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THERMODYNAMIC PROPERTIES OF *cis*-2-BUTENE FROM 15° TO 1,500°K[1]

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ABSTRACT

The following properties of a sample of *cis*–2–butene, 99.94 percent pure, were measured: (1) the specific heat of solid and of liquid from 15° to 300°K, (2) heat of fusion at the triple point (130.25 int. joule g^{-1}), (3) triple-point temperature ($-138.900 \pm 0.008°$ C), (4) heats of vaporization at several temperatures between 246° and 293°K, and (5) vapor pressure from 200° to 296°K. With these experimental data, calculations were made of (1) the normal boiling temperature (3.718°C), (2) volume of the saturated vapor, (3) enthalpy and entropy of the solid and the liquid from 0° to 300°K, and (4) entropy, enthalpy, and specific heat of the vapor in the ideal gas state from 245° to 300°K. Thermodynamic functions for *cis*–2–butene in the ideal gas state from 300° to 1,500°K were calculated from spectroscopic data. Thermodynamic data for the *cis-trans* isomerization of 2–butene are included.

CONTENTS

I. INTRODUCTION

The measurements and calculations described in this paper constitute a continuation of the program of obtaining data on the properties of materials that are of interest in the chemistry of synthetic rubber.

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[1] The investigation reported in this paper is part of a joint program with the Cryogenic Laboratory, The Pennsylvania State College, on the C_4 hydrocarbons.

The properties measured include the specific heat at saturation pressure of solid and of liquid *cis*-2-butene from 15° to 300° K, heat of fusion, heat of vaporization at several temperatures between 246° and 292° K, and vapor pressure over the temperature range 200° to 296° K. These experimental data were used to calculate: (1) the volume of the saturated vapor, (2) enthalpy and entropy of the solid and the liquid from 0° to 300° K, and (3) enthalpy, entropy, and specific heat of the vapor in the ideal gas state from 245° to 300° K.

A frequency assignment for the internal vibrations of *cis*-2-butene based upon the infrared absorption and Raman spectra reported by Gershinowitz and Wilson [10],[2] was used to calculate the barrier restricting internal rotation of the methyl groups from the gaseous specific heat data of Kistiakowsky and Rice [9]. The spectroscopic value for the entropy of *cis*-butene in the ideal gas state involving this barrier is in good agreement with the experimental value of the entropy determined from the calorimetric data. From this frequency assignment and value for the barrier, tables were computed for the thermodynamic functions of *cis*-2-butene in the ideal gas state from 300° to 1,500° K.

II. MATERIAL

The *cis*-2-butene used for these measurements was prepared in a pure state by M. R. Fenske, of The Pennsylvania State College, and was further purified at the Bureau by two fractional crystallizations, in which about one-third of the original sample of 122 g was discarded. A volatile impurity, which may have been air, was removed by condensing the material into a trap surrounded by liquid air while maintaining a high vacuum on the trap. Sixty-four grams of the material thus purified was used in the calorimetric investigations. The amount of impurity in this sample, assuming the impurity to be insoluble in solid *cis*-butene, was computed from measurements taken with the calorimeter, which gave the melting temperature as a function of the fraction melted. The temperature at which 50 percent of the sample was melted was found to be 0.0116° K lower than the temperature at which 99+ percent was melted. This corresponds to a "liquid soluble, solid insoluble" impurity of 0.057 mole percent.

III. APPARATUS

This investigation was carried out with the same apparatus used for the measurements on 1,3-butadiene. The calorimeter was similar to the adiabatic vacuum type of Southard and Brickwedde [1], but was modified somewhat for the measurement of heats of vaporization and to improve the temperature distribution and for ease of control. A manuscript on 1,3-butadiene [2], giving a complete description of the apparatus, methods of measurement, and correlation of the data, has been prepared.

IV. SPECIFIC HEAT

The data from which the specific heats were calculated were obtained in two sets of measurements of the heat capacity of the calorimeter and contents, first with a large amount of material in the calorimeter

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[2] Figures in brackets indicate the literature references at the end of this paper.

and then with a small amount. If G_b is the heat capacity of the calorimeter plus an amount of material M_b, and G_a is the heat capacity of the calorimeter plus an amount of material M_a, then the specific heat of the material in the condensed state at saturation pressure is

$$C_{sat.}=\frac{G_b-G_a}{M_b-M_a}+T\frac{d}{dT}\left(v\frac{dP}{dT}\right),^{3} \qquad (1)$$

where T is the absolute temperature, v is the specific volume of the condensed phase, and P is the vapor pressure. This relation was derived from equation 11 of the paper by N. S. Osborne [3]. The first term of the right-hand member of equation 1 would be the specific heat if the substance were not volatile. The last term of this equation takes account of the heat required to vaporize some of the material during a heat-capacity determination so as to maintain saturation vapor pressure. In the present experiment, the large mass, M_b, consisted of 64.235 g of *cis*-2-butene, and the small mass, M_a, was 0.740 g.

The values of v, the specific volume of the liquid, were obtained from a table compiled by Cragoe [4]. Values of dP/dT were obtained from vapor-pressure equation 5, p. 7. At temperatures below 85°K no measurements were made with the small amount of material in the calorimeter, G_a being taken as the heat capacity of the completely empty calorimeter, as determined by earlier measurements, M_a being zero of course. This was permissible, since below 165° K the last term in equation 1 is negligible. At temperatures between 85° and 130° K, inclusive, the specific heats were calculated by both methods, first from the values of G_a and M_a obtained in this investigation, and then with the earlier values of G_a for the empty calorimeter and the value zero for M_a. This was done as a check on the reproducibility of the measurements. The maximum difference between the two sets of values for the specific heats in this temperature region was about 1 part in 1,200, and the mean deviation was 1 part in 2,500. The values reported here were obtained by averaging the two sets of values.

Figure 1 gives the specific heat of *cis*-2-butene, and the second column of table 1 gives the results of the specific heat-determinations tabulated at 5-degree intervals. The values at 5° and 10° K were calculated by using the equation

$$C_{sat.}=0.7381\mathrm{D}\left(\frac{150}{T}\right),$$

where **D** is the Debye specific-heat function. The numerical constants were chosen to fit the data at 15°, 20°, and 25° K.

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[3] This relation was derived by Harold J. Hoge.

