molecule or the assumption that a certain fraction of the acetone molecules dissociate directly into two methyl radicals and carbon monoxide. The fraction is a function of the absorbed wave length.

3. A mechanism is advanced to account for the facts.

4. Biacetyl is formed largely as a result of a wall reaction, although some homogeneous reaction between acetyl radicals must occur.

5. The best value for the energy of activation for dissociation of the acetyl radical into carbon monoxide and a methyl radical is about 18 kcal.

ROCHESTER, NEW YORK RECEIVED APRIL 20, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of Isobutane

BY J. G. ASTON, R. M. KENNEDY AND S. C. SCHUMANN

The comparison of the entropy values for gaseous ethane obtained by use of the third law with those calculated from the spectroscopic data has indicated that the potential hindering the internal rotation of the methyl group is 3150 cal.[1] Similarly a potential of 4200 cal. hindering the internal rotation of the methyl groups in tetramethylmethane (neopentane) has been inferred.[2,3,4] From these results Pitzer has interpolated the potential hindering the internal rotation of the three methyl groups in isobutane to be 3800 cal.[5] The following paragraphs describe an investigation of the thermal properties of isobutane extending down to 11.9°K. which shows the hindering potential to be 3870 cal. if certain assumptions about the vibration spectrum are valid.

Preparation and Purification of Isobutane.—Tertiary butyl alcohol, purified by distillation followed by several recrystallizations to constant melting point (m. p. 23.83–23.91°), was dehydrated at 300 to 310° by passing it through a horizontal tube 80 cm. long, 2.1 cm. in diameter, packed for 76 cm. with a mixture of 90% alumina (80 mesh) and 10% Pyrex glass wool. The effluent vapor was passed first through a condenser to remove as much water as possible, next through three scrubbers filled with 25% sodium hydroxide and lastly through a tube 40 cm. long, 1.8 cm. in diameter and packed with dry alumina. The vapor was collected in a series of solid carbon dioxide–acetone traps. The alcohol was added at a rate of 100 cc. per hour. A total of 650 cc. of crude liquid isobutylene was obtained—a yield of 85%.

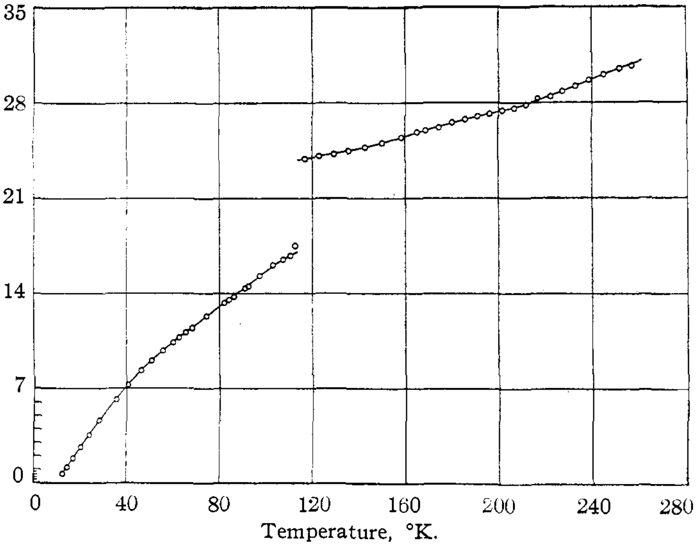

Fig. 1.—Molal heat capacity of isobutane.

Two hundred cc. of the isobutylene thus prepared was hydrogenated over 12 cc. (36 g.) of Raney nickel previously washed five times with *t*-butyl alcohol. The hydrogen pressure was kept constant at 1000 lb./sq. in. (67 atm.). At 16° the hydrogenation went to completion in two and one-half hours. After the reaction was completed, the material was condensed into a high pressure cylinder. The yield was 84.7% of isobutane.

