114.1	V
4	173.271–175.937	164.9	58.4	106.5	
5	171.842–175.190	183.4	71.7	111.7	
6	171.553–175.246	191.9	79.0	112.9	
		Accepted value		113.4 ± 1	

was already present at the start of the heating period. For this reason these values were given no weight in obtaining the accepted value.

Heat of Fusion.—No measured values of the heat of fusion were found in the literature. The present measurements are summarized in Table VII.

TABLE VII

HEAT OF FUSION OF METHYL BROMIDE

Temp. interval, °K.	Corr. heat input per mole	$\int C_p dT$	ΔH cal./mole
177.826–182.511	1545	115	1430
178.006–181.879	1524	95	1429
175.556–181.742	1574	146	1428
	Average value		1429 ± 2

Heat of Vaporization.—The methyl bromide was vaporized from the calorimeter into the 5-liter measuring bulb mentioned previously. A constant pressure regulating device described by Giauque and Johnston[7] was used. Table VIII contains a summary of the individual measurements. The value given by Hsia,[9] and that calculated from equation (2) and Berthelot's equation are also included.

TABLE VIII

HEAT OF VAPORIZATION OF METHYL BROMIDE

Boiling point, 276.66°K.; molecular weight, 94.950.

No. mole vaporized	Time of energy input, min.	ΔH at 760 mm. cal./mole
0.22073	47	5714
.22870	48	5719
.22616	48	5711
	Average value	5715 ± 6
From vapor pressure equation (2). (This includes a Berthelot correction of −189 cal.)		5716
Value of Hsia		5885

Entropy from Calorimetric Data.—The calculation of the entropy of methyl bromide at the boiling point, 276.66°K., from calorimetric data is summarized in Table IX.

TABLE IX

ENTROPY OF METHYL BROMIDE FROM CALORIMETRIC DATA

0–15°K., Debye extrapolation, ($hc\nu/k$ = 91)	0.61
Solid, 15–173.75°K., graphical	19.328
Transition, 113.4/173.75	0.653
Solid, 173.75–179.44°K., graphical	0.489
Fusion, 1429/179.44	7.964
Liquid, 179.44–276.66°K., graphical	8.034
Vaporization, 5715/276.66	20.657
Entropy of actual gas at the boiling point	57.74 ± 0.1
Correction for gas imperfection	0.12
Entropy of ideal gas at 1 atm. and 276.66° K.	57.86 cal./deg. per mole

The correction for gas imperfection was obtained from the expression

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

Measured values of the critical temperature and critical pressure could not be found in the literature. T_c was estimated to be 475°K. and P_c to be 68 atm.

Entropy from Spectroscopic and Molecular Structure Data.—Stevenson and Beach[10] recently have calculated the entropy of methyl bromide at 298.10°K. The same frequencies and molecular constants were used in the present calculation at the boiling point

C–Br = 1.91 ± 0.06 Å.[11]
C–H = 1.09 Å.
H–C–H = 111°

The values used for the natural constants were those given in the "International Critical Tables." From the above data the moments of inertia times 10^{40} g. cm.^{2} were found to be $I_1 = 5.36$ and $I_2 = I_3 = 85.3$. The symmetry number σ was taken equal to 3.

The following vibration frequencies were used.[12–14]

cm. $^{-1}$	Weight
$\nu_1 = 2900$	1
$\nu_2 = 3061$	2
$\nu_3 = 1305$	1
$\nu_4 = 1450$	2
$\nu_5 = 610$	1
$\nu_6 = 957$	2

Table X contains a summary of the calculation. An uncertainty of ±0.06 Å. in the C–Br distance affects the entropy by ±0.12 cal./deg. per mole. The entropy effect due to the presence of isotopes and of nuclear spin has been neglected.

TABLE X

ENTROPY OF METHYL BROMIDE AT ONE ATMOSPHERE FROM SPECTROSCOPIC AND MOLECULAR STRUCTURE DATA

	T = 276.66°K.	T = 298.10°K.
$S_{\text{trans.}} = 3/2\ R \ln M + 5/2\ R \ln T - R \ln P - 2.300$	39.203	39.572
$S_{\text{rot.}} = R/2 \ln I_1I_2I_3 \times 10^{120} + 3/2\,R \ln T - \text{R} \ln 3 - 6.851$	18.226	18.448
$S_{\text{vib.}} = \Sigma_{\nu_1 \text{ to } \nu_6} S_{\text{Einstein}}$	0.563	0.720
Entropy in cal./deg. per mole	57.99	58.74

The good agreement between the experimental entropy at the boiling point, 57.86 ± 0.10 cal./deg. per mole and the spectroscopic value, 57.99, further establishes the validity of using the third law of thermodynamics in conjunction with low temperature calorimetric data to obtain the entropies of compounds containing methyl groups.

The experimental entropy (ideal gas) at 298.10°K. is 58.61 cal./deg. per mole, and the spectroscopic value (ideal gas) is 58.74 cal./deg. per mole.

