[Contribution from the School of Chemistry and Physics, The Pennsylvania State College]

The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of Butene-1. The Zero Point Entropy of the Glass. The Entropy of the Gas from Molecular Data

By J. G. Aston, H. L. Fink,[1] A. B. Bestul,[1] E. L. Pace[1] and G. J. Szasz

It has been possible to crystallize butene-1 for the first time and thus obtain thermal data on the crystal down to 11.5°K. leading to entropies of crystal, liquid and gas. In addition, it has been possible to cool the glass down to 13°K. and obtain a value for the residual entropy in the glass at the absolute zero. The present paper records the experimental data and conclusions from this work.

Experimental

Purification of Butene-1 Samples.—The sample of butene-1 on which the heat capacities in series I–VIII and the heats of fusion were measured was obtained from Professor M. R. Fenske, of the Petroleum Refining Laboratory of The Pennsylvania State College, as an original sample of 124 g., prepared by dehydrating *n*-butyl alcohol over activated alumina at 475–500° and reported to be quite pure. This sample was dried by slowly passing three times over activated alumina, previously baked for twenty-four hours at 225°. The sample was then distilled through the laboratory low temperature fractionating column (twelve theoretical plates). A middle portion of the take off, of approximately 37 cc., measured at 85°K., was withdrawn as the calorimetric sample. This sample was freed of air by alternately warming nearly to the boiling point, cooling to liquid air temperatures, and pumping off any vapor remaining over the sample. It was then introduced into the calorimeter in the customary manner.[2a,b] This sample was found to contain 0.49 mole per cent. impurity as determined from equilibrium temperatures observed during melting.

A second sample of butene-1, obtained from the Phillips Petroleum Company and prepared by dehydrating *n*-butyl alcohol over activated alumina at 427°, was used to take all the other measurements. The sample was withdrawn directly from the cylinder in which it was shipped and passed through activated alumina in order to dry it. The removal of the air from the sample was accomplished partly before and partly after the introduction of the sample into the calorimeter. Before introduction, the sample was alternately warmed to the boiling point and cooled to liquid air temperature several times while any residual air was removed by the high vacuum pumping system. After the sample was condensed in the calorimeter, air was found to be present despite the elaborate precautions which had been taken to remove it. Therefore, before the vapor pressure measurements, a procedure was employed which consisted of distilling two 10-cc. portions (from an original sample of 35 cc.) out of the calorimeter, and the evacuation of the residual air remaining over the remaining sample and over the distillates at liquid air temperature after each distillation. Thus, the vapor pressure measurements were taken with the residual 15-cc. sample that did not exhibit a measurable pressure at liquid air temperatures. The amount of air present (a pressure of 0.2 mm. at 90°K.) in this sample during the heat capacity measurements (taken before this operation) was not sufficient to affect the accuracy of the results. For the heats of vaporization the two ten-cc. distillates were returned to the calorimeter, the whole cooled to liquid air temperatures and re-evacuated.

The Phillips sample of butene-1 was found to have 0.46 mole per cent. of impurity from its melting point curve assuming the impurity to be liquid soluble, solid insoluble.

The Heat Capacity Measurements.—The heat capacities were measured in calorimeter C, as previously described.[2a,b] Standard thermocouple S-7 was used as standard and S-4 as a check. Prior to the measurements comparison against oxygen vapor pressures had shown no significant change in calibration since the last comparison.[2b] During the measurements the copper wire of S-4 to the ice junction had to be replaced. At the end of the measurements the indications of the standard thermocouples were checked against oxygen vapor pressures. For S-4 the indications corresponded to 0.04° lower and for S-7 0.02° lower than in the last comparison.