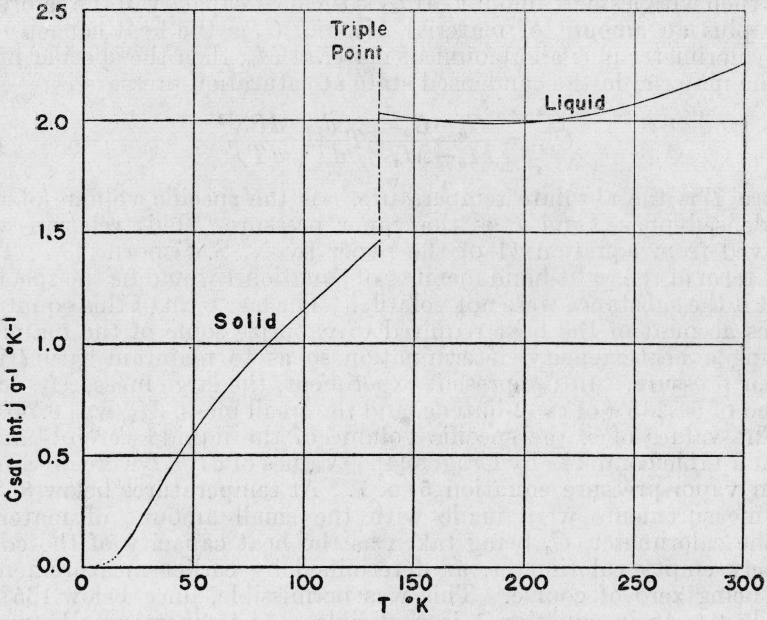

FIGURE 1.—*Specific heat of solid and liquid cis-2-butene.*

TABLE 1.—*Specific heat, entropy, and enthalpy*[a] *of solid and of liquid cis-2-butene at saturation pressure*

[13.4114 cal mole^{-1}=1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	$C_{sat.}$	$S_{sat.}$	$\int_0^T C_{sat.}\,dT$	$\int_0^T V_{sat.}\frac{dP}{dt}\,dt$	$(H_{sat.}-E_0^s)$
			SOLID		
°K	*Int. j g^{-1} °K^{-1}*	*Int. j g^{-1} °K^{-1}*	*Int. j g^{-1}*	*Int. j g^{-1}*	*Int. j g^{-1}*
0	0	0	0	0	0
5	[b].00213	.0007	.0027	----------------	.0027
10	[b].01703	.0057	.0426	----------------	.0426
15	.05645	.0190	.214	----------------	.214
20	.1197	.0435	.648	----------------	.648
25	.1969	.0783	1.434	----------------	1.434
30	.2812	.1216	2.629	----------------	2.629
35	.3669	.1714	4.248	----------------	4.248
40	.4496	.2258	6.291	----------------	6.291
45	.5280	.2834	8.737	----------------	8.737
50	.6012	.3428	11.562	----------------	11.562
55	.6705	.4034	14.743	----------------	14.743
60	.7370	.4646	18.264	----------------	18.264
65	.7979	.5261	22.103	----------------	22.103
70	.8551	.5873	26.237	----------------	26.237
75	.9091	.6482	30.649	----------------	30.649
80	.9602	.7085	35.323	----------------	35.323
85	1.0102	.7682	40.249	----------------	40.249
90	1.0584	.8273	45.422	----------------	45.422
95	1.1040	.8858	50.829	----------------	50.829
100	1.1482	.9435	56.460	----------------	56.460
105	1.1916	1.0006	62.310	----------------	62.310
110	1.2349	1.0570	68.376	----------------	68.376
115	1.2790	1.1129	74.660	----------------	74.660
120	1.3237	1.1682	81.166	----------------	81.166
125	1.3694	1.2232	87.899	----------------	87.899
130	1.4164	1.2778	94.863	----------------	94.863
134.26	1.4584	1.3242	100.99	----------------	100.99

See notes at end of table.

TABLE 1.—*Specific heat, entropy, and enthalpy*[a] *of solid and of liquid cis-2-butene at saturation pressure*—Continued

T	$C_{sat.}$	$S_{sat.}$	$\int_0^T C_{sat.} dT$	$\int_0^T V_{sat.} \frac{dP}{dt} dt$	$(H_{sat.}-E_0^s)$
LIQUID					
°K	*Int. j g⁻¹ °K⁻¹*	*Int. j g⁻¹ °K⁻¹*	*Int. j g⁻¹*	*Int. j g⁻¹*	*Int. j g⁻¹*
134. 26	2. 0334	2. 2944	231. 24	----------	231. 24
135	2. 0318	2. 3055	232. 75	----------	232. 75
140	2. 0209	2. 3792	242. 88	----------	242. 88
145	2. 0114	2. 4500	252. 96	----------	252. 96
150	2. 0035	2. 5180	263. 00	----------	263. 00
155	1. 9974	2. 5836	273. 00	----------	273. 00
160	1. 9923	2. 6470	282. 97	----------	282. 97
165	1. 9876	2. 7082	292. 92	----------	292. 92
170	1. 9840	2. 7675	302. 85	----------	302. 85
175	1. 9823	2. 8249	312. 76	----------	312. 76
180	1. 9801	2. 8808	322. 67	----------	322. 67
185	1. 9803	2. 9350	332. 57	----------	332. 57
190	1. 9817	2. 9878	342. 47	----------	342. 47
195	1. 9840	3. 0393	352. 39	----------	352. 39
200	1. 9867	3. 0896	362. 31	----------	362. 31
205	1. 9903	3. 1387	372. 26	----------	372. 26
210	1. 9950	3. 1867	382. 22	0. 01	382. 23
215	2. 0009	3. 2337	392. 21	. 01	392. 22
220	2. 0081	3. 2798	402. 23	. 01	402. 24
225	2. 0166	3. 3250	412. 29	. 02	412. 31
230	2. 0264	3. 3695	422. 40	. 02	422. 42
235	2. 0372	3. 4132	432. 56	. 03	432. 59
240	2. 0484	3. 4562	442. 77	. 04	442. 81
245	2. 0602	3. 4985	453. 04	. 05	453. 09
250	2. 0731	3. 5403	463. 38	. 06	463. 44
255	2. 0871	3. 5814	473. 77	. 07	473. 85
260	2. 1018	3. 6221	484. 25	. 09	484. 34
265	2. 1178	3. 6623	494. 79	. 11	494. 91
270	2. 1348	3. 7020	505. 43	. 13	505. 56
275	2. 1529	3. 7414	516. 14	. 16	516. 30
280	2. 1716	3. 7803	526. 96	. 19	527. 15
285	2. 1912	3. 8190	537. 86	. 22	538. 08
290	2. 2119	3. 8572	548. 87	. 26	549. 13
295	2. 2335	3. 8952	559. 98	. 30	560. 28
298. 16[c]	*2. 2480*	*3. 9191*	*567. 08*	*. 33*	*567. 41*
300	2. 2564	3. 9330	571. 21	. 35	571. 56

[a] The enthalpy is referred to $H_0^s=E_0^s$, the internal energy of solid *cis*-butene at 0°K.

[b] Extrapolated, using Debye function, 0.7381D (150/T).

[c] =25°C.

V. HEAT OF FUSION AND TRIPLE-POINT TEMPERATURE

The heat of fusion was determined by measuring the amount of electric energy required to heat the calorimeter and contents from a temperature, T_1, below the triple point to a temperature, T_2, above the triple point. If this measured energy is Q_t, then the heat, Q_f, required to melt the contents is

$$Q_f=Q_t-\int_{T_1}^{T_f} G_s dT-\int_{T_f}^{T_2} G_l dT, \tag{2}$$

where T_f is the triple-point temperature, G_s is the heat capacity of the calorimeter and contents below the triple point, and G_l is the heat capacity of the calorimeter and contents above the triple point. Two determinations were made, the data and results of which are given in table 2. The mean value of these determinations is 130.25 int. j g^{-1}. The triple-point temperature of the sample used was 134.248°K. As mentioned in section II, measurements were made which gave the solid-liquid equilibrium temperature as a function of the fraction melted. By the use of this function, the triple-point temperature of pure *cis*-2-butene was found to be 134.260°K, or −138.900°C. Although the error arising from this operation is small, an uncertainty of ±0.008° should be assigned to these values of temperature, because differences this large are sometimes found between the scales of standardized platinum resistance thermometers when they are compared at this temperature [17].

