[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 *n*-Butane[1]

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From a recent comparison of the entropy of propane obtained from low temperature thermal data with that calculated from molecular constants, Kemp and Egan[2] have assigned a restricting potential of 3300 cal. to the internal rotation of the methyl groups in the propane molecule.

In the case of *n*-butane it is reasonable to assume that a restricting potential of equal magnitude will be associated with the methyl groups on the ends of the molecule. On this assumption the calculation of the potential restricting the rotation of the two ethyl groups about the middle C–C bond awaits an independent experimental value of the entropy.

The entropy of *n*-butane is of interest in another connection. Kassel[3] has pointed out that discrepancies of several entropy units exist in the entropy difference between *n*- and iso-butane when this difference is calculated by different methods as follows: (1) from equilibrium measurements upon the isomerization reaction[4]; (2) from incomplete calorimetric data and the third law[5,6] and (3) from molecular data[7] based upon arbitrary assignment of the unknown restricting potentials. Since the incomplete calorimetric data used for the third law calculation extended only to about 70°K., the entropies obtained by application of the third law could be considerably in error.

In the present paper complete and more accurate heat capacities down to 11.8°K. are presented. It is shown that the rotation of ethyl groups about the central C–C bond is restricted by a potential of considerable magnitude. Values for the entropy difference of *n*- and iso-butane obtained by the three methods are in better agreement when the new calorimetric data for *n*-butane are used for method (2) and the new potential or its equivalent frequency for method (3).

Preparation and Purification of *n*-Butane.—The *n*-butane was prepared by Mr. R. B. Greenburg of this Laboratory by condensing carefully purified ethyl iodide with metallic sodium. By this method the product was free from substances boiling near 0°. The reaction product was twice distilled through the laboratory low temperature fractionating column. Vapor pressure measurements on the first and last portions of the final middle fraction indicated that no further purification could be effected by distillation. The sample taken for calorimetric measurement was dried with phosphorus pentoxide and freed from the last traces of air before being condensed into a weighed glass sample bulb.

The Heat Capacity Measurements.—The apparatus, methods, temperature scale and accu-

TABLE I

THE MOLAL HEAT CAPACITY OF *n*-BUTANE

Mol. wt., 58.121. 0.46761 mole in calorimeter. 0°C. = 273.16°K.

Temp., °K.	C_p cal./deg.	ΔT °K.
	Series I	
60.72	10.412	5.2
66.27	11.313	5.6
72.30	12.109	6.0
79.32	13.161	6.7
85.76	14.052	5.9
92.28	14.927	6.0
98.17	15.72	5.5
103.55	16.39	5.0
113.77	19.92	5.7
119.80	20.13	6.0
126.78	20.47	6.8
142.22	27.12	5.6
149.50	27.42	5.9
156.03	27.73	5.6
162.29	27.71	6.2
168.49	27.93	6.0
174.59	27.92	5.8
180.83	27.99	6.1
	Series II	
88.59	14.367	6.9
96.29	15.41	6.7
	Series III	
12.73	0.494	1.7
15.05	0.793	2.4
18.44	1.510	3.9
22.36	2.455	3.6
26.71	3.419	4.1
31.53	4.724	5.0
36.89	5.862	5.2
42.03	6.980	4.4
48.87	8.426	5.3
54.59	9.412	5.5
74.07	12.412	5.9
	Series IV	
130.17	20.74	4.0
133.39	21.19	2.0
139.88	27.07	5.5
186.63	28.22	4.7
191.76	28.32	4.4
196.83	28.51	4.7
203.24	28.71	4.6
209.00	28.78	3.9
215.94	29.11	4.4
222.71	29.29	4.7
230.81	29.62	4.5
238.43	29.84	4.4
247.01	30.36	4.6
251.43	30.89	4.8
262.04	31.30	4.3
268.14	31.46	3.8
	Series V	
59.62	10.276	5.3
65.35	11.242	5.7

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Boston meeting of the American Chemical Society, September, 1939.

[2] Kemp and Egan, THIS JOURNAL, **60**, 1521 (1938).

[3] Kassel, *ibid.*, **59**, 2745 (1937).