Table I

The Molal Heat Capacity of Butene-1

Mol. wt. 56.104; 0.35048 mole, 99.51 mole per cent. pure, in calorimeter for series I–VIII; 0.40090 mole, 99.54 mole per cent. pure, in calorimeter for series IX and X; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
Crystal Series VI		Series V		Series II	
12.84	0.636	77.27	12.59	40.22	7.906
14.34	0.815	Series VII		43.18	8.437
16.42	1.162	80.42	12.93	46.85	9.216
18.54	1.591	Series IV		52.79	10.48
21.39	2.374	82.65	13.32	58.61	19.43
24.62	3.087	85.36	15.55	61.92	27.78
27.58	3.806	Glass and Supercooled Liquid Series III		66.51	27.33
30.20	4.467	13.70	1.507	72.50	27.01
36.23	5.916	14.86	1.584	Normal Liquid Series I	
42.22	7.353	16.49	1.920	89.80	26.14
46.94	8.289	18.28	2.271	94.78	25.92
50.36	8.791	20.77	2.956	99.43	25.75
53.04	9.246	24.92	4.008	Series X	
56.42	9.724	29.23	5.301	96.14	25.74
65.51	11.16	33.90	6.231	105.65	25.53
71.93	12.00	39.79	7.675	124.62	25.28
77.99	12.68	45.24	8.982	135.98	25.24
81.02	13.18	50.71	10.18	144.39	25.18
Series VIII		56.53	12.40	153.77	25.22
60.31	10.41	61.24	27.58	163.67	25.39
64.39	11.01	65.68	32.75	174.60	25.69
72.10	12.02	71.00	26.80	184.79	25.95
Series IX				194.55	26.18
63.86	10.96			204.92	26.45
68.21	11.62			215.36	26.76
72.74	12.19			237.71	27.73
78.36	12.90			248.39	28.17
				258.51	28.46

---

[1] Phillips Petroleum Fellow, 1944.

[2] (a) Aston and Messerly, This Journal, **58**, 2354 (1936); (b) Messerly and Aston, *ibid.*, **62**, 886 (1940).

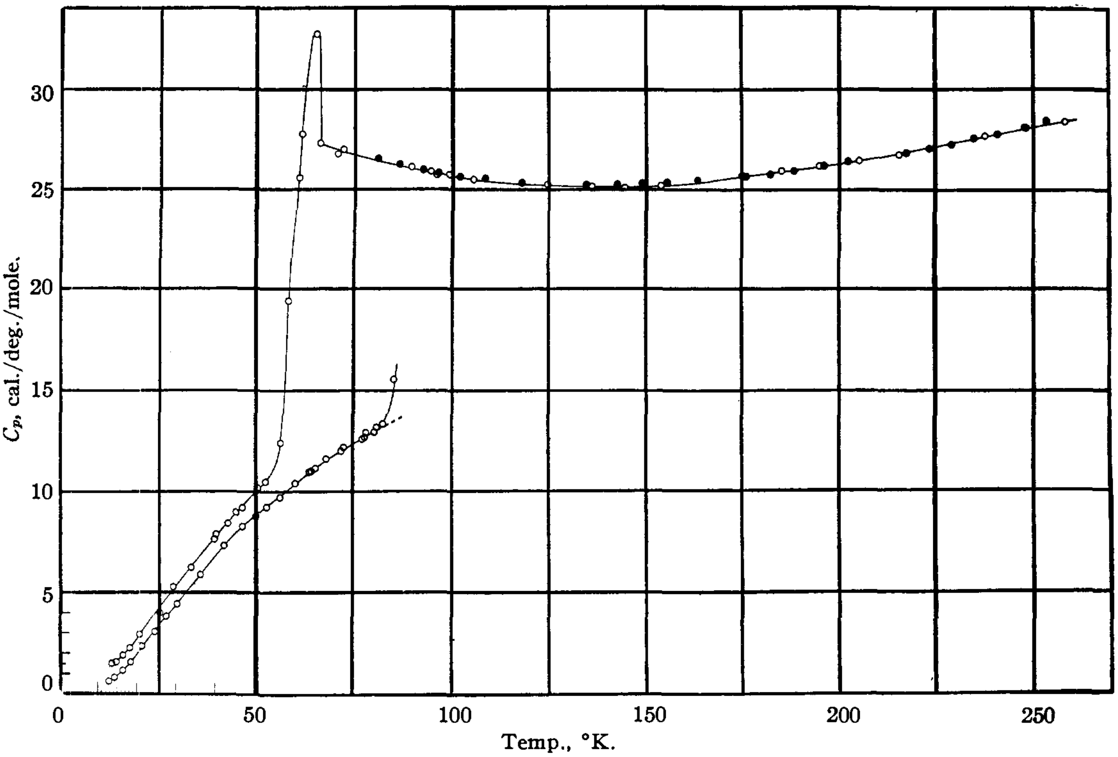

Fig. 1.—The molal heat capacity of butene-1: ○, this research; ●, Todd and Parks.