TABLE 2.—*Heat of fusion of cis-2-butene*

[13.4114 cal mole $^{-1}$=1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

Run	T_1	T_2	Q_T	$\int_{T_1}^{T_f} G_s dT$	$\int_{T_f}^{T_2} G_l dT$	Q_f	$L_f=Q_f/M$ (M=64.235 g)
	°K	*°K*	*Int. j*	*Int. j*	*Int. j*	*Int. j*	*Int. j g^{-1}*
1	128.00	136.59	9858.4	1019.4	474.2	8364.8	130.22
2	117.69	136.26	11404.0	2626.0	408.6	8369.4	130.29

VI. HEAT OF VAPORIZATION

The heat of vaporization was determined by measuring the electric power required to keep the temperature of the calorimeter constant while withdrawing vapor from the calorimeter at an almost constant rate. The amount of vapor withdrawn during a measured interval of time was determined by allowing the vapor to condense into a weighing flask cooled with solid CO_2 and weighing the flask before and after each run. The rate of withdrawal of vapor varied from 16 to 20 g per hour for the different runs. Previous experience with the calorimeter in measuring the heat of vaporization of 1,3-butadiene had shown that the values obtained for the heat of vaporization were independent of the rate of withdrawal of vapor. The above rate was chosen because the necessary energy input could be conveniently measured with it, and the material withdrawn during a run of from 40 to 60 minutes could be accurately weighed.

The heat of vaporization, L_v, was calculated from the experimental data by means of the relation

$$L_v=\frac{Q}{M}\left(1-\frac{v}{V}\right), \tag{3}$$

where Q is the amount of electric energy required to keep the temperature of the calorimeter constant while a mass, M, of vapor was withdrawn, v is the specific volume of the liquid, and V is the specific volume of the vapor. If all the vapor produced were withdrawn from the calorimeter and included in the mass, M, Q/M would be the heat of vaporization. However, some of the vapor produced does not leave the calorimeter but fills the space vacated by the evaporated liquid. This is accounted for by the factor $(1-\frac{v}{V})$. Values of v, the specific volume of the liquid, were obtained from a table by Cragoe [4], and values of V, the specific volume of the vapor, were determined from the equation of state (section VIII) and the vapor-pressure equation (section VII).

In table 3 the results of the measurements of the heat of vaporization are given. It was found that the heat of vaporization as a function of temperature could be represented by the following equation, the constants of which were obtained by the method of least squares:

$$L_v \text{ (int. j g}^{-1}) = 542.53 + 0.07217T - 0.0019098T^2, \tag{4}$$

where T is in degrees Kelvin. The *maximum* deviation of the seven observed results from values obtained from the equation is 0.13 percent and the *average deviation* is 0.08 percent.

TABLE 3.—*Heat of vaporization of cis-2-butene*

[13.4114 cal mole^{-1} =1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	Q/M	1-(v/V)	L_v
°*K*	*Int. j g*$^{-1}$		*Int. j g*$^{-1}$
246. 18	444. 47	0. 99892	443. 99
252. 43	440. 15	. 99854	439. 51
252. 44	440. 18	. 99854	439. 54
263. 29	429. 98	. 99766	428. 97
272. 36	421. 51	. 99663	420. 09
279. 70	415. 32	. 99556	413. 48
292. 25	403. 33	. 99311	400. 55

VII. VAPOR PRESSURE

The vapor pressures of a sample of cis-2-butene in the calorimeter were measured with a mercury manometer connected to the calorimeter for this purpose. The heights of the mercury columns were read on a mirror-backed glass scale, having 1-mm divisions, supported in contact with the manometer tubes. For pressures below 1 atmosphere, one arm of the manometer was evacuated. For pressures between 1 and 2 atmospheres this manometer arm was open to the atmosphere, atmospheric pressure being measured with a precision barometer. The inside diameter of the manometer tubes was 10 mm. The readings were corrected for capillary depression due to different meniscus heights and reduced to standard conditions (0°C and g=980.665 cm sec^{-2}). The heights were read to 0.1 mm Hg, although hundredths millimeter were carried after averaging and computing the corrections.

The results of the vapor pressure measurements are given in table 4. It was found that the observed data could be represented within the accuracy of measurement by the equation

$$\log_{10}P = 12.64318 - \frac{1808.945}{T} - 0.0162822T + 1.6686 \times 10^{-5}T^2, \tag{5}$$

in which the pressures are expressed in millimeters of mercury at standard conditions (0° C and g=980.665 cm sec^{-2}), and where T, the Kelvin temperature, is equal to 273.160°+t° C. Values of vapor pressure computed from this equation are given in column 3 of table 4, and the differences between the observed and calculated pressures are given in column 4. The normal boiling point of cis-2-butene, obtained by setting P equal to 760 mm Hg in equation 5, is 276.878° K, or 3.718° C. From Raoult's law a nonvolatile impurity of 0.057 mole percent (sec. II) corresponds to an error of 0.016° C in boiling point.

TABLE 4.—*Vapor pressure of cis-2-butene in millimeters of mercury at standard conditions*

[0° C and g=980.665 cm sec^{-2}]

T[1]	$P_{obs.}$	$P_{calc.}$	ΔP obs.−calc.	T[1]	$P_{obs.}$	$P_{calc.}$	ΔP obs.−calc.
°*K*	*mm* Hg	*mm* Hg	*mm* Hg	°*K*	*mm* Hg	*mm* Hg	*mm* Hg
203.070	13.09	13.09	0.00	266.454	501.51	501.68	−.17
210.612	23.15	23.18	−.03	273.720	672.53	672.73	−.20
217.790	38.29	38.25	+.04	276.849	759.14	759.15	−.01
225.057	61.12	61.12	.00	279.862	850.50	850.35	+.15
233.085	98.58	98.55	+.03	284.304	1000.27	1000.19	+.08
241.613	157.18	157.15	+.03	288.680	1167.07	1167.13	−.06
250.031	240.04	240.09	−.05	293.045	1354.53	1354.38	+.15
258.338	353.25	353.37	−.12	295.919	1489.85	1489.91	−.06
266.444	501.46	501.48	−.02				

[1] T °K=273.160°+t °C.

VIII. PROPERTIES DERIVABLE FROM THE CALORIMETRIC AND VAPOR-PRESSURE DATA

1. ENTROPY AND ENTHALPY OF SOLID AND OF LIQUID

In table 1, column 3, values of the entropy, $S_{sat.}$, of *cis*-2-butene in the solid and the liquid states at saturation pressure are given at 5-degree intervals. These were obtained by a tabular integration of values of $C_{sat.}/T$ by means of Simpson's rule. Values $(H_{sat.}-E_0^s)$ of the enthalpy of the condensed phases at saturation pressure relative to the internal energy, E_0^s, of solid *cis*-butene at 0°K are given in column 6, table 1. These were obtained from the following relations:

$$H_{sat.}-E_0^s=\int_0^T C_{sat.}dT+\int_0^T v_{sat.}\left(\frac{dP}{dT}\right)_{sat.}dT \tag{6a}$$

for the solid, and

$$H_{sat.}-E_0^s=\int_0^T C_{sat.}dT+\int_0^T v_{sat.}\left(\frac{dP}{dT}\right)_{sat.}dT+L_f \tag{6b}$$

for the liquid, where $v_{sat.}$ is the specific volume of the condensed phase in equilibrium with vapor, P is the vapor pressure, and L_f is the heat of fusion. The integrals were evaluated by the tabular method mentioned above. Values of dP/dT were obtained by differentiating the vapor-pressure equation 5, and values of $v_{sat.}$ were taken from the table by Cragoe [4].