[4] Montgomery, McAteer and Franke, *ibid.*, **59**, 1768 (1937).

[5] Huffman, Parks and Barmore, *ibid.*, **53**, 3884 (1931).

[6] Parks, Shomate, Kennedy and Crawford, *J. Chem. Phys.*, **5**, 359 (1937).

[7] Pitzer, *ibid.*, **5**, 473 (1937).

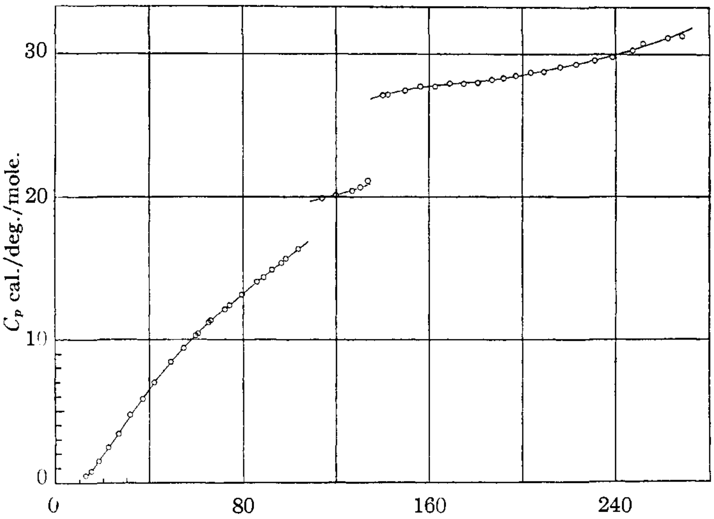

Fig. 1.—The molal heat capacity of *n*-butane.

racy were as already described.[8] The defined calorie was taken as 4.1835 international joules. The density of the liquid was obtained from the data of Coffin and Maass.[9] The molal heat capacities are listed in Table I and graphed in Fig. 1.

Table II

Molal Heat Capacity of *n*-Butane

T, °K.	C_p cal./deg. A. and M.	C_p cal./deg. H., P. and B.	T, °K.	C_p cal./deg. A. and M.	C_p cal./deg. H., P. and B.
12	0.38		134.87	M. p.	
15	0.78		140	27.16	27.15
20	1.08		150	27.50	27.35
25	3.08		160	27.74	27.50
30	4.30		170	27.86	27.60
40	6.56		180	28.03	27.87
50	8.60		190	28.28	28.15
60	10.29		200	28.58	
70	11.84	12.45	210	28.90	
80	13.30	13.55	220	29.23	
90	14.61	14.60	230	29.63	29.45
100	15.94	15.94	240	30.02	
107.53	Transition pt.		250	30.54	
110	19.83		260	31.10	30.90
120	20.14	21.5	270	31.65	
130	20.64		272.66	B. p.	

Data upon the heat capacity of *n*-butane have been obtained by Parks, *et al.*[5,6] Table II gives heat capacities interpolated from our data at rounded values of the temperature and compared with the data of Huffman, Parks and Barmore.[5] The agreement at the higher temperatures is somewhat better than indicated in Table II from a statement of Parks, Shomate, Kennedy and Crawford[6] that the original data on *n*-butane were somewhat over-corrected at the higher temperatures.

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 III. Column 1 gives the absolute temperature as read by standard thermocouple S-7. Column 2 gives the observed pressure and column 3 the difference between the observed pressure and that calculated from the temperature by means of equation (1)

$$\mathrm{Log}_{10} P_{\mathrm{mm.}} = -\frac{2352.900}{T} - 16.49230 \log_{10} T + 0.01111869\, T + 48.64763 \quad (1)$$

All the measurements except the one marked (*a*) were taken with the calorimeter full of material. This measurement was taken after a third of the material had been removed for heat of vaporization measurements.

Table III

The Vapor Pressure of *n*-Butane

Boiling point, 272.66 °K. 0 °C. = 273.16 °K. (*g* for State College = 980.124; "I. C. T.")