Summary

The heat capacity of condensed methyl bromide has been measured from 15°K. to the boiling point.

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(10) Stevenson and Beach, *J. Chem. Phys.*, **6**, 25 (1938); **6**, 108 (1938).

(11) Lévy and Brockway, THIS JOURNAL, **59**, 1662 (1937).

(12) Bennett and Myer, *Phys. Rev.*, **32**, 888 (1928).

(13) Barker and Plyler, *J. Chem. Phys.*, **3**, 367 (1935).

(14) Adel and Barker, *ibid.*, **2**, 627 (1934).

This substance has a transition in the solid about 5.7° below the melting point. Equilibrium in the transition was attained very slowly and the methyl bromide could be superheated or supercooled one or two-tenths of a degree above or below the transition point, 173.75 ± 0.15°K.

The melting point was found to be 179.44 ± 0.05°K., the boiling point 276.66 ± 0.05°K., the heat of transition 113.4 ± 1 cal./mole, the heat of fusion 1429 ± 2 cal./mole, and the heat of vaporization 5715 ± 6 cal./mole.

Vapor pressure measurements have been made on liquid methyl bromide and the results have been represented by the following equation

liquid methyl bromide, 203 to 278°K. (0°C. = 273.10°K.)

$$\log_{10}P(\text{Int. cm. Hg}) = -(1541.437/T) + 8.49274 - 0.00424740T + 1.7599 \times 10^{-6}T^2$$

The density of methyl bromide gas at 298.10°K. and one atmosphere was found to be 3.9739 ± 0.0009 grams/liter.

The entropy of methyl bromide (ideal gas) at one atmosphere and at the boiling point, 276.66°K., has been calculated from calorimetric data to be 57.86 ± 0.10 cal./deg. per mole and compared with the value 57.99 obtained from spectroscopic data.

The good agreement indicates that it is correct to use the third law value in thermodynamic calculations. It also gives more experimental substantiation to the assumption made in the calculation of potential barriers in compounds containing methyl groups, namely, that the entropies of these compounds may be obtained correctly from low temperature calorimetric data.

The experimental entropy (ideal gas) at 298.10°K. is 58.61 cal./deg. per mole, and the spectroscopic value (ideal gas) is 58.74 cal./deg. per mole.

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[CONTRIBUTION FROM THE BURROUGHS WELLCOME & CO. U. S. A. EXPERIMENTAL RESEARCH LABORATORIES]

2-Alkyl-1,2,3,4-tetrahydroisoquinoline Hydrochlorides[1]

BY JOHANNES S. BUCK AND WALTER S. IDE

With a view to carrying out a detailed pharmacological examination of the effects of various 2-alkyl groups on the action of tetrahydroisoquinolines, three series of 2-alkyl-1,2,3,4-tetrahydroisoquinolines were prepared. One series has no nuclear substituents, the second carries 6,7-dimethoxy groups and the third has 6,7-dihydroxy groups. Hydrochlorides were chosen for pharmacological reasons. In no case was a substituent present in the 1-position.

The preparation of the unsubstituted compounds was carried out substantially according to the method of Wedekind, *et al.*[2] and offered no particular difficulties. However, a general method was required for future work, and Wedekind's procedure could not be applied to the substituted derivatives. owing to the relative inaccessibility of substituted isoquinolines. Attempts were made to N-alkylate homoveratrylamine by the Decker[3] method with a view to cyclizing the alkylated amines,[4] but these did not succeed with alkyl groups larger than ethyl, the alkiodides of the Schiff bases being non-crystalline and the homogeneity of the secondary amine being therefore in doubt. However, some 2-ethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline was made by this route, from ethylhomoveratrylamine.

Direct alkylation of 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline[5] with ethyl iodide gave considerable amounts of quaternary compound and unchanged material, with some of the desired 2-ethyl derivative.[6] The method, however, was regarded as unsatisfactory. Similar objections apply to the use of toluene sulfonic esters.[7] Attempts to alkylate by means of α-bromo acids[8] gave only the hydrobromide of the starting material.

Finally, 6,7-dimethoxy-3,4-dihydroisoquinoline was investigated. This readily formed crystalline

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(1) This work is part of a joint research being carried out in collaboration with a pharmacological group at the above laboratories. The pharmacological data were contributed by this group.

(2) Wedekind and Oechslen, *Ber.*, **34**, 3986 (1901); Wedekind and Ney, *ibid.*, **42**, 2138 (1909); **45**, 1298 (1912).

(3) Decker and Becker, *Ann.*, **395**, 362 (1913).

(4) *Cf.* Buck, THIS JOURNAL, **56**, 1769 (1934).

(5) Forsyth, Kelly and Pyman, *J. Chem. Soc.*, **127**, 1659 (1925), but prepared from homoveratrylamine by the method of German Patent 257,138 (*cf.* ref. 4.).

(6) *Cf.* German Patent 270,859.

(7) *Cf.* Földi, *Ber.*, **55**, 1535 (1922).

(8) *Cf.* Bischoff and Mintz, *ibid.*, **25**, 2314 (1892).