The integrations were checked by performing the additional integration $\int_0^T S_{sat.}dT$ and also obtaining values of $TS_{sat.}$. Since

$$\int_0^T S_{sat.}dT=TS_{sat.}-\int_0^T C_{sat.}dT-L_f, \tag{7}$$

an error in the integrations involved in the calculations of $H_{sat.}$ will appear when comparing the values obtained for the two sides of this equation.

2. SPECIFIC VOLUME OF THE VAPOR

The heat of vaporization and vapor-pressure data were used to compute the specific volume of the saturated vapor by means of the Clausius-Clapeyron relation.

$$V-v=\frac{L_v}{T\left(\frac{dP}{dT}\right)_{sat.}}, \tag{8}$$

where V and v are the volumes of the saturated vapor and liquid, respectively, L_v is the observed heat of vaporization (table 3), T is the Kelvin temperature, and $(dP/dT)_{sat.}$ is the temperature derivative of the vapor-pressure equation, 5. Values of V thus obtained are given in table 5.

TABLE 5.—*Volumes of saturated cis-2-butene vapor derived from calorimetric and vapor-pressure data*

T[1]	P (saturation pressure)	V	PV/RT
°*K*	*mm* Hg	*ml g*$^{-1}$	
246.18	198.62	1359.7	0.9869
252.43	269.26	1027.6	.9862
252.44	269.40	1027.3	.9863
263.29	438.95	651.69	.9775
272.36	637.66	459.92	.9687
279.70	845.24	353.85	.9620
292.25	1318.7	232.74	.9448

[1] T °K=273.16°+t °C.

If an equation of state of the form

$$\frac{pV}{RT}=1-\frac{k}{VT^2} \tag{9}$$

is assumed, values of k may be obtained from the experimental values of p, V, and T. Thus

$$k=VT^2\left(1-\frac{pV}{RT}\right). \tag{10}$$

Figure 2 shows the values of k obtained in this way. Also included in figure 2 are values of k computed from the direct measurements of volume made by Roper [5]. There are rather large differences at low temperatures between the values of k calculated from our calorimetric and vapor-pressure data and the values of k calculated from Roper's measurements, but the agreement at higher temperatures is good. The disagreement at low temperatures is perhaps not surprising, since the pressures are so low (limited by the vapor pressure) that pV/RT is nearly equal to 1. The value 1.075×10^6 ml g^{-1} °K^2 was selected for k. We think that ±10 percent is a reasonable probable error for this value.

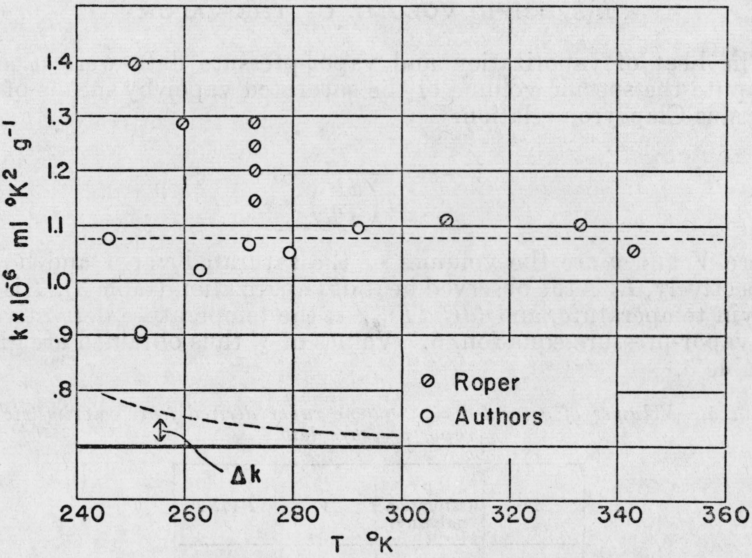

FIGURE 2.—*Experimental values of k in the equation of state, eq 9.*

The horizontal dotted line at $k=1.075\times10^6$ ml °K² g⁻¹ represents the value of k chosen in this investigation. The interval, Δk, bounded by the dotted curve and the horizontal line near the bottom of the graph, represents the error in k that would result from an error of 1 part in 1,000 in $V_{sat.}$, the specific volume of the saturated vapor.

3. THERMAL PROPERTIES OF THE VAPOR

The results thus far obtained were used to compute the enthalpy, entropy, and specific heat at constant pressure of *cis*-2-butene in the ideal gas state. The differences between the enthalpy or entropy of the ideal gas at a pressure of 1 atmosphere and the enthalpy or entropy of the real gas at saturation pressure were obtained from the equation of state, 9, and the thermodynamic relations:

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T \tag{11}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \tag{12}$$

where H is the enthalpy, V is the volume, T is the absolute temperature, p is the pressure, and S is the entropy. The difference between the enthalpy of the ideal gas and that of the saturated vapor in int. j g⁻¹ is

$$H^\circ - H_{sat.} = \frac{3kR}{V_{sat.}T},$$

where k has the value of 1.075×10^6 ml g⁻¹ °K², R is the gas constant for butene in int. j g⁻¹ °K⁻¹ (0.148168), $V_{sat.}$ is the volume of the saturated vapor in ml g⁻¹, and T is the temperature in degrees kelvin.

The difference between the entropy of the ideal gas at 1 atmosphere and that of the real gas at saturation pressure in int. j g^{-1} $°K^{-1}$ is

$$S^\circ_{1\ atm}-S_{sat.}=R\left(\frac{k}{V_{sat.}T^2}+\ln\frac{R'T}{p_{1\ atm}V_{sat.}}\right),$$

where the constants and the properties of the gas are expressed in the same units as those given above for the enthalpy difference, except for the gas constant R', which is in units consistent with those used for p, V, and T. With p expressed in atmospheres and $V_{sat.}$ in ml g^{-1}, R' is 1.4625 atm ml g^{-1} $°K^{-1}$.

Table 6 gives values of the enthalpy of *cis*-2-butene at intervals of 5 degrees between 245° and 300°K and at 298.16°K (25°C) derived from calorimetric and vapor-pressure data. In column 2 are values of the enthalpy of the saturated liquid from table 1. In column 3 are values of the enthalpy of vaporization calculated by means of equation 4. The values at 295°, 298.16°, and 300°K are extrapolations above the range of temperatures included in the measurements of heats of vaporization, but it is improbable that a significant error resulted from the extrapolation. Column 4 gives values of the enthalpy of the saturated vapor, column 5 the differences between the enthalpy of the ideal gas and that of the saturated vapor, and column 6 the enthalpy of the ideal gas. In column 7 are values of the specific heat at constant pressure, C_p°, of the ideal gas. Column 7 entries are actually values of $\Delta H^\circ/\Delta T$ with $\Delta T=10$ degrees. Since dH°/dT is not changing rapidly, the ratio of these finite differences is very nearly equal to the derivative.