The crude isobutane was first purified by passing it through three wash bottles of concentrated sulfuric acid, then through three sulfuric acid scrubbing towers, a potassium hydroxide tube and a phosphorus pentoxide tube. The condensed gas was then fractionated through the laboratory low temperature column. The sample was dried over phosphorus pentoxide before being condensed in the sample bulb. Alternate cooling to liquid air temperature, with evacuation to 10^{-6} mm. of mercury, and thawing removed the last traces of air before the bulb was sealed off and weighed ready for introduction of the sample into the apparatus in the customary manner.[2]

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(1) Kemp and Pitzer, THIS JOURNAL, **59**, 276 (1937).

(2) Aston and Messerly, *ibid.*, **58**, 2354 (1936).

(3) Aston, Siller and Messerly, *ibid.*, **59**, 1743 (1937).

(4) Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

(5) Pitzer, *ibid.*, **5**, 473 (1937).

The Heat Capacity Measurements.—The apparatus, method and temperature scale were as already described.[2,6] Calorimeter C with thermocouples S-4 and S-7 was used. The heat capacity measurements are listed in Table I and plotted in Fig. 1. One defined calorie was taken equal to 4.1833 international joules.

TABLE I

THE HEAT CAPACITY OF ISOBUTANE

Mol. wt. 58.121; 0.42322 mole in calorimeter; 0°C. = 273.16°K.

Temp., °K.	C_p, cal./deg./mole	Approximate rise, °K.
Series III		
12.53	0.664	1.3
14.57	1.146	2.1
17.16	1.823	3.2
20.54	2.648	3.4
24.20	3.576	4.4
28.45	4.660	4.1
35.74	6.195	1.2
40.51	7.234	8.1
46.45	8.298	4.3
50.90	9.045	4.6
55.68	9.782	4.8
Series I		
62.79	10.756	5.6
68.42	11.443	5.5
74.57	12.341	5.3
82.22	13.308	9.3
86.47	13.761	7.6
92.69	14.522	3.8
97.51	15.28	5.1
103.16	16.10	5.8
107.50	16.48	2.8
110.57	16.75	3.0
112.58	17.50	1.3
113.74	Fusion	
116.94	23.88	6.1
123.11	24.13	5.8
129.43	24.23	6.2
135.80	24.51	5.8
142.84	24.76	6.1
150.13	25.07	5.8
158.46	25.48	5.5
165.22	25.87	5.3
168.70	25.94	5.2
174.45	26.19	5.0
180.31	26.56	4.8
185.87	26.80	4.9
190.99	27.03	4.7
196.10	27.22	4.6
201.52	27.48	4.5
206.56	27.61	4.8
211.63	27.86	4.7
216.78	28.33	4.8
222.27	28.47	5.2
227.31	28.86	5.0
232.89	29.21	4.9
238.57	29.67	5.5
245.04	30.07	5.3
251.94	30.50	5.1
257.02	30.66	3.5
261.44	Vaporization	
Series II (solid)		
60.12	10.378	5.1
65.73	11.115	5.1
84.31	13.556	6.8
91.20	14.380	6.1

Table II gives the heat capacities interpolated from our data at rounded values of the absolute temperature and compared with the values of Parks, *et al.*[7]

The Melting Point of Isobutane.—The equilibrium temperature of solid and liquid isobutane was observed over a period of eight hours with various fractions of the sample melted as estimated from the heat input. From these results and the heat of fusion, the liquid-soluble solid-insoluble impurity present was found to be 0.0015 mole per cent. Table III summarizes the data on the melting point. The final value taken is 113.74 ± 0.05°K. (−159.43°). Values recorded in the literature are −145.0°[8] and −160.0°[7] (all in degrees C.).

TABLE II

COMPARISON OF HEAT CAPACITY VALUES FOR ISOBUTANE

T, °K.	C_p, cal./deg./mole (This research)	C_p, cal./deg./mole (Parks, *et al.*[7])	Dev., %
20	2.520		
30	5.026		
40	7.350		
50	8.876		
60	10.339		
70	11.718		
80	12.985	12.92	−0.54
90	14.315	14.39	+ .49
100	15.62	15.70	+ .51
110	16.74		
120	23.97	23.94	− .17
130	24.28	24.33	+ .21
140	24.63	24.71	+ .32
150	25.05	25.09	+ .16
160	25.52	25.52	0
170	26.03	25.97	− .23
180	26.50	26.42	− .31
190	26.94	26.88	− .22
200	27.33	27.35	+ .04
210	27.81	27.81	0
220	28.37	28.31	− .21
230	28.99	28.86	− .45
240	29.71	29.46	− .87
250	30.38	30.12	− .85
260	31.00	30.82	− .58

TABLE III

MELTING POINT OF ISOBUTANE, 0°C. = 273.16°K.