In most cases the time of energy input for the heat capacities was measured by means of the laboratory automatic timer, which was checked against the Arlington time signals. In the remaining cases the time was measured directly by a calibrated tenth-second stop watch. One calorie was taken as equal to 4.1833 international joules. The values obtained for the heat capacities are listed in Table I, and plotted against the absolute temperature in Fig. 1 as open circles. The solid circles in Fig. 1 represent the data of Todd and Parks[3] which differ on the average by 0.27% from the results of the present investigation and by a maximum of 0.71%. The heat capacities in Table I near the melting point have not been corrected for premelting but the dotted curve in Fig. 1 represents our estimate of this correction. The temperature rises can be estimated from the intervals between successive points in a given series. Corrections to the heat capacities for vaporization into the filling line were made using the density values listed by Coffin and Maass.[4] Below 30°K., because of large heat leak and rapidly changing resistance thermometer derivatives, the error in these heat capacities may rise to as much as 5% at the lowest temperatures. Between 30 and 200°K., the accuracy is about 0.3%, falling off to about 0.5% at higher temperatures because of radiation.

TABLE II

THE MOLAL HEAT CAPACITY OF BUTENE-1 AT ROUNDED TEMPERATURES

Mol. wt. 56.104; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules

Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
Crystal		110	25.48
12	0.481	120	25.32
15	0.921	130	25.19
20	1.963	140	25.19
25	3.174	150	25.20
30	4.417	160	25.33
35	5.625	170	25.55
40	6.808	180	25.78
50	8.774	190	26.04
60	10.36	200	26.32
70	11.76	210	26.63
80	12.88	220	27.00
		230	27.40
Liquid		240	27.80
90	26.12	250	28.18
100	25.73	260	28.55

Method of Crystallization and Melting Point of Butane-1.—After the second cooling of the Petroleum Laboratory sample of butene-1 to liquid hydrogen temperatures and subsequent warming, crystallization started at 72°K. and continued for a period of two days as indicated by cessation of the warm drift of the calorimeter. A value of the heat of fusion was determined by the usual method after the warm drifts had ceased.

The equilibrium temperature of solid and

---

(3) Todd and Parks, THIS JOURNAL, 58, 134 (1936).

(4) Coffin and Maass, *ibid.*, 50, 1427 (1928).

liquid butene-1 was observed over a period of thirty-one hours with increasing fractions of the sample melted as estimated from the heat input and heat leak corrections. From these results and the heat of fusion, the impurity present was found to be 0.49 mole per cent., assuming no solid solution. The mole per cent. impurity calculated[5] from the premelting heat capacities is only 0.075. The higher value from the melting curve could be due to lack of equilibrium or the lower value from the premelting heat capacities could be due to solid solution.

A similar determination of the equilibrium temperatures during melting for a sample of butene-1 supplied by Phillips Petroleum Company gave a value of the liquid-soluble solid-insoluble impurity of 0.46 mole per cent. This value may also be too high. Tables III and IV summarize the data on the melting point. The last column of these tables gives the equilibrium temperature calculated from the equation

$$\Delta T = \frac{RT^2}{\Delta H} N_0^2 \frac{100}{x} \qquad (1)$$

where ΔT is the lowering from the melting point of the pure substance, ΔH is the heat of fusion, T is the melting point of the pure compound, N_2^0 is the mole fraction of the impurity in the completely melted sample and x is the per cent. melted when the lowering is ΔT.

TABLE III

MELTING POINT OF BUTENE-1

(Petroleum Refining Laboratory Sample)

0 °C. = 273.16 °K.