Table 7 is similar to table 6, except that corresponding values of entropy are given.

TABLE 6.—*Enthalpies, heat of vaporization, and specific heat of cis-2-butene derived from calorimetric and vapor-pressure data*

[The superscript (°) designates the ideal gas state. E_0^s is the internal energy of solid *cis*-butene at 0°K. 13.4114 cal $mole^{-1}=1$ int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	$(H_{sat.\ liq.}-E_0^s)$	L_v	$(H_{sat.\ vap.}-E_0^s)$	$H^\circ-H_{sat.\ vap.}$	$(H^\circ-E_0^s)$	$C_p^\circ=\frac{dH^\circ}{dT}$
°K	*Int. j g^{-1}*	*Int. j g^{-1}*	*Int. j g^{-1}*	*Int j g^{-1}*	*Int. j g^{-1}*	*Int. j g^{-1} °K^{-1}*
245	453.09	445.58	898.67	1.36	900.03	----------------
250	463.44	441.21	904.65	1.68	906.33	1.262
255	473.85	436.75	910.60	2.05	912.65	1.267
260	484.34	432.19	916.53	2.47	919.00	1.277
265	494.91	427.54	922.45	2.97	925.42	1.288
270	505.56	422.79	928.35	3.53	931.88	1.299
275	516.30	417.95	934.25	4.16	938.41	1.316
280	527.15	413.01	940.16	4.88	945.04	1.332
285	538.08	407.97	946.05	5.68	951.73	1.352
290	549.13	402.85	951.98	6.58	958.56	1.375
295	560.28	397.62	957.90	7.58	965.48	1.398
298.16	*567.41*	*394.27*	*961.68*	*8.27*	*969.95*	----------------
300	571.56	392.30	963.86	8.68	972.54	1.423

TABLE 7.—*Entropies of cis-2-butene derived from calorimetric and vapor-pressure data*

[The superscript (°) designates the standard ideal gas state. Entropy, *S*, of the solid at 0°K equals zero. 13.4114 cal mole^{-1} = 1 int. j g^{-1}. Atomic weights: C = 12.010, H = 1.008]

T	$S_{sat.\ liq.}$	$\Delta S = L_v/T$	$S_{sat.\ vap.}$	$S^\circ_{1\ atm.} - S_{sat.\ vap.}$	$S^\circ_{1\ atm.}$
°*K*	*Int. j g*$^{-1}$ °*K*$^{-1}$	*Int. j g*$^{-1}$ °*K*$^{-1}$	*Int. j g*$^{-1}$ °*K*$^{-1}$	*Int. j g*$^{-1}$ °*K*$^{-1}$	*Int. j g*$^{-1}$ °*K*$^{-1}$
245	3.4985	1.8187	5.3172	−0.2037	5.1135
250	3.5403	1.7648	5.3051	−.1664	5.1387
255	3.5814	1.7127	5.2941	−.1305	5.1636
260	3.6221	1.6623	5.2844	−.0960	5.1884
265	3.6623	1.6134	5.2757	−.0627	5.2130
270	3.7020	1.5659	5.2679	−.0311	5.2368
275	3.7414	1.5198	5.2612	−.0005	5.2607
280	3.7803	1.4750	5.2553	+.0292	5.2845
285	3.8190	1.4315	5.2505	+.0579	5.3084
290	3.8572	1.3891	5.2463	+.0857	5.3320
295	3.8952	1.3479	5.2431	+.1127	5.3558
298.16	*3.9191*	*1.3223*	*5.2414*	*+0.1294*	*5.3708*
300	3.9330	1.3077	5.2407	+0.1389	5.3796

IX. ESTIMATES OF PROBABLE ERRORS IN THE MEASUREMENTS AND IN THE VALUES OF PROPERTIES DERIVED FROM THE CALORIMETRIC DATA

The accuracy of measurements made with the calorimeter used for the *cis*-butene investigation is discussed in more detail, with a description of the calorimeter, in a paper on an investigation of butadiene [2].

The probable error[4] assigned to specific-heat values in table 1 above 40°K is 0.1 percent and to the heat of fusion, 0.07 percent. It is believed that, as a result of increased experience, the probable error of measurement of heats of vaporization of *cis*-butene is 0.1 percent instead of the 0.15 percent for the butadiene investigated earlier. Errors in the temperature scale are on the average much smaller than 0.1 percent of the absolute temperature, hence they do not introduce appreciable calorimetric errors. The enthalpy and entropy of solid *cis*-butene at 40°K are small compared with the enthalpy and entropy of the liquid, hence even though the errors in specific-heat determinations are probably larger than 0.1 percent below 40°K, these errors below 40°K have little effect upon the errors in the enthalpy and entropy values given in tables 1, 6, and 7 for the liquid.

The effect of impurities on the specific heat is another possible source of error that should be considered, although it cannot be evaluated in the present experiment. In measurements on butadiene [2], the specific heat of the solid seemed to be rather sensitive to a small impurity, although the specific heat of the liquid was unaffected. The specific heat at 80°K of a sample of solid butadiene that contained 0.055 mole percent of impurity was more than 1 percent higher than that of a pure sample. This difference between the pure and slightly impure samples diminished rapidly at higher and lower temperatures, but it was appreciable over a temperature range of 50 degrees. Since the present measurements were made on only one sample of *cis*-2-butene, no information concerning the effect of impurities was obtained.

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[4] As used in this paper, the term "probable error" is the author's estimate of that error which is just as likely to be exceeded as not. Actual computations of probable error were not carried out, because in some cases systematic errors may have been much larger than accidental errors, and in other cases there were insufficient data to justify such a computation.

Leaving out any errors that might have resulted from impurities, it is reasonable to assign a probable error of 0.1 percent to the values of the entropy and enthalpy of the saturated vapor in tables 6 and 7.

In estimating the errors in the values of the enthalpy and entropy of the ideal gas in tables 6 and 7, it is necessary to consider the error in the equation of state used to determine the differences between the properties of the real and ideal gas. In figure 2, it appears that a probable error of 10 percent should be assigned to the selected value (1.075×10^6 ml g^{-1} °K^2) of k. This corresponds to an error in $(H^\circ-E_0^s)$ of 0.015 percent at 245°K and about 0.09 percent at 300°K. By combining the probable error of the calorimetric measurements with the probable error arising from the equation of state, the probable error of the values of $(H^\circ-E_0^s)$ in table 6 is 0.11 percent at 245°K and increases to 0.14 percent at 300°K. An error of 10 percent in the value of k will cause an error of only 0.03 percent in the value of S° at 300°K, hence the probable error to be assigned to the values of S° in table 7 is 0.13 percent.

Since an average slope of an $(H^\circ-E_0^s)$ versus T graph may be determined from values of $(H^\circ-E_0^s)$ at the two ends of the graph, the probable error of the slope $dH^\circ/dT=C_p^\circ$ was estimated from values of the probable errors in $(H^\circ-E_0^s)$ at 245° and 300° K. The probable error obtained for C_p° values in table 6 is about 0.030 j g^{-1} °K^{-1}, or 2.3 percent.