Melted, %	Total time, min.	T, °K. Res. Th.	T, °K. Thermocouple S-4	T, °K. Thermocouple S-7
7	110	113.732	113.705	113.721
17	175	113.736	113.726	113.745
27	235	113.736	113.722	113.738
48	310	113.736	113.730	113.743
68	385	113.736	113.718	113.732
88	490	113.735	113.728	113.724
Mean of last four values		113.736	113.724	113.734
Accepted value		113.74 ± 0.05°K.		

The Vapor Pressure Measurements.—In view of the high purity of the sample, the accuracy, except at the lowest pressures, is determined solely by the temperature. The results are given in Table IV. Column 1 gives the observed pressure, column 2 the absolute temperature as read by the resistance thermometer calibrated against standard thermocouple S-7, column 3 gives the difference between the observed pressure and that calculated from the temperature by means of the equation (1)

$$\text{Log } P_{\text{mm.}} = -\frac{1716.687}{T} - 6.38879 \log_{10} T + 0.0024132\, T + 24.260325 \quad (1)$$

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(6) Messerly and Aston, THIS JOURNAL, **62**, 886 (1940).

(7) Parks, Shomate, Kennedy and Crawford, *J. Chem. Phys.*, **5**, 360 (1937).

(8) Coffin and Maass, THIS JOURNAL, **50**, 1427 (1928).

TABLE IV

THE VAPOR PRESSURE OF ISOBUTANE

0°C. = 273.16°K.; boiling point, 261.44°K.; g for State College = 980.124, "I. C. T."

P obsd., Int. mm. Hg.	T obsd., °K.	P obsd. − P calcd.[a] mm.	T calcd. − T obsd. °K.
11.37	188.070	−0.009	−0.010
31.96	201.456	+ .033	+ .014
86.85	216.729	+ .003	+ .001
174.26	229.053	− .01	− .001
391.02	245.584	− .05	− .003
498.08	251.089	.00	.000
572.67	254.399	.00	.000
716.13	259.922	− .04	− .001
763.44	261.551	+ .05	+ .002

[a] Log $P_{\text{mm.}}$ = $1716.687/T - 6.38879 \log T + 0.0024132\ T + 24.260325$.

All the measurements were taken with the calorimeter full of material. From equation (1) the boiling point of isobutane was found to be 261.44 ± 0.02°K. (−11.72°). Values recorded in the literature are: −13.4,[9] −10.9,[8] −12.2,[10] and −10.2[11] (all in degrees C.).

The Heat of Fusion and Heat of Vaporization.—The methods have been described before,[2,6] and the results are given in Table V and Table VI.

TABLE V

HEAT OF FUSION OF ISOBUTANE

Mol. wt., 58.121; 0.42322 mole; melting point, 113.74 ± 0.05°K.

Temp. interval, °K.	Heat input, cal./mole	$\int C_p dT$ cal./mole	ΔH fusion cal./mole
111.679–115.742	1221.5	135.7	1085.8
111.079–117.498	1303.9	219.1	1084.8
110.721–116.348	1272.1	186.1	1085.5
		Average	1085.4 ± 0.5
Measured (Parks, *et al.*)[7]			1075.2

TABLE VI

THE HEAT OF VAPORIZATION OF ISOBUTANE AT THE BOILING POINT

Mol. wt., 58.121; boiling point, 261.44°K.