Temp., °K.	Pressure, int. mm. Hg.	ΔP Calcd. − Obsd.	ΔT Obsd. − calcd.
195.117	9.90	−0.308	−0.265
212.678	36.26	+ .017	+ .008
226.286	85.59	+ .079	+ .015
235.832	145.58	− .010	− .001
246.521	249.53	− .046	− .004
256.214	238.77	− .009	− .001
262.277	503.34	− .023	− .001
266.799	604.97	+ .028	+ .001
270.407	697.13	+ .016	+ .001
272.037[a]	742.20	− .017	− .001
272.816	764.50	+ .035	+ .001

The Transition, Melting and Boiling Points of *n*-Butane.—The equilibrium temperature of solid and liquid *n*-butane was observed over a period of twelve hours with various fractions of the sample melted as estimated from the heat input. From these results and the heat of fusion, the solid insoluble impurity present in the sample was found to be 0.001 ± 0.001 mole per cent. The purity of the sample was also estimated from the slight rise of the heat capacity as the melting

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[8] Aston and Messerly, This Journal, **58**, 2354 (1936); **62**, 886 (1940).

[9] Coffin and Maass, *ibid.*, **50**, 1433 (1928).

point was approached, and found to be about 0.001 mole per cent. The final value for the melting point was taken as 134.87 ± 0.05°K. (−138.29°C.). Other values reported for the melting point are −135.0°C.,[10] and 134.1°K.[5]

The solid–solid equilibrium temperature was observed in a similar way with increasing fractions of the material in the high temperature form. About eight hours was required after the addition of energy for equilibrium to be attained, and for this reason the transition temperature of *n*-butane is not recommended for use as a thermometric fixed point. Our value for this point is 107.56 ±0.10°K. (−165.60°C.). Huffman, Parks and Barmore[5] report 107.0°K. for the transition temperature. Data on the melting and transition temperatures are summarized in Table IV.

TABLE IV

TRANSITION AND MELTING TEMPERATURES OF *n*-BUTANE

0°C. = 273.16°K.

Date	% in high temp. phase	*T*, °K. resistance thermometer	*T*, °K. thermocouple S-7	*T*, °K. thermocouple S-4
5/2/39		Transition Temperature		
10:00 A.M.—added energy to calorimeter				
11:45 A.M.	21	107.651	107.663	107.650
12:50 P.M.	21	107.627	107.635	107.622
2:00 P.M.	21	107.593	107.615	107.598
3:45 P.M.	21	107.589	107.618	107.602
4:00 P.M.—added energy				
8:25 P.M.	54	107.529	107.567	107.548
12:00 P.M.	54	107.557	107.594	107.592
5/3/39				
12:30 A.M.—added energy				
8:00 A.M.	95	107.434	107.474	107.459
11:00 A.M.	95	107.478	107.474	107.446
1:25 P.M.	95	107.533	107.517	107.502
Transition temperature, 107.56 ± 0.10 °K.				
4/24/39		Melting Temperature		
2:45 P.M.	0.1	132.772	132.767	132.753
4:00 P.M.	8	134.871	134.873	134.860
7:30 P.M.	25	134.873	134.880	134.874
8:30 P.M.	25	134.873	134.880	134.874
10:00 P.M.	50	134.874	134.879	134.874
11:40 P.M.	90	134.874	134.874	134.868
Melting point, 134.87 ± .05 °K.				

By solving equation (1) for one atmosphere, 272.66 ± 0.03°K. (−0.50°C.) is obtained as the normal boiling point of *n*-butane. Other values reported for the boiling point are: −0.3,[11] −0.6,[12] −0.5[9] and +0.5[13] (all in °C.).

The Heat of Transition, Fusion and Vaporization.—The methods have been described before.[8] The results are given in Tables V, VI and VII.

TABLE V

HEAT OF TRANSITION OF *n*-BUTANE

Transition point, 107.56 ± 0.10 °K. 0 °C. = 273.16 °K. Mol. wt., 58.121.

Temp. interval, °K.	Total input, cal./mole	$\int C_p\, dT$, cal./mole	ΔH cal./mole
105.604–111.804	681.8	188.5	493.3
105.118–111.232	677.7	184.5	493.6
104.792–111.854	707.8	412.8	495.0
		Average	494.0 ± 1

TABLE VI

HEAT OF FUSION OF *n*-BUTANE

Melting point, 134.87 ± .05 °K. 0 °C. = 273.16 °K. Mol. wt., 58.121.

