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## Thermodynamic Properties of Ethylbenzene Vapor from 300° to 1500°K

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In this paper are presented tables of the more important thermodynamic functions of ethylbenzene in the ideal gas state from 300° to 1500°K. These functions were calculated using spectroscopic, structural, and calorimetric data. Six investigations of the Raman spectrum of ethylbenzene and three of the infra-red absorption spectrum were available for an assignment of frequencies to the intramolecular vibrations. Included in the paper is a calculation from calorimetric data of the enthalpy and entropy of saturated vapor at 294°K relative to the solid at 0°K. This paper completes a report on a determination of the thermodynamic properties of ethylbenzene covering the solid, liquid, and vapor phases, extending from 0° to 1500°K. All the experimental results are presented in detail in preceding papers.

### I. INTRODUCTION

THIS paper completes a report on a determination of the thermodynamic properties of ethylbenzene covering the solid, liquid, and vapor phases and extending from 0° to 1500°K. Properties of the solid and liquid phases from 0° to 300°K are reported in an earlier paper,<sup>1</sup> and a calorimetric measurement of the specific heat of the vapor at 373.16°K in still another paper.<sup>2</sup> The present paper covers the vapor, in the ideal gas state, from 300° to 1500°K.

The calorimetric data on the solid and liquid<sup>1</sup> were used to obtain a so-called calorimetric value for the entropy of ethylbenzene at 294°K in the ideal gas state, relative to the solid at 0°K. This entropy value and the calorimetric value for the specific heat of the vapor<sup>2</sup> were used with spectroscopic and structural data for ethylbenzene to calculate the tables of thermodynamic data for gaseous ethylbenzene presented here. The frequencies of the intramolecular vibrations of ethylbenzene used in these calculations were taken insofar as possible from the infra-red absorption and Raman spectra of ethylbenzene. Other frequencies were derived or were assumed to be the same as for the corresponding motions in closely related compounds. The frequency

assignment for toluene by Pitzer and Scott<sup>3</sup> facilitated the interpretation of the ethylbenzene spectra. The barriers restricting internal rotation of the methyl and ethyl groups in ethylbenzene, used in the thermodynamic calculations, were selected to obtain the best agreement between the spectroscopic and calorimetric values for the entropy and specific heat of the vapor. The barriers thus obtained were 2700 and 1300 cal. mole<sup>-1</sup> for the methyl and ethyl groups, respectively.

Included in the paper is a calculation from calorimetric data of the enthalpy and entropy of saturated ethylbenzene vapor at 294°K relative to the crystalline solid at 0°K.

### II. CALORIMETRIC VALUES OF THE ENTHALPY AND ENTROPY OF THE VAPOR

Table I is a summary of the calculations of the enthalpy and entropy of ethylbenzene vapor, relative to the solid at 0°K.

The enthalpy and entropy of saturated vapor were calculated for the temperature, 294°K, at which the heat of vaporization had been measured calorimetrically. The calorimetric data for these calculations were taken from the earlier paper.<sup>1</sup>

The differences between the properties of the real and ideal gases were computed using the Berthelot equation of state and thermodynamic relations for  $(\partial S/\partial p)_T$  and  $(\partial H/\partial p)_T$ . The for-

<sup>1</sup> Russell B. Scott and Ferdinand G. Brickwedde, "Thermodynamic Properties of Solid and Liquid Ethylbenzene, 0° to 300°K," J. Research Nat. Bur. Stand. **35**, Dec. (1945).

<sup>2</sup> Russell B. Scott and Jane W. Mellors, "Specific Heats of Gaseous 1,3-Butadiene, Isobutene, Styrene and Ethylbenzene," J. Research Nat. Bur. Stand. **34**, 243 (1945).

<sup>3</sup> Kenneth S. Pitzer and Donald W. Scott, "The Thermodynamics and Molecular Structure of Benzene and Its Methyl Derivatives," J. Am. Chem. Soc. **65**, 803 (1943).

mulas for the differences are:

$$H^0 - H_{\text{sat. vap}} = \int_{p_{\text{sat.}}}^0 \left( \frac{\partial H}{\partial p} \right)_T dp$$

$$= -\frac{9}{128} RT_c \left( 1 - 18 \frac{T_c^2}{T^2} \right) \frac{p_{\text{sat.}}}{p_c} \quad (1)$$

and

$$S^0_{(1 \text{ atmos.})} - S_{\text{sat. vap}}$$

$$= \int_{p_{\text{sat.}}}^{p^*} \left( \frac{\partial S}{\partial p} \right)_T dp + R \ln_e \frac{p^*}{p_{(1 \text{ atmos.})}}$$

$$= R \left[ \ln_e \frac{p_{\text{sat.}}}{p_{(1 \text{ atmos.})}} + \frac{27}{32} \frac{T_c^3}{T^3} \frac{p_{\text{sat.}}}{p_c} \right], \quad (2)$$

where the superscript <sup>0</sup> refers to the ideal gas state and  $p^*$  is a pressure so low that ethylbenzene vapor is essentially an ideal gas. The critical constants used in the Berthelot equation were  $T_c = 619.6^\circ\text{K}$  and  $p_c = 38.1$  atmospheres, as reported by Altschul.<sup>4</sup>