Moles vaporized	Mean temp. of vapor, °K.	Total input, cal./mole	$\int C_p dT$,[a] cal./mole	ΔH at 261.435°K., cal./mole
0.05561	258.46	5,531.1	405.3	5092.8
.04278	258.45	5,587.1	463.4	5080.8
.06210	258.75	5,679.6	565.7	5094.0
			Average	5089.6 ± 8
Measured (Dana, *et al.*)[14]				5095
Calculated from equation (1) and critical data of Seibert and Burrell[13] (Berthelot correction 246.2 cal.)				5022

[a] This is the correction to the mean temperature of vaporization. Column 3 minus the sum of columns 5 and 4 give the correction from the mean temperature to the normal boiling point.

In measuring the heat of vaporization, the sample vaporized was condensed into a weighed glass sample bulb immersed in an ammonium chloride–ice–water eutectic mixture. The eutectic temperature was found to be −15.30°. The actual temperature of vaporization was obtained from the vapor pressure during vaporization, and the heat of vaporization then corrected to the normal boiling point. For this purpose the heat capacity data on the liquid together with those of Sage and Lacey[12] for the gas were used. To get the change of heat of vaporization under saturated conditions, data of state are necessary. In lieu of these the modified Berthelot equation was used. The final values for the actual gas at the normal boiling point are given in Table VI.

The heat of vaporization also has been calculated from thermodynamics using equation (1) and the modified Berthelot equation, with the critical data of Seibert and Burrell[13]: T_c = 133.7° C., P_c = 36.54 atm. This value is listed in Table VI. Its deviation from the calorimetric value is merely a check on the assumption of the modified Berthelot equation which appears to give corrections to the real gas volume which are about 35% too large. The experimental value, of Dana, *et al.*,[14] listed in Table VI is the only other experimental one we have found in the literature. This result is an average of several values obtained with crude apparatus and agreement with the result of this investigation is therefore excellent.

The Entropy from Thermal Data.—The calculation at the boiling point and 298.16°K. is summarized in Table VII for the liquid and the gas. The correction for gas imperfection is based on the modified Berthelot equation of state. The entropy of the gas at 298.16°K. has been calculated using the extrapolated data of Sage and Lacey.[12] For completeness the entropy for the liquid at 298.16°K. has been extrapolated from the experimental data.

The Entropy from Molecular Data.—For the translational and external rotational entropy of the rigid molecule, the expression given by Pitzer[5] can be used with sufficient accuracy.

$$S_{t+r} = 15.22 + 4R \ln T \qquad (2)$$

The frequency assignment was based on the Raman data of Kohlrausch and Köppl[15] and the

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(9) Burrell and Robertson, THIS JOURNAL, **37**, 2482 (1915).

(10) Hückel and Rassmann, *J. prakt. Chem.*, **136**, 30 (1933).

(11) Peters and Lohmar, *Beiheft Z. Ver. deutsch. Chem.*, No. **12**, *Angew. Chem.*, **50**, 40–42 (1937).

(12) Sage and Lacey, *Ind. Eng. Chem.*, **29**, 1309 (1937).

(13) Seibert and Burrell, THIS JOURNAL, **37**, 2683 (1915).

(14) Dana, Jenkins. Burdick and Timm, *Refrig. Eng.*, **12**, 387 (1926).

(15) Kohlrausch and Köppl, *Z. physik Chem.*, **B26**, 209 (1934).

TABLE VII

THE ENTROPY OF ISOBUTANE FROM THERMAL DATA

Mol. wt., 58.121; 0 °C. = 273.16 °K.

	E. u./mole
0–12.53 °K. Debye extrapolation	0.247
12.53–113.74 °K. graphical	16.115
113.74 °K. fusion 1085.4/113.74	9.543
113.74–261.44 °K. graphical	22.030
261.44 °K. vaporization 5089.6/261.44	19.468
Entropy real gas 261.44 °K., 1 atm.	67.40
Gas imperfection correction[a]	0.12
Entropy ideal gas 261.44 °K., 1 atm.	67.52 ± 0.10
261.44–298.16 °K.	2.91
Entropy ideal gas 298.16 °K. 1 atm.	70.43 ± 0.15
Entropy saturated liquid 298.16 °K.	52.09 ± 0.1

[a] $S_{\text{ideal}} - S_{\text{actual}} = 27\ RT_c^3P/32\ T^3P_c$. $P_c = 36.54$ atm. $T_c = 133.7$ °C.