Temp. interval, °K.	Total input, cal./mole	$\int C_p\, dT$, cal./mole	ΔH fusion, cal./mole
133.497–138.178	1287.8	175.1	1112.7
133.370–138.203	1294.4	177.3	1114.1
132.720–137.656	1294.5	180.3	1114.2
		Average	1113.7 ± 1

TABLE VII

HEAT OF VAPORIZATION OF *n*-BUTANE

Mol. wt., 58.121. Boiling point, 272.66 °K.

Moles vaporized	Mean temp. of vapn., °K.	Total input, cal./mole	$\int C_p\, dT$, cal./mole	ΔH at 272.66°K. cal./mole
0.04950	273.62	5807.9	471.7	5346
0.04996	273.70	5758.0	411.3	5357
				5351 ± 15
Measured (Dana, *et al.*,[12] 1926)				5324
Calculated from eq. (1) and state data of Visser[14]				5350
Calculated from eq. (1) and modified Berthelot eq. (T_c = 152.01 °C.[14]; P_c = 37.47 atm.[15]; correction = 213 cal.)				5372

During the vaporization, the pressure was held constant by having the condensation bulb immersed in a well-stirred cryostat of finely shaved ice and water. The heat of vaporization has also been calculated by thermodynamics using equation (1) with (a) state data of Visser[14] and (b) the modified Berthelot equation with T_c = 152.01°C.; P_c = 37.47 atm.[15]

The agreement of the experimental value with that calculated using the state data of Visser is a good check on the accuracy of the latter. The deviation of the value calculated using the modified Berthelot equation is sufficiently small to justify the use of the modified Berthelot equation in correcting to the ideal gas state.

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[10] Timmermans, *Bull. soc. chim. Belg.*, **25**, 300 (1911).

[11] Burrell and Robertson, THIS JOURNAL, **37**, 2188 (1915).

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

[13] Kohlrausch and Köppl, *Z. physik. Chem.*, **26B**, 209 (1934).

[14] Visser, *Comm. Phys. Lab. Univ. Leiden*, No. 138 (1913).

[15] Beattie, THIS JOURNAL, **61**, 24 (1939).

The Entropy from Thermal Data.—The calculation is summarized in Table VIII. 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 from heat capacity data of Sage and Lacey.[16] The entropy of the superheated liquid at 298.16°K. has been obtained by extrapolating the liquid C_p curve.

TABLE VIII

THE ENTROPY OF *n*-BUTANE

Mol. wt., 58.121. 0°C. = 273.16°K.

	E. u./mole
0–10°K., Debye extrapolation	0.150
10–107.55°K., graphical	14.534
107.55°K., transition 494.0/107.56	4.593
107.55–134.89°K., graphical	4.520
134.89°K., fusion 1113.7/134.87	8.255
134.89–272.66°K., graphical	20.203
272.66°K., vaporization 5351/272.66	19.62
Entropy real gas, 272.66°K., 1 atm.	71.88
Gas imperfection correction[a]	0.17
Entropy ideal gas, 272.66°K., 1 atm.	72.05±0.2
Entropy ideal gas, 298.16°K., 1 atm.[b]	74.0
Entropy liquid, 298.16°K.	55.2

[a] $S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c$. P_c = 37.47 atm., T_c = 152.01°C.[16] [b] Using gaseous C_p data of Sage and Lacey.[17]

The Thermodynamic Functions from Thermal and Molecular Data.—Pitzer[7] has calculated the entropy of *n*-butane using 3400 and 3800 cal./mole for the potentials restricting rotation about the two end C–C bonds and the middle C–C bond, respectively. He used an arbitrary frequency assignment. We have reversed this calculation using 3300 cal./mole for the methyl group potential (in accord with the results of Kemp and Egan[2] for propane), and using our experimental entropy value together with the C-chain vibrational frequency assignment of Kohlrausch and Köppl[13] to determine the restricting potential or torsional frequency which may be formally associated with the restricted rotation of the two ethyl groups about the middle C–C bond. This calculation is summarized in Table IX. The butane molecule is assumed to exist in two pseudo-rigid forms. In the one form, the so-called "straight" form, the carbon atoms all lie in one plane in a zigzag configuration (*i. e.*, the potential minima are taken as for the D_{3d} configuration of ethane). The other "bent" form is obtained from the "straight" by a rotation of one ethyl group through 120° about the middle C–C bond. The terms "bent" and "straight" are remarkably non-descriptive, but have been retained to conform with previous usage.[7]