Melted, %	Total time, min.	T, °K. S-7	T, °K. Res. therm.	T, °K. Calcd.
11.9	250	87.459	87.470	87.093
32.5	310	87.595	87.595	87.563
47.1	440	87.652	87.655	87.646
56.2	1215	87.671	87.663	87.676
65.1	1360	87.690	87.691	87.698
74.0	1575	87.712	87.707	87.714
82.8	1870	87.727	87.722	87.727
(100)	(Extrapolated)		87.745	87.745
Melting point of pure butene-1			87.83 ± 0.02 °K. (−185.33 °C.)	
Mole per cent. impurity			0.49	

TABLE IV

MELTING POINT OF BUTENE-1

(Phillips Petroleum Company Sample)

0 °C. = 273.16 °K.

Melted, %	Total time, min.	T, °K. S-7	T, °K. Res. therm.	T, °K. Calcd.
13.0	580	87.346	87.346	87.210
33.5	1240	87.593	87.593	87.572
54.3	1335	87.673	87.662	87.660
64.7	1445	87.687	87.687	87.682
74.9	1525	87.705	87.704	87.698
87.3	1605	87.707	87.716	87.713
(100)	(Extrapolated)		87.725	87.724
Melting point of pure butene-1			87.80 ± 0.02 °K. (−185.36 °C.)	
Mole per cent. of impurity			0.46	

The discrepancies between Tables III and IV which lead to a melting point of the pure material deduced from the Phillips sample 0.03° higher than from the Petroleum Refining Laboratory sample may be due to the lack of equilibrium due to the high viscosity of the liquid. The calorimeter took unusually long to reach a constant temperature in each case. The length of time to reach equilibrium produced large corrections due to heat leak which makes the fraction melted in error by several per cent. This could also account, in part, for the discrepancies. The average of the two values of the melting point is 87.82 ± 0.02°K. This is the only value of the melting point of butene-1 reported, as it has apparently never been crystallized previously.

The Vapor Pressures.—The vapor pressure measurements were made on the 15-cc. sample discussed above. The results of the determinations, made as described previously,[2a,b] are presented in Table V. Column 1 gives the absolute temperature as read on the resistance thermometer (calibrated against S-4 and S-7), column 2 gives the corresponding pressure, column 3 gives the pressure calculated from the equation

$$\log_{10} P\text{mm} = -1360.869/T + 1.672647 \log_{10} T - 0.00495236T + 5.242833 \qquad (2)$$

Column 4 gives the difference between the pressure observed and that calculated from equation 2.

TABLE V

THE VAPOR PRESSURE OF BUTENE-1

0 °C. = 273.16 °K.; g for State College = 980.124 (I. C. T.)

T obs., °K.	P obs. Int. mm. Hg	P calcd. Int. mm. Hg	$P_{\text{obs.}} - P_{\text{calcd.}}$[a] Int. mm. Hg This research	L. and R.[6]
199.061	18.43	18.45	−0.02	+1.6
204.733	28.03	28.03	.00	+1.9
214.626	54.89	54.87	+ .02	+2.5
231.202	146.54	146.53	+ .01	+2.9
245.604	304.55	304.53	+ .02	+2.0
252.642	420.39	420.39	.00	+1.4
258.765	547.23	547.25	− .02	+1.0
264.363	687.56	687.64	− .08	+1.1
266.841	758.06	758.20	− .14	+1.1
After distilling off one-third of the sample				
247.168	327.73	327.71	+0.02	+2.0
258.396	538.78	538.90	− .12	+1.0
266.064	735.39	735.64	− .25	+1.0

[a] $\log_{10} P\text{mm.} = -1360.869/T + 1.672647 \log_{10} T - 0.00495236T + 5.242833. \qquad (2)$

The most complete vapor pressure data up to now are those of Lamb and Roper.[6]

In the last column of Table V are given the values of the difference between the observed pressure and that calculated from the equation of

---

[5] Johnston and Giauque, THIS JOURNAL, 51, 3194 (1929).

[6] Lamb and Roper, *ibid.*, 62, 806 (1940).