X. COMPARISON OF RESULTS OF THE CALORIMETRIC AND VAPOR-PRESSURE MEASUREMENTS WITH RESULTS OF OTHER OBSERVERS

Todd and Parks [6] measured the specific heat of *cis*-2-butene from 90° to 266° K. The values they report are, in general, somewhat larger than the values given in this paper. The discrepancy is greatest at temperatures between 110° and 170° K, attaining a maximum value of 0.9 percent. At both ends of the temperature range they covered the agreement is good, about 0.2 percent. The heat of fusion reported by Todd and Parks is only 0.1 percent higher than that obtained in this investigation.

The vapor pressure of *cis*-2-butene has been reported by Lamb and Roper [7], and by Kistiakowsky, Ruhoff, Smith, and Vaughan [8]. Figure 3 shows the deviations of the reported values from equation 5. The values reported by these observers are somewhat higher than those obtained in this investigation. Since two of the impurities, *trans*-2-butene and air, likely to be present in *cis*-2-butene have higher vapor pressures than *cis*-butene, it is believed that the lower values obtained in this investigation are an indication of a purer sample.

The specific heat of gaseous *cis*-2-butene was determined by Kistiakowsky and Rice [9], who used an adiabatic expansion method by which the heat capacity is determined from the change in temperature that results from an isentropic expansion. The equation of state of the gas is important for this method, since, in effect, the specific heat is determined from the ratio of the work done by the gas in the isentropic expansion to the measured change of temperature, and the work done is calculated with the aid of the equation of state of the gas. Table 8 shows the dependence upon the equation of state of the specific heats of *cis*-2-butene determined by the adiabatic expansion method. The authors of the present paper prefer equation of state 9 to the equation of state proposed by Roper [5]. The 10-percent probable error that the authors have placed upon the constant k in equation of state 9 gives rise to the following probable errors in the specific heats: (1) in C_p at 1 atm, at 298.58° K, 0.0077 int. j g^{-1} $°K^{-1}$; at 332.85°, 0.0063; and at 371.24°, 0.0050 int. j g^{-1} $°K^{-1}$; (2) in C_p° at 298.58° K, 0.0052 int. j g^{-1} $°K^{-1}$; at 332.85°, 0.0044; and at 371.24°, 0.0036.

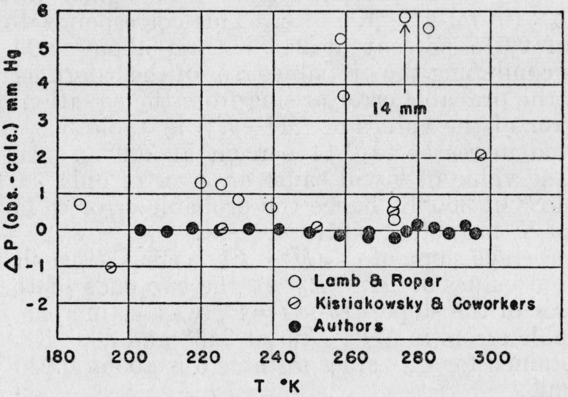

FIGURE 3.—*Deviations of observed vapor pressures from equation 5.*

TABLE 8.—*Heat capacities of gaseous cis-2-butene: (1) as reported by Kistiakowsky and Rice [9], who used Roper's equation of state, (2) as calculated from the data of Kistiakowsky and Rice by using the equation of state, eq 9, of this paper, and (3) as calculated from spectroscopic data*

[The superscript (°) refers to the ideal gas state. 13.4114 cal $mole^{-1}$ = 1 int. j g^{-1}. Atomic weights: C= 12.010, H=1.008]

T	From the paper of Kistiakowsky and Rice, using the conversion factor in their paper 9 and —			From experimentat data of Kistiakowsky and Rice and equation of state [9] of the present paper		Calculated from spectroscopic data
	Equation of state, $pV=RT$	Roper's equation of state				
	C'_p	Real gas C_p at 1 atm	C°_p	Real gas C_p at 1 atm	C°_p	C°_p
° K	*Int. j g^{-1} ° K^{-1}*	*Int. j g^{-1} ° K^{-1}*	*Int. j g^{-1} ° K^{-1}*	*Int. j g^{-1} ° K^{-1}*	*Int. j g^{-1} ° K^{-1}*	*Int. j g^{-1} ° K^{-1}*
298. 58	1. 377	1. 496	1. 446	1. 454	1. 429	1. 432
332. 85	1. 519	1. 606	1. 572	1. 582	1. 563	1. 565
371. 24	1. 675	1. 737	1. 716	1. 725	1. 711	1. 718

The experimental value of C_p° for gaseous *cis*-2-butene derived from the vapor-pressure and calorimetric measurements on the liquid reported in this paper (see table 6) is 1.416 int. j g^{-1} ° K^{-1} at 298.58° K. This is 2.1 percent lower than the value of Kistiakowsky and Rice based on Roper's [5] equation of state, and 0.9 percent lower than the value derived from the experimental data of Kistiakowsky and Rice, using the equation of state 9. In section IX it is shown that the probable error in the values of C_p° derived from the experimental data reported in this paper, based upon probable errors from all sources, was 2.3 percent. The agreement of the C_p° values derived from our measurements with the values in table 8 derived from direct measurements on the gas by Kistiakowsky and Rice is a confirmation of the accuracy of the present measurements in the range 245° to 300° K.

XI. THERMODYNAMIC FUNCTIONS FROM 300° TO 1,500° K DERIVED FROM SPECTROSCOPIC DATA

Gershinowitz and Wilson [10] investigated the infrared absorption and Raman spectra of *cis*- and *trans*-2-butene. Their measurements covered the full range of the fundamental frequencies of the intramolecular motions. Weak lines were measured, and in the case of *trans*-2-butene the polarization of the Raman lines was determined. Polarization data on *cis*-2-butene were not reported.

Because the *cis*-2-butene molecule has C_{2v} symmetry, all internal motions are optically active, and all are allowed in both the infrared and Raman spectra with the exception of the A_2 vibrations (symmetrical with respect to C_{2v} axis and asymmetrical with respect to the σ_x and σ_y planes), which are forbidden in the infrared absorption spectra.

In working out an assignment of frequencies, use was made of the *trans*-2-butene assignment which had previously been worked out [11]. Because of the C_{2h} symmetry of *trans*-2-butene, the fundamental vibrations are either Raman or infrared active, but not both. This with the Raman polarization observations of *trans*-2-butene make possible a more certain assignment of frequencies. In the assignment of the carbon skeleton frequencies, the *cis-trans* relationships in the spectra of 1,2-dichloroethylene and 1,2-dibromoethylene [12] served as a guide in the use of the *trans*-2-butene frequencies. The results of O. Burkard's normal coordinate calculation [12] were helpful also.

The frequencies in reciprocal centimeters used for the calculation of the thermodynamic properties of *cis*-2-butene from 300° to 1,500° K were as follows:

C *skeleton frequencies*—
  A_1: ω_1, 1669; ω_2, 883; ω_3, 304.
  A_2: ω_6, 402.
  B_2; ω_4, 986; ω_5, 583.

Frequencies due to C–H *groups*—
  δ's: 1233, 1267.
  γ's: 1018, 1047.

Frequencies due to CH_3 *groups*—
  δ's: 1267, 1389, 1436, 1462, 1473, 1541,.
  γ's: 685, 883, 1047, 1233.