TABLE IX

CALCULATION OF POTENTIALS RESTRICTING ROTATION ABOUT MIDDLE BOND OF *n*-BUTANE

Mol. wt., 58.121. Reduced moment of methyl group, 5.0 × 10^{-40} g. cm.[2] Reduced moment of ethyl group, 32.2 × 10^{-40} g. cm.[2] C–C = 1.53 Å. C–H = 1.11 Å. Tetrahedral angle between bonds = 109°28′.

	E. u./mole at 272.66°K. St.	E. u./mole at 272.66°K. Bent
Translation–rotation entropy		
Straight form 16.00 + 4 *R* ln *T*	60.57	62.00
Bent form 17.43 + 4 *R* ln *T*		
Vibrational entropy		
C, chain vibrations, Kohlrausch and Köppl[13]	3.85	4.02
H, vibrations, cm.$^{-1}$ = 950(10); 1455 (8); 3000(10)		
Internal restricted rotational entropy		
2 methyl groups	3.84	3.84
Restricting potential = 3300±400 cal.		
	68.26	69.86
A Entropy of mixture, 31 mole per cent. Straight form; 69 mole per cent. Bent form, assuming no heat of transformation	70.61±0.5	
B Calorimetric entropy	72.05±0.2	
C Difference, B − A, due to torsion about middle bond	1.44±0.7	
Frequency of vibration corresponding to C from Einstein function	272±150 cm.$^{-1}$	

The translation-rotation entropy is obtained by well-known methods. The symmetry number of each form is 2. The entropy of the bent form has been increased by *R* ln 2 to account for the optical isomerism of the bent form. The constant term in the equation for $S_{\text{trans.} + \text{rot.}}$ of the straight form differs from that obtained by Pitzer[7] by 0.33 e. u. The reduced moment of the ethyl group is 32.3 × 10^{-40} instead of 18.0 × 10^{-40} given by Pitzer. To $S_{\text{trans.} + \text{rot.}}$ for each form is added the vibrational contribution. The mole fraction of each form is obtained by assuming that the energy of the two forms is equal, or that the ΔH for the transformation is zero. There is reason to believe that this energy difference, if not zero, is small. If it were as large as 1500 cal., one form would predominate to the extent of about 90% at the boiling point. The existence of appreciable quantities of the two forms is necessary

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(16) Sage and Lacey, *Ind. Eng. Chem.*, **27**, 1484 (1935).

(17) Lambert and Lecomte, *Ann. phys.*, **10**, 566 (1938).

to account for all the observed Raman and infrared lines.[13,17] On this assumption, then, the entropy of the mixture is computed and compared with the experimental entropy. It is found that a torsional frequency of 272 cm.$^{-1}$ must be assigned to bring the two into agreement. This frequency corresponds to a potential barrier of the order of 30,000 cal./mole.

Since the unknown torsional frequency or its equivalent potential was obtained by a difference method, it is in error by the sum of the error in frequency assignment and the experimental error in the entropy, and is thus uncertain to almost 100% of its value. The only conclusion that can be made is that the absolute magnitude of the restraining potential appears to be quite large.

When this potential or equivalent frequency is used for the calculation of thermodynamic functions at higher temperatures, however, a different situation exists. Any error in frequency assignment will be compensated for by an equivalent error in the torsional frequency. In Table X are given values for the thermodynamic functions of n-butane at various temperatures calculated from two different vibrational frequency assignments.[13,17] Complete tables of these functions will be published elsewhere.

TABLE X

THERMODYNAMIC FUNCTIONS OF n-BUTANE CALCULATED FROM $S^\circ_{272.7} = 72.05 \pm 0.2$ e. u.