Lamb and Roper. The sample used by Lamb and Roper may have contained air as indicated by the deviations between their pressures and ours and from the extreme difficulty we found in removing air from the sample.

From equation 2 the normal boiling point is 266.91°K. (−6.25°C.). Previous values given for the normal boiling point are 267.1°K. (−6.1°C.)[4], 266.86°K. (−6.30°C.),[6] 267.0°K. (−6.2°C.),[7] 266.84°K. (−6.32°C.),[8] 266.5°K. (−6.7°C.).[9]

The Heat of Fusion.—The data were obtained in the usual manner using the Petroleum Refining Laboratory sample. The results are summarized in Table VI. The correction for premelting was calculated assuming 0.075 mole per cent. impurity.

TABLE VI

HEAT OF FUSION OF BUTENE-1

Mol. wt. 56.104; 0.35048 mole; melting point 87.83 ± 0.02°K.; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Temp. interval °K.	Cor. heat input, cal./mole	$\int C_p\,dT$ cal./mole	Pre-melting	ΔH fusion cal./mole
78.773–89.085	1214.3	296.7	1.3	918.9
83.505–90.639	1149.1	232.6	2.7	919.2
84.210–89.792	1096.9	179.2	3.4	921.1
			Average	919.7 ± 2.2

Heats of Vaporization.—The methods employed in the determination of the heat of vaporization have been described previously.[10a,b] The same calorimeter with which the heats of fusion and the heat capacity measurements were taken, was used. The results are summarized in Table VII. In the first four vaporizations, the vaporized sample was condensed in a bulb surrounded by liquid air, and its volume was measured later in a three-liter calibrated bulb. In the last two, the vaporized material was collected directly over mercury at constant pressure in the three-liter calibrated bulb. In calculating the weights from the volumes the measured densities were used.

TABLE VII

THE MOLAL HEAT OF VAPORIZATION OF BUTENE-1

Mol. wt. 56.104; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Moles vaporized	Mean temp. of vaporization, °K.	Total heat input, cal./mole	$\int C_p\,dT$ cal./mole	ΔH at mean temp. of vaporization to real gas state cal./mole obs.	calcd.[a]
0.11515	202.305	5937.1	−102.2	6039.3	6035.6
.14419	202.853	5988.6	− 35.6	6024.2	6030.1
.11780	218.865	5811.2	− 53.0	5864.2	5859.6
.10681	242.232	5469.9	−104.8	5574.7	5577.9
.13142	266.454	5100.1	−149.7	5249.8	5244.5
.12135	266.722	5066.6	−169.5	5236.1	5240.5

[a] Calculated from $\Delta H = 6595.06 + 4.49954T - 0.0359104T^2$.

The Vapor Densities.—The vapor densities, obtained by a previously described method,[10b] are summarized in Table VIII.

TABLE VIII

THE VAPOR DENSITIES OF BUTENE-1 AT 298.16°K.

Pressure, atm.	Density, g./cc.	P/d obs.	P/d calcd.[a]	B, liter/mole[c]
1.00163	0.00236600	423.343	423.304	−0.611
0.96913	.00228783	423.602	423.674	− .617
.46647	.00108623	429.440	429.361	− .604
.17225	.00039820	432.572	432.644	− .628
.00000[b]	....	.....	434.503	.....

[a] Calculated from $P/d = 434.503 - 4733.4d$. [b] Extrapolated. [c] Calculated using a molecular weight of 56.307.

The experimental data are represented by the equation

$$P/d = 434.503 - 4733.4d \qquad (3)$$

in which the pressure is expressed in atmospheres and the density in g./cc. The data can also be represented by the equation

$$d/P = 0.0000615187P + 0.00230067 \qquad (4)$$

in the same units as the preceding one. The two equations give substantially the same values for the limiting density and virial coefficient B.

The molecular weight obtained by the method of limiting density was 56.307 as compared to the calculated value of 56.104 for the pure material. This could be due to adsorption on the glass bulb and/or in stopcocks.