theoretical treatment of Mecke.[16] The frequencies used, in cm.$^{-1}$, were

Carbon skeleton: $\nu(\pi)$, 796; $^2\nu(\sigma)$, 967; $\delta(\pi)$, 372; $^2\delta(\sigma)$, 436
CH$_3$ (internal): $^{10}\nu$, 2900; $^3\delta(\pi)$, 1355; $^6\delta(\sigma)$, 1453
Hydrogen (external): ($^6\delta_1$, 950); $^2\delta_2$, 1167

The frequency in parentheses is an average value obtained by analogy with other molecules. The calculation of the entropy at the normal boiling point and 298.16°K. is summarized in Table VIII.

TABLE VIII

THE ENTROPY OF ISOBUTANE FROM SPECTROSCOPIC AND MOLECULAR DATA

	Entropy, cal./deg./mole T = 261.44 °K.	 T = 298.16 °K.
Translation + external rotation of rigid molecule	59.47	60.51
Vibrational ($^6\delta_1$ = 950)	0.40	0.69
Vibrational (other modes)	2.59	3.44
Restricted rotation of three methyl groups (V=3870, $I \times 10^{40}$ = 5.2 g. cm.^{2})	(5.08)	5.79
Total	(67.54 ± 0.10)	70.43 ± 0.10
Experimental	67.54 ± .10	70.43 ± .15

The potential of 3870 cal. hindering the three methyl groups was calculated from Pitzer's tables[4] to give the best fit with the experimental data at the boiling point, so that column 2 of Table VIII is merely a record of this calculation.

The use of 950 cm.$^{-1}$ for the six modes of vibration (δ_1) is merely the result of a guided guess. These frequencies are predominantly those in which the hydrogen bonds bend so that the angles they make with each other within each methyl group do not change. The calculation of an average value from the results of Sage and Lacey gives too high a value to be reasonable (1850 cm.$^{-1}$). If, however, such a value were accepted, the potential restricting internal rotation which is required to yield an entropy value in agreement with experiment is 3200 cal. In Table IX are listed in column 2 values of the heat capacity of the real gas, calculated at several temperatures using $^6\delta_1$ = 950 cm.$^{-1}$ and V = 3870. In column 3 are listed similar values using $^6\delta_1$ = 1850 cm.$^{-1}$, V = 3200. Inasmuch as the last two numbers were chosen to fit best the experimental entropy as well as the gaseous heat capacities, the values in column 3 should agree with the experimental values in column 4. Instead this is only true at one temperature. The curves of the two sets of values cross. We are inclined to believe for this reason alone that the experimental heat capacity values on the gas are in error. For this reason they have been given no weight except for the small extrapolation of the experimental entropy to 298.16°K., which would introduce a negligible error. On the other hand, there is much evidence that such frequencies as those in question seldom (if ever) have values much greater than 1200 cm.$^{-1}$ and have an average value close to 950 cm.$^{-1}$. Thus our choice could hardly be in error by greater than 50 cm.$^{-1}$, which would not change the value of the potential by more than 125 cal. In addition the uncertainty in the experimental entropy introduces about 130 calories uncertainty into the potential, making a total of about 250 calories uncertainty. Of course, the value of 3870

TABLE IX

COMPARISON OF GASEOUS HEAT CAPACITIES FOR ISOBUTANE

T	C_p (V = 3875, ν = 950),[a] cal./deg./mole	C_p (V = 3200, ν = 1850),[a] cal./deg./mole	C_p (Sage and Lacey), cal./deg./mole
300	24.48	21.94	22.80
320	25.91	22.92	23.52
340	27.30	23.98	24.28
360	28.67	25.03	25.14
380	30.02	26.07	26.03
400	31.35	27.15	26.97
420	32.60	28.21	27.46
440	33.80	29.26	29.00

[a] Corrected to real gas state at 1 atmosphere using the modified Berthelot equation of state with P_c = 36.54 atm., T_c = 133.7 °C.

$$C_p \text{ real} - C_p \text{ ideal} = \frac{81}{32}\frac{RT_c^3}{P_c}\frac{P}{T^3}$$

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(16) Mecke, *Z. physik. Chem.*, **B36**, 347 (1937).

calories per degree per mole is only correct if the potential function is sinusoidal with three equal minima.