$-(F^0 - E^0_0)/T$, cal./deg./mole

T, °K.	(1)	(2)	(3)
272.7	58.23	58.28	57.93
300	59.59	59.66	59.31
700	76.05	76.59	76.58
1300	97.31	97.43	97.25

$(H^0 - E^0_0)/T$, cal./deg./mole

T, °K.	(1)	(2)	(3)
272.7	13.82	13.77	14.12
300	14.63	14.49	14.92
700	26.92	26.85	27.09
1300	39.73	39.69	39.86

S, cal./deg./mole

T °K.	(1)	(2)	(3)
272.7	72.05	72.05	72.05
300	74.22	74.15	74.23
700	103.42	103.44	103.67
1300	137.04	137.12	137.11

The columns of Table X headed (1), (2) and (3) contain values of the function calculated from the experimental entropy value at 272.66°K. and (1) the vibrational frequency assignment of Kohlrausch and Köppl[13]:

Straight form, cm.$^{-1}$...	835	326	1058	250	954
Bent form, cm.$^{-1}$......	788	428	1060	185	980

Torsion frequency calculated from $S^\circ_{272.7}$ = 272 cm.$^{-1}$

(2) the vibrational frequency assignment of Lambert and Lecomte[17]:

Straight form, cm.$^{-1}$...	1050	785	380	892	690
Bent form, cm.$^{-1}$.......	990	833	350	950	430

Torsion frequency calculated from $S^\circ_{272.7}$ = 138 cm.$^{-1}$

(3) the vibrational frequency assignment of Kohlrausch and Köppl assuming the presence of only the bent form; torsion frequency calculated from $S^\circ_{272.7}$ = 179 cm.$^{-1}$.

The calculation assuming the presence of only the straight form could not be made because the difference between the experimental and calculated entropy in this case is too great to be accounted for on any basis. The hydrogen bending and stretching vibrations were taken in all cases as 950(10), 1455(8), and 3000(10) cm.$^{-1}$. Table X shows that values of the thermodynamic functions for n-butane obtained in this way are practically independent of uncertainties in frequency assignment or of theoretical treatment, and are probably reliable at the highest temperature to about ±0.5 cal./deg./mole.

That the agreement in the values given in columns (1), (2), and (3) is not fortuitous is evident when the shape of the curves representing the value of $(E/T)_{\text{Einstein}}$ and $(F/T)_{\text{Einstein}}$ as a function of $\tilde{\nu}/T$ is considered.

The function $(E/T)_{\text{Einstein}}$ plotted against $\tilde{\nu}/T$ may be considered linear over a wide range of values of $\tilde{\nu}/T$. The same is true for $(F/T)_{\text{Einstein}}$ for a smaller range of values. Within such a range, however, the total $S_{T\,\text{vib.}}$ depends only on the average value of the frequencies used, and is independent of the particular frequency assignment made as long as

$$\sum_1^n \tilde{\nu}_i \Big/ n = \tilde{\nu}_{\text{av.}} \qquad (2)$$

When the total $S_{\text{vib.}}$ is known at a particular temperature from an experimental measurement, it may be used with an uncertain and incomplete frequency assignment to calculate an unknown and equally uncertain frequency. However, as long as the uncertain frequencies do not extend over too great a range, any complete assignment thus obtained will fulfil condition (2), since the total $S_{\text{vib.}}$ including the torsional S is a constant determined by the experimental S. At higher temperatures the range of values of $\tilde{\nu}/T$ over which, for a given error, (F/T) may be considered as linear decreases. For a given range of uncertainty in $\bar{\nu}$ at low temperature, the range over which (F/T) need be considered linear also decreases with increasing temperature ($\bar{\nu}/T$ is the parameter involved), so that the total vibrational entropy calculated at any temperature will be, with relatively small error, independent of a considerable uncertainty in the original assignment.

This principle must of course be used with reasonable discretion, but may be of considerable help with practical computations. To the best of our knowledge it has not been stated explicitly before. It is this very lack of sensitivity of the (E/T) and (F/T) functions which prevents the use of experimental entropy values to obtain accurate molecular data. The same is not true for the heat capacity function. Over certain critical temperature regions for each frequency the heat capacity is quite sensitive to changes in the vibrational frequency assignment. In this connection it may be noted that at 1000°K. a change in the heat capacity of 2 cal./deg./mole over a hundred degrees will produce only 0.2 e. u. difference in the entropy and correspondingly smaller differences in (E/T) and (F/T).