The mean value of the virial coefficient, defined by

$$PV = RT\,(1 + (B/V)) \qquad (5)$$

(where P is the pressure, V the molecular volume of the gas in liters and R the gas constant in suitable units) calculated from the data of four separate measurements is −0.615 liter/mole at 298.16° K. A value of −0.654 liter/mole was obtained by Roper[11] under the same conditions. It is also possible to calculate the virial coefficient B from the heats of vaporization and the Clausius–Clapeyron equation

$$dP/dT = \Delta H/T\Delta V \qquad (6)$$

The results of this calculation are summarized in Table IX. Column 1 gives the temperature, column 2 gives the pressure, column 3 the value of dP/dT obtained by differentiating equation 2 and substituting, column 4 gives the value of the molal heat of vaporization (ΔH), column 5 gives the molal volume of the liquid (V_L)[4], column 6 gives the molal volume of the gas (V_g) calculated

$$\Delta V = V_g - V_L \qquad (7)$$

from equations 6 and 7, and column 7 gives the value of B calculated from equation 5, while column 8 gives the value of B obtained by Roper.[11] Our values below 0.34 atm. are undoubtedly in error due to the small value of B/V and to the inaccuracies in dP/dT at the low pressures. The

---

(7) Coffin, Sutherland and Maass, *Can. J. Research*, **2**, 267 (1930).

(8) Benoliel, M. S. thesis, The Pennsylvania State College, 1940.

(9) Hurd and Goldsby, THIS JOURNAL, **56**, 1812 (1934).

(10) (a) Aston, Fink and Schumann, *ibid.*, **65**, 341 (1943); (b) Aston, Sagenkahn, Szasz, Moessen and Zuhr, *ibid.*, **66**, 1171 (1944).

(11) Roper, *J. Phys. Chem.*, **44**, 835 (1940).

TABLE IX

THE SECOND VIRIAL COFFICIENTS (B) OF BUTENE-1 FROM HEATS OF VAPORIZATION AND VAPOR PRESSURES

T, °K.	P, atm.	dp/dT, mm./deg.	ΔH, cal./mole	V_e, liters/mole	V_g, liters/mole	B, liters/mole this research	B, liters/mole Roper[11]
202.305	0.03094	1.7267	6039.3	0.081	542.720	+6.3	−1.94
202.853	.03220	1.7863	6024.2	.081	521.884	+5.0	−1.92
218.865	.09431	4.4192	5864.2	.083	190.384	−0.05	−1.55
242.232	.34067	12.662	5574.7	.086	57.134	−1.18	−1.16
266.454	.98247	29.128	5249.8	.090	21.321	−0.89	−0.89
266.722	.99279	29.362	5236.1	.090	21.075	−0.93	−0.89

check with Roper at 0.34 atm. and above is gratifying.

The Entropy from the Calorimetric Data.—The calculation of the absolute entropy of the liquid at the melting point and at the normal boiling point from the low temperature heat capacity data on the crystal is summarized in Table X, along with the calculation for the liquid at the melting point from the low temperature heat capacity data on the glass. The difference between the two values of the entropy of the liquid at the melting point gives directly the value of the residual entropy of the glass at 0°K. This residual entropy value was found to be 3.01 cal./deg./mole. There is no doubt that the heat capacity values on the glass do not represent equilibrium values for the phase, considered as a highly viscous liquid, and that different values could be obtained depending on the history of the glass[12] and hence the meaning of such a value is not very definite. Other values obtained for residual entropies of glasses are those for glycerol[13a,b,c] and ethyl alcohol[14] which were 4.6 and 2.6 cal./deg./mole, respectively.

TABLE X

THE MOLAL ENTROPY OF BUTENE-1 CRYSTAL AND LIQUID

Mol. wt., 56.104; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

	Cal./deg./mole		Cal./deg./mole
0–20.00°K. Debye extrapolation (six degrees of freedom) Crystal, θ = 149,	0.714	Glass, θ = 126,	1.116
20.00–87.82°K. ($\int C_p \, d \ln T$ – analytical) crystal	10.970	Glass and liquid	18.032
Crystal at 87.82°K.	11.684 ± 0.03		
Fusion (919.7/87.82)	10.473		
Liquid at 87.82°K.	22.157 ± 0.06		19.148 ± 0.06
Liquid 87.82–266.91°K. ($\int C_p \, d \ln T$ – analytical)	28.950 ± 0.08		
Liquid at 266.91°K.	51.107 ± 0.14		

Residual entropy in glass at 0°K. 22.16 − 19.15 = 3.01 e. u.