C–H *stretching frequencies*—
  ν's: 2874, 2877, 2931(2), 2979(2), 3034(2).

The C=C torsional frequency, ω_6 for *cis*-2-butene was estimated by Harold W. Woolley, who used a force-constant calculation based on the frequencies of other molecules. If we consider the two halves of the molecule as rigid, the estimate based on the C=C torsion in ethylene was 535 cm^{-1}. The estimate based on the value 270 cm^{-1}

assumed [11] for the C=C torsional frequency, ω_6 in *trans*-2-butene was 470 cm^{-1}. The sign of the difference [ω_6 (*cis*)$-\omega_6$ (*trans*)] was easily verified from general considerations for the case of identical torsional constants. A more detailed calculation was made in which bonds attached to the doubly bonded carbons were assumed to be equally flexible for all directions of bending, with bending constants determined from other molecules. As before, the ethylene torsional frequency was used to evaluate a torsion constant for the double bond. Torsional frequencies thus estimated were 374 cm^{-1} for *cis*-dichloroethylene, 342 cm^{-1} for *cis*-dibromoethylene, and 368 cm^{-1} for *cis*-2-butene. These estimated frequencies for *cis*-dichloroethylene and *cis*-dibromoethylene are 31 cm^{-1} and 30 cm^{-1}, respectively, lower than the observed frequencies assigned by Kohlrausch [12] to these ethylene halides. The assignment of the observed *cis*-2-butene frequency 402 cm^{-1} to the torsional vibration, ω_6 appeared logical, since the difference 34 cm^{-1} between the assigned and estimated values for *cis*-2-butene is nearly the same as the differences for the ethylene halides.

The following bond lengths and angles were assumed for *cis*-2-butene: C=C distance, 1.36 A; C—C distance, 1.54 A; C—H distance, 1.09 A; $\angle$H—C—H = 109°28′; $\angle$C—C=C = 125°16′; $\angle$H—C—C = 109°28′. From these assumed values it follows that the product of the principal moments of inertia, *ABC*, is 1.85×10^{-114} g^3 cm^6 and the reduced moment of inertia for each rotating methyl group is 5.02×10^{-40} g cm^2 [12].

Good agreement of spectroscopic values for the specific heat of gaseous *cis*-2-butene with the calorimetric values is obtained with a value of 700 cal $mole^{-1}$ for the barriers restricting internal rotation of the methyl groups. Table 8 shows the agreement. Agreement of the absolute values and the trends with temperature are significant. The calorimetric value for the entropy, $S°$, of *cis*-2-butene in the ideal gas state at 300° K is 72.148 cal $mole^{-1}$ $°K^{-1}$. A probable error of ±0.094 cal $mole^{-1}$ $°K^{-1}$ was assigned to the calorimetric value at 300° K. The difference between the spectroscopic and calorimetric values is 0.210 cal $mole^{-1}$ $°K^{-1}$. The authors consider this agreement of the spectroscopic and calorimetric entropy values satisfactory after making allowances for (1) the uncertainties in the experimental values of the specific heat $C_p°$, (table 8) from which the barrier of 700 cal $mole^{-1}$ was calculated, and in the assumption that the barriers to rotation of the two methyl groups can be represented by two independent barriers of the form $V=(1/2)\ V_0\ (1-\cos 3\theta)$, and (2) for a possible effect of impurities in the *cis*-butene sample on the calorimetric value for $S°$ (see section IX).

In tables 9 and 10 are tabulated the thermodynamic functions for *cis*-2-butene in the ideal gas state calculated with barriers of 700 cal $mole^{-1}$ restricting rotation of the methyl groups and with the preceding frequency assignment. The contributions to the thermodynamic functions arising from hindered rotation were calculated with the aid of the 1942 tables published by Pitzer and Gwinn [13]. The principles and methods involved in the calculations have been discussed by Aston [14].

TABLE 9.—*Thermodynamic functions of cis-2-butene in the idea gas state*

[$H°$ and $E_0°$ are enthalpies at $T°$ and 0°K, respectively, referred to the enthalpy of the elements in the standard state at 0°K. $\Delta H°$ is the heat of formation from the elements in their standard states at T°K. $H_0°=E_0°$=3,670 cal mole^{-1}. 13.4114 cal mole^{-1}=1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	$\frac{H°-E_0°}{T}$	$H°$	$\Delta H°$	$C_p°$
°*K*	*cal °C^{-1} mole^{-1}*	*cal mole^{-1}*	*cal mole^{-1}*	*cal °C^{-1} mole^{-1}*
298.16	13.50	7,700	−1,400	19.17
300	13.53	7,730	−1,440	19.27
400	15.63	9,920	−3,020	24.56
500	17.93	12,630	−4,370	29.57
600	20.24	15,810	−5,490	33.96
700	22.48	19,410	−6,380	37.74
800	24.60	23,350	−7,090	41.00
900	26,59	27,600	−7,620	43.83
1,000	28.44	32,110	−8,010	46.28
1,100	30.16	36,840	−8,280	48.41
1,200	31.76	41,780	−8,430	50.25
1,300	33.24	46,890	−8,490	51.85
1,400	34,62	52,140	−8,490	53.23
1,500	35.90	57,520	−8,440	54.44

TABLE 10.—*Thermodynamic functions of cis-2-butene in the ideal gas state at 1-atmosphere pressure*

[$F°$ and $E_0°$ are the free energy at T°K and the internal energy at 0°K, respectively, referred to the internal energy of the elements in their standard states at 0°K. $\Delta F°$ and K are the free-energy changes and equilibrium constants, respectively, for the reaction forming *cis*-C_4H_8 from its elements at T°K. $E_0°$=3,670 cal mole^{-1}. 13.4114 cal mole^{-1}=1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	$-\left(\frac{F°-E_0°}{T}\right)$	$S°$	$-F°$	$\Delta F°$	$\log_{10} K$
°*K*	*cal °C^{-1} mole^{-1}*	*cal °C^{-1} mole^{-1}*	*cal mole^{-1}*	*cal mole^{-1}*	$\frac{-\Delta F°/RT}{2.3026}$
298.16	58.32	71.82	13,720	16,030	−11.763
300	58.41	71.94	13,850	16,140	−11.757
400	62.59	78.22	21,370	22,230	−12.151
500	66.32	84.24	29,490	28,710	−12.553
600	69.79	90.03	38,200	35,440	−12.910
700	73.07	95.56	47,480	42,340	−13.221
800	76.21	100.81	57,300	49,360	−13.485
900	79.22	105.81	67,630	56,440	−13.708
1,000	82.12	110.56	78,450	63,590	−13.898
1,100	84.91	115.07	89,730	70,760	−14.059
1,200	87.61	119.37	101,460	77,950	−14.197
1,300	90.21	123.46	113,600	85,140	−14.314
1,400	92.73	127.35	126,150	92,340	−14.415
1,500	95.16	131.06	139,080	99,540	−14.504

The internal energy, or enthalpy, of *cis*-2-butene in the ideal gas state at 0°K, that is $E_0°$, was calculated by using (1) the value −29,820 cal mole^{-1} of Prosen and Rossini [15] for $\Delta H_{298.16°}$, the enthalpy change for the formation of gaseous *n*-butane from its elements in their standard states at 25°C; (2) the value of Kistiakowsky, Ruhoff, Smith, and Vaughan [8], −28,570 cal mole^{-1}, for $\Delta H_{355°}$, the enthalpy change for the gas-phase hydrogenation of *cis*-2-butene to *n*-butane at 355°K corrected to the new atomic weight of carbon; (3) 1,408 cal mole^{-1} for the difference between the enthalpies of gaseous *n*-butane at 355° and 298.16°K [11]; (4) enthalpy differences for *cis*-2-butene from table 9; and (5) enthalpies of C and H_2 from reference [16]. The value obtained for E_0° was 3,670 cal mole^{-1}.