A comparison of our calorimetric value of the entropy with other experimental and calculated values is given in Table XI.

TABLE XI

THE ENTROPY OF *n*-BUTANE

	$S_{272.7}$	$S_{298.1}$
Parks, *et al.*[5,6] (1931), revised (1937), calorimetric	73.9	75.8±0.8
Calculated, Pitzer[7] (1937), potentials of 3400 and 3800	72.8	75.1±1.0
This research, calorimetric	72.05±0.2	74.0±0.2
Calculated, by Pitzer's method,[2] potentials of 3300 and 30,000 cal.	72.05	74.1

In column 1 of Table XII are given values for the entropy difference of iso- and *n*-butane as calculated from the equilibrium data, method (1), on the one hand and from the third law entropy data on *n*-butane combined with the value calculated from the molecular data, method (2), on the other. For method (2) to be complete, calorimetric data on iso-butane have been obtained and are in progress of computation. When the potentials or equivalent frequencies are determined empirically, methods (2) and (3) are identical. In Table XI is also included an entropy difference calculated by method (3) assuming free rotation. While the other two methods are in agreement, the assumption of free rotation yields a negative value which is too high by more than can be accounted for on the basis of error. The results, therefore, speak against free rotation in either compound. A preliminary calculation of the entropy of iso-butane from calorimetric data down to 11°K. indicates that deviation of the third law results from those obtained from the equilibrium data is somewhat larger than indicated above.

TABLE XII

n-BUTANE $\longrightarrow$ *i*-BUTANE (ΔS_{298})

ΔS_{298}	
−2.08±0.55	Equilibrium measurement, Montgomery,[4] *et al.* (1937)
−3.2 ±1.0	*i*-Butane, calculated (Pitzer,[7] 1937) *n*-Butane, This Research (third law or calculated)
−4.1	Calculated. free rotation, Kassel (1936)[3]

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Summary

1. The heat capacity of *n*-butane has been determined from 12°K. to the boiling point.

2. The transition point of *n*-butane is 107.56 ± 0.10°K. (−165.60°C.); the melting point is 134.87 ± 0.05°K. (−138.29°C.) and the boiling point is 262.66 ± 0.03°K. (−0.50°C.).

3. The heats of transition, fusion and vaporization at the boiling point are, respectively: 494.0 ± 1, 1113.7 ± 2 and 5351 ± 15 cal./mole.

4. The vapor pressure of *n*-butane from 210°K. to the boiling point is given by the equation

$$\mathrm{Log}_{10} P_{\mathrm{mm.}} = -\frac{2352.900}{T} - 16.49230 \log_{10} T + 0.01111869\,T + 48.64763$$

5. The molal entropy of the ideal gas at the boiling point calculated from the experimental data is 72.05 ± 0.2 e. u.

6. The molal entropies of the ideal gas and the superheated liquid at 298.16°K. are, respectively, 74.0 ± 0.2 and 55.2 ± 0.3 e. u.

7. The rotation of the ethyl groups of *n*-butane is hindered by a potential of the order of 30,000 cal./mole.

8. It is shown that reliable thermodynamic functions for *n*-butane at high temperatures may be obtained despite uncertainty in the vibrational frequency assignment.

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Aqueous Solubilities of Some Aliphatic Ketones

BY P. M. GINNINGS, DOROTHY PLONK AND ELOISE CARTER

In view of the dearth of information in the literature as to the solubility in water of aliphatic ketones and the relationships already found between the molecular structure and solubility of aliphatic alcohols,[1] the aqueous solubilities of twelve such ketones have now been measured.

The solubilities (Table I) were determined by the same volumetric method as was used for the alcohols, and are considered accurate to within 0.05 weight per cent. except that 0.20 weight per cent. should probably be allowed in nos. 1 and 2. The ketones were of the best Eastman Kodak Co. grade except nos. 5, 8, 9 and 10, which were prepared from the corresponding secondary alcohols by the method of Yohe.[2] All were purified by fractional distillation through a 1-meter column, usually from barium oxide. Nos. 1, 3, 6, 8 and 12 were further purified by means of sodium bisulfite.