The calculations of the entropy of the ideal gas at 200, 230°K., the normal boiling point and 298.16°K. are given in Table XI. The corrections to the ideal gas state were made using Roper's virial coefficients.

The Entropy from Molecular Data.—Since the time when the thermodynamic quantities of butene-1 were first calculated by Pitzer,[15] little further information has become available from which to get a better frequency assignment and molecular model. The Raman spectrum of the liquid is too complicated to analyze.[16]

Employing Pitzer's original treatment, we have used the entropy of the vapor at the normal boiling point, 266.91°K., to solve for the barrier hindering the mutual internal rotation of the ethyl and vinyl groups with respect to each other.

For this calculation the product of the principal moments of inertia was taken as

$$ABC = 1.53 \times 10^{-114} \text{ (g. cm.}^2)^3$$

TABLE XI

THE MOLAL ENTROPY OF GASEOUS BUTENE-1 AT CERTAIN TEMPERATURES

Mol. wt., 56.104; 0°C. = 273.16°K.

	Cal./deg./mole			
	200.00°K.	230.00°K.	266.91°K.	298.16°K.
Liquid at melting point	22.157 ± 0.06	22.157 ± 0.06	22.157 ± 0.06	22.157 ± 0.06
87.82 − T°K. (analytical)[b]	21.025 ± 0.06	24.763 ± 0.07	28.950 ± 0.08	32.248 ± 0.10
Vaporization at T°K.[a]	30.293 ± 0.06	24.914 ± 0.06	19.624 ± 0.04	15.912 ± 0.06
Gas imperfection correction	0.012	0.045	0.142	0.264
Correction to 1 atm.	−7.247	−3.402	0	+2.105
Entropy ideal gas at T°K., 1 atm.	66.24 ± 0.20	68.48 ± 0.21	70.87 ± 0.21	72.69 ± 0.30
From Molecular Data:				
Pitzer, V = 4500	65.96	68.29	70.86	73.08
Calcd. model, V = 2200	65.98	68.35	70.92	73.20

[a] Calculated from $\Delta H = 6595.06 + 4.49954T - 0.0359104T^2$. [b] Above 258°K. the heat capacities were extrapolated analytically.

---

(12) Nelson and Newton, THIS JOURNAL, **63**, 2178 (1941).

(13) (a) Gibson and Giauque, *ibid.*, **45**, 93 (1923); (b) Simon and Lange, *Z. Physik*, **38**, 227 (1926); (c) Ahlberg, Blanchard and Lundberg, *J. Chem. Phys.*, **5**, 539 (1937).

(14) Kelley, THIS JOURNAL, **51**, 779 (1929).

(15) K. S. Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

(16) Kahovec and Kohlrausch, *Z. physik. Chem.*, **B46**, 165 (1940).

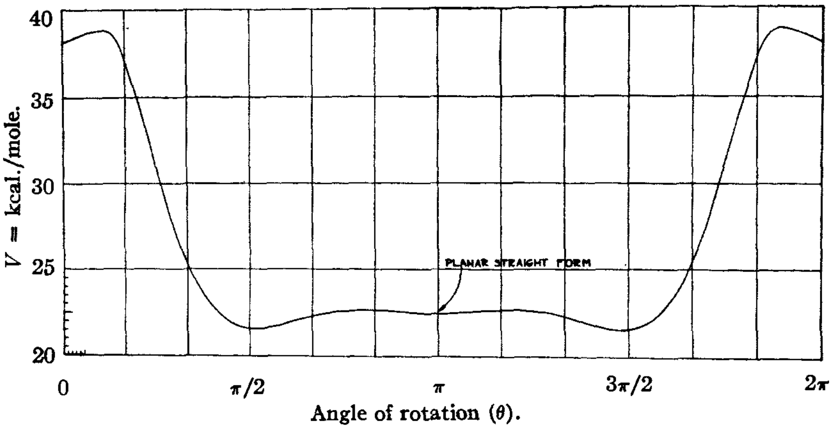

Fig. 2.—The potential energy of the ethyl group in butene-1.