Using $\delta_1 = 950$ cm.$^{-1}$ and $V = 3870$ for the restricting potential, tables of S, F/T and H/T can be compiled which are not in error by more than a few tenths of a calorie per degree per mole up to 1500°K.[17] It is important to realize that the small error is due to the fact that the potential was chosen to give the best fit with the experimental data and not to the accuracy of the molecular data.

Acknowledgment.—We wish to thank the Standard Oil Development Company, without whose aid this work would not have been possible. Dr. G. H. Messerly kindly helped with the experimental work on the thermal data. The extremely pure sample of isobutane was prepared by Dr. R. B. Greenburg and Mr. R. E. Meyer.

Summary

1. The heat capacity of isobutane has been determined from 12°K. to the normal boiling point.
2. The melting point of isobutane is 113.74°K. (−159.42°C.) and the boiling point is 261.44°K. (−11.72°C.).
3. The heats of fusion and vaporization at the boiling point are 1085.4 calories/mole and 5089.6 calories/mole, respectively.
4. The vapor pressure of isobutane from 200°K. to the boiling point is given by the equation:

$$\text{Log } P_{\text{mm.}} = -1716.687/T - 6.38879 \log T + 0.0024132\, T + 24.260325$$

5. The molal entropy of the liquid at the boiling point is 47.94 ± 0.10 e. u. The molal entropy of the ideal gas at the boiling point calculated from the experimental data is 67.52 ± 0.10 e. u.
6. The molal entropy of the liquid at 298.16°K. extrapolated from the experimental data is 52.09 ± 0.10 e. u. The molal entropy of the ideal gas from the experimental data at 298.16°K. is 70.43 ± 0.15 e. u.
7. In order to make the entropy calculated from the spectroscopic and molecular data agree with the experimental value at the boiling point it is necessary to assume that the potential hindering internal rotation of the methyl groups is 3870 cal.
8. The results of this investigation seem to indicate errors in existing heat capacity data on the gas.

State College, Penna. Received June 5, 1940

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[17] See Aston and Messerly, This Journal, **62**, 1917 (1940), for a discussion of the cancellation of errors in this type of calculation.

[Contribution from the Department of Chemistry, the Creighton University]

The Partial Pressure of Hydrogen Chloride from its Solutions in the Mono-halobenzenes at 25°

By S. James O'Brien and Joseph B. Byrne

In previous papers[1,2] measurements of the partial pressure of hydrogen chloride from its solutions in a number of solvents were reported. Since work of this kind provides information which may be of assistance in studying the nature of acid–base reactions and the bonding present between solvent molecules, similar determinations are being made in other solvents. In this paper measurements of the vapor pressure of hydrogen chloride from its solutions in the four monohalobenzenes at 25° are reported. These measurements were undertaken since conclusions concerning the basicity of chlorobenzene derived from measurements of the solubility of hydrogen chloride at one atmosphere[3] disagree with those obtained from the shift of the 3.46 μ absorption band of hydrogen chloride.[4,5] The shift of the infrared band indicates a proton-attracting tendency for chlorobenzene that is approximately the same as that of benzene. A negative deviation of hydrogen chloride from the law of Raoult in chlorobenzene solutions of about the same magnitude as that shown in benzene solutions[1] might, then, be expected. The solubility measurements of Bell,[3] however, indicate a rather large positive deviation. Measurements were made to determine whether such a deviation persists at lower pressures and whether such a deviation is to be

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[1] S. J. O'Brien, C. L. Kenny and R. A. Zuercher, This Journal, **61**, 2504 (1939).

[2] S. J. O'Brien and C. L. Kenny, *ibid.*, **62**, 1189 (1940).

[3] R. P. Bell, *J. Chem. Soc.*, 1371 (1931).

[4] D. Williams, *Phys. Rev.*, **50**, 719 (1936).

[5] W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).