TABLE I

No.	d^{25}_4 of pure ketone and b. p. °C. (760 mm.)	Temp., °C.	Wt. % ketone		d^{20}_4, $^{25}_4$, $^{30}_4$ of the liquid phases	
					Water rich	Ketone rich
	Butanone-2					
1[a,b]	0.8007	20	27.33	88.41	0.9620	0.8353
	80.7–80.8	25	25.57	88.28	.9611	.8322
		30	24.07	88.15	.9615	.8270
	3-Methylbutanone-2					
2	0.8189	20	6.53	97.61	.9908	.8328
	93.1–94.0	25	6.08	97.43	.9901	.8284
		30	5.68	97.24	.9890	.8238
	Pentanone-2					
3	0.8018	20	5.95	96.70	.9903	.8147
	102.2–102.3	25	5.51	96.52	.9897	.8103
		30	5.18	96.32	.9887	.8059
	Pentanone-3					
4[c]	0.8116	20	5.08	98.55	.9925	.8195
	101.6–101.9	25	4.81	98.38	.9915	.8150
		30	4.50	98.17	.9901	.8108
	3-Methylpentanone-2					
5	0.8083	20	2.26	98.05	.9926	.8328
	117.4–117.5	25	2.09	97.97	.9944	.8131
		30	1.93	97.83	.9935	.8088
	4-Methylpentanone-2					
6	0.7969	20	2.04	97.59	.9951	.8092
	115.6–115.7	25	1.91	97.93	.9944	.8018
		30	1.78	97.80	.9932	.7981
	3,3-Dimethylbutanone-2					
7	0.8012	20	2.04	98.35	.9954	.8097
	106.0–106.1	25	1.90	98.24	.9946	.8053
		30	1.77	98.14	.9933	.8010
	Hexanone-2					
8	0.8072	20	1.75	97.88	.9959	.8154
	127.5–127.6	25	1.64	97.75	.9950	.8117
		30	1.53	97.64	.9938	.8079
	4-Methylpentanone-3					
9	0.8059	20	1.63	98.79	.9959	.8128
	115.0–115.1	25	1.52	98.69	.9952	.8088
		30	1.42	98.60	.9941	.8047
	Hexanone-3					
10	0.8111	20	1.57	98.47	.9962	.8175
	123.6–123.7	25	1.47	98.38	.9952	.8134
		30	1.38	98.30	.9943	.8087
	2,4-Dimethylpentanone-3					
11	0.7900	20	0.59	99.24	.9976	.8044
	125.4–125.5	25	.57	99.19	.9966	.8003
		30	.56	99.15	.9953	.7962
	Heptanone-2					
12	0.8115	20	0.44	98.69	.9978	.8177
	151.2–151.3	25	.43	98.59	.9967	.8141
		30	.40	98.48	.9953	.8098

[a] Park and Hofman, *Ind. Eng. Chem.*, **24**, 134 (1932), give data for Nos. 1, 3, 8 and 12 at room temperatures (about 25°). [b] Evans, *Ind. Eng. Chem. Anal. Ed.*, **8**, 208 (1936), has measured no. 1 at 20° using a volumetric method obtaining 26.7 wt. %. [c] Gross, Saylor and Gorman, THIS JOURNAL, **55**, 650 (1933), have measured no. 4 accurately at 30°, obtaining 4.48 wt. %.

Discussion

The most important factor is of course the molecular size (nos. 1, 3, 8 and 12) as the smallest ketone is the most soluble (acetone is soluble in water in all proportions). In a group of isomeric ketones, solubility tends to increase as molecular structure becomes more compact (nos. 3 and 2; 10 and 9; 8, 6, 5 and 7). Most unexpected was the effect of the position of the carbonyl group. In alcohols increasing solubility follows move-

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[1] For instance, unsaturated alcohols, Ginnings, Herring and Coltrane, THIS JOURNAL, **61**, 807 (1939).

[2] Yohe, Lauder and Smith, *J. Chem. Education*, **10**, 374 (1933).