The value of E_0° for *trans*-2-butene is 2,455 cal mole^{-1} [11], and accordingly the heat of the *cis-trans* isomerization of 2-butene at 0°K is 1.2 kcal mole^{-1}. The greater energy of *cis*-butene is attributed principally to mutual potential energy of the methyl groups, which, in *cis*-butene, are in close proximity.

The low value, 700 cal mole^{-1}, for the barriers restricting rotation of the methyl groups in *cis*-butene is interesting in view of this closeness of approach of the methyl groups and the possible steric hindrance when in rotation. In *trans*-butene, in which the groups are well separated, the barriers are 1,900 cal mole^{-1} [11]. Although the difference between the maximum and minimum values of the potential energy of the field in which the methyl groups rotate is smaller for *cis*-butene than for *trans*-butene, the minimum value of the potential is higher for *cis*- than *trans*-butene. This is inferred from the higher value of E_0° for *cis*-butene than for *trans*-butene. Consideration of repulsions between hydrogen atoms in a Fischer-Hirschfelder model for *cis*-butene makes it seem plausible that the difference between the maximum and minimum values of the potential restricting rotation of the methyl groups should be small. With the model, one sees that as the methyl groups rotate hydrogen atoms are so close for all orientations of the methyl groups that there is no place where the minimum in potential can be very low.

Pitzer and Scott [18] obtained 2,000 cal mole^{-1} for the barriers restricting rotation of the methyl groups in *ortho*-xylene. In *ortho*-xylene and in *cis*-2-butene the relative spatial positions of the two methyl groups and the two proximate nonmethyl hydrogen atoms are similar. However, in *cis*-butene the separation of the two methyl groups is somewhat greater than in *ortho*-xylene, and the separation of the nonmethyl hydrogen and methyl group somewhat less. If repulsions between H atoms are a determining factor for barriers, a lower barrier in *cis*-2-butene is reasonable.

XII. *CIS-TRANS* ISOMERIZATION OF 2-BUTENE

In table 11 are given for the *cis-trans* isomerization of 2-butene

$$cis\text{-2-butene} \rightleftharpoons trans\text{-2-butene}$$

in the ideal gas state, the following properties: (1) the heat of isomerization, equal to $-\Delta H^\circ$; (2) the standard entropy change; (3) the standard free-energy change; (4) the equilibrium constant, K, equal to exp.$(-\Delta F^\circ/RT)$; and (5) the equilibrium proportion of *trans*-2-butene in a mixture of *cis-trans* isomers, equal to $K/(1+K)$. The *cis*-2-butene data used in compiling table 11 were taken from tables 9 and 10, and the *trans*-2-butene data from reference [11]

Table 11.—*Standard enthalpy, entropy, and free-energy changes, equilibrium constant, and equilibrium concentration for the reaction cis-2-butene$\rightleftharpoons$trans-2-butene in the ideal gas state*

T	Heat of reaction, $-\Delta H^\circ$	Standard entropy change, ΔS°	Standard free-energy change, ΔF°	Equilibrium constant, K $\frac{[trans\text{-}C_4H_8]}{[cis\text{-}C_4H_8]}$	Equilibrium proportion, $\frac{[trans\text{-}C_4H_8]}{[cis+trans\ C_4H_8]}$
°*K*	*cal mole*$^{-1}$	*cal mole*$^{-1}$	*cal mode*$^{-1}$		
298.16	1,045	−3.50	−778	3.72	0.788
300	1,048	−3.49	−779	3.70	.787
400	899	−2.25	−749	2.57	.720
500	790	−1.580	−684	1.99	.666
600	752	−1.253	−675	1.76	.638
700	688	−0.983	−701	1.66	.624
800	594	−.743	−719	1.57	.611
900	517	−.574	−759	1.53	.605
1,000	487	−.487	−789	1.49	.598
1,100	507	−.461	−885	1.50	.600
1,200	527	−.439	−927	1.48	.597
1,300	541	−.416	−973	1.46	.593
1,400	469	−.335	−972	1.42	.587
1,500	276	−.184	−1,004	1.40	.583

Table 12.—*Comparison of equilibrium constants K for the reaction cis-2-butene$\rightleftharpoons$trans-2-butene*

[Derived from (1) calculations based on spectroscopic data, (2) catalyzed equilibrium concentrations of C_4 hydrocarbons measured by Frey and Huppke [19], and (3) short-period uncatalyzed thermal-decomposition products of *n*-butene and *iso*pentane by Frey and Hepp [20]]

T	K (spectroscopic values from table 11)	K (experimental values)[a]	Source of experimental value
°*K*			
623	1.74	1.7 and 1.6, (1.6)	Frey and Huppke [19].
673	1.68	1.5, (1.6)	Do.
723	1.64	1.4, (1.6)	Do.
848	1.55	2.1 and 1.7	Frey and Hepp [20].

[a] The values in parentheses were obtained from Frey and Huppke's equilibrium constants for the dehydrogenation reactions of *n*-butane to *trans*-2-butene and to *cis*-2-butene. K(*cis*→*trans*-butene)$=K$(*n*-butane→*trans*-butene)/K(*n*-butane→*cis*-butene). Values not in parentheses are ratios of the measured *trans*-*cis* butene concentrations. The 2 sets of Frey and Huppke values in column 3 are based on the same *cis*- and *trans*-2-butene concentration data and should agree within experimental accuracy.

As with other isomerization reactions, the equilibrium constant, K, and the equilibrium proportions of the *cis* and *trans* isomers are independent of pressure.

Frey and Huppke [19] measured the concentrations of the isomeric butenes in equilibrium with normal butane at 350°, 400°, and 450° C. In their investigation, equilibrium was established by passing the vapors over a heated chromium-oxide catalyst. The Frey and Huppke experimental values for K without parentheses in column 3 of table 12 are ratios of their measured equilibrium concentrations of the *trans* and *cis* isomers. The values in parentheses are ratios of Frey and Huppke's equilibrium constants for the dehydrogenation reactions of *n*-butane to *trans*- and to *cis*-2-butene: K(*cis*→*trans*-2-butene)$=K$(*n*-butane→*trans*-2-butene)/K(*n*-butane→*cis*-2-butene). The two sets of Frey and Huppke values in column 3 are based on the same *cis*- and *trans*-2-butene concentration data and should agree witnin experimental error. Frey and Hepp [20] measured the concentrations of the *cis* and *trans* isomers of 2-butene in the primary products of the uncatalyzed thermal decomposition of *n*-butane and *iso*pentane at 575° C for 25 seconds and 12 seconds, respectively.

The spectroscopic and experimental values of K agree within the limits of error of the experimental data.

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