The reduced moment for the mutual rotation of the ethyl and vinyl groups was

$$I_{\text{red}} = 13.37 \times 10^{-40} \text{ g. cm.}^2$$

and the reduced moment for the internal rotation of the methyl groups was

$$I_{\text{red}} = 5.0 \times 10^{-40} \text{ g. cm.}^2$$

A potential of 3600 cal. was assumed to hinder the internal rotation of the methyl groups. The expression for the entropy of translation and total rotation (including internal rotation not corrected for restriction) is

$$S_{\text{t+r+int.rot.}} = 22.875 \log T + 15.854 \qquad (8)$$

The barrier obtained was 4500 cal. The entropies calculated at 200, 230 and 298.16°K. with this barrier are included in Table XI (second row from the bottom).

A calculation of the potential energy as an ethyl group rotates with respect to a vinyl group can be made on the basis of hydrogen repulsions alone with the constants of the potential function deduced from the potential barriers of simple hydrocarbons.[17] This leads to the curve shown in Fig. 2 where θ is the angle of rotation of the vinyl group with respect to the ethyl group. The value, θ equals π, corresponds to the position with the carbon atoms staggered in the plane, usually referred to as the straight configuration.

If the actual situation is at all like that given by this curve, one would expect two stereoisomers of the configuration corresponding to $\pi/2$ and $3\,\pi/2$. It has been arbitrarily assumed that each of these occupies $^1/_3$ of a revolution. Corresponding to this supposition the above calculation has been repeated using equation 8 with $R \ln 2$ added for the entropy of mixing of these isomers and $R \ln 3$ subtracted to allow of their being limited to $^1/_3$ of a revolution. The barrier thus obtained is 2200 cal. The results at 200, 230 and 298.16°K. are also tabulated in Table XI (bottom line).

Acknowledgments.—We thank Phillips Petroleum Company and Professor M. R. Fenske for making available the samples of butene-1. Financial aid for the greater portion of this investigation was furnished by Phillips Petroleum Company. The work was carried out coöperatively with the Cryogenic Laboratory of the U. S. Bureau of Standards and is part of a program on the thermodynamic properties of the four carbon hydrocarbons. Much of the apparatus was purchased with funds provided by the National Research Council.

Summary

1. Butene-1 has been crystallized for the first time.
2. The heat capacities of crystalline butene-1 have been measured from 11°K. to the melting point; of butene-1 glass, from 12.5 to 78°K.; of the liquid, from the melting point (87.82°K.) to the normal boiling point.
3. The solid–liquid equilibrium temperature and heat of fusion have been determined.
4. The vapor pressures have been determined from 199 to 267°K. and the results represented by an equation leading to a value for the normal boiling point.
5. The heats of vaporization have been determined from 202 to 267°K. and a quadratic equation derived to represent them.
6. Vapor densities have been measured at 298.16°K. and a value of the virial coefficient calculated from the results. Values of the virial coefficient at lower temperatures have been calculated using the equations for the vapor pressures and heats of vaporization.
7. From the heat capacities, a value has been calculated for the difference in entropy between butene-1 crystal and glass at 0°K. as well as values for the entropy of the saturated vapor and ideal gas at 200, 230°K., the normal boiling point and 298.16°K.
8. The calorimetric entropy of the ideal gas at one atmosphere and 266.91°K. (70.87 ± 0.21 e. u.) has been used, in conjunction with assumed molecular data, to calculate two alternative values of the barrier hindering the mutual relative rotation of the ethyl and vinyl groups. Entropies have been calculated from the molecular data with these barriers and compared with the experimental values at 200, 230, and 298.16°K.

STATE COLLEGE, PENN. RECEIVED MARCH 26, 1945

---

[17] Aston, Isserow, Szasz and Kennedy, *J. Chem. Phys.*, **12**, 337 (1944).