TABLE I. Summary of calculations of enthalpy and absolute entropy of ethylbenzene vapor. [The superscript (°) designates the ideal gas state.  $E_0^*$  is the internal energy of solid ethylbenzene at  $0^\circ\text{K}$ . 1 cal. = 4.18330 int j. Atomic weights: C = 12.010, H = 1.0080.]

Enthalpy	cal. mole <sup>-1</sup>
$H_{\text{sat. liq}} - E_0^*$ at $294^\circ\text{K}$	9,434.
$L_v$ at $294^\circ\text{K}$	10,155.
$H_{\text{sat. vap}} - E_0^*$ at $294^\circ\text{K}$	19,589.
$H^0 - H_{\text{sat. vap}}$ at $294^\circ\text{K}$	1.5
$H^0 - E_0^*$ at $294^\circ\text{K}$	19,590.
$H_{298.16^\circ\text{K}}^0 - H_{294^\circ\text{K}}^0$	127.1
$H_{298.16^\circ\text{K}}^0 - E_0^*$	19,717.
Entropy	cal. mole <sup>-1</sup> °K <sup>-1</sup>
$S_{\text{sat. liq}}$ at $294^\circ\text{K}$	60.40
$\Delta S_{\text{vaporization}} (= L_v/294)$	34.54
$S_{\text{sat. vap}}$ at $294^\circ\text{K}$	94.94
$S_{1 \text{ atmos.}}^0 - S_{\text{sat. vap}}$ at $294^\circ\text{K}$	-9.17
$S_{1 \text{ atmos.}, 294^\circ\text{K}}^0$	85.77
$S_{1 \text{ atmos.}, 298.16^\circ\text{K}}^0 - S_{1 \text{ atmos.}, 294^\circ\text{K}}^0$	0.429
$S_{1 \text{ atmos.}, 298.16^\circ\text{K}}^0$	86.20

<sup>4</sup> Michael Altschul, "On the Critical Constants of Some Organic Compounds," Zeits. f. physik. Chemie **11**, 576 (1893).

Tables V and VI were used to compute the increases in enthalpy and entropy from  $294^\circ\text{K}$  to the standard reference temperature  $298.16^\circ\text{K}$  ( $25^\circ\text{C}$ ).

### III. THE MEASURED SPECIFIC HEAT OF THE VAPOR AT $373.16^\circ\text{K}$

The specific heat  $C_p$  of ethylbenzene vapor measured at  $373.16^\circ\text{K}$  with a flow calorimeter has already been reported in detail.<sup>2</sup> The calorimeter was of the adiabatic type in which measurements were made in a steady state of the change in temperature of a stream of ethylbenzene vapor after passage over an electric heater in which electrical energy was dissipated at a constant measured rate.

The experimental values for  $C_p$  at  $373.16^\circ\text{K}$  are  $38.22 \pm 0.20$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> at the pressure of the measurement, 175 mm Hg, and  $38.06 \pm 0.20$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> at zero pressure or for the ideal gas state.

### IV. THERMODYNAMIC FUNCTIONS, $300^\circ$ TO $1500^\circ\text{K}$ , FROM SPECTROSCOPIC DATA

#### 1. Intramolecular Vibrational Frequencies

There have been six independent investigations of the Raman spectrum of ethylbenzene and three of its infra-red absorption spectrum. All intramolecular vibrations are active in both the Raman and the infra-red absorption spectra. The observed spectral frequencies to  $1700 \text{ cm}^{-1}$  are listed in Tables II and III. Numbers and letters in parentheses after frequency values are the measures of intensity reported by the original investigators. No Raman polarization data are available. Apparently no complete assignment of frequencies to the intramolecular vibrations of ethylbenzene exists in the literature. The assignment adopted for the thermodynamic calculations is given in Table IV, where the frequencies of toluene and benzene are given for comparison. Ethylbenzene frequencies in parentheses were not observed. These were derived or were assumed to be the same as for the corresponding motions in closely related compounds. Except for the C—H stretching vibrations, the frequencies were taken insofar as possible from the ethylbenzene spectra.

The frequency  $290 \text{ cm}^{-1}$  for the phenyl vibration  $18B$  of ethylbenzene was obtained from a

TABLE II. Reported Raman frequencies in  $\text{cm}^{-1}$  of liquid ethylbenzene from 0 to  $1700 \text{ cm}^{-1}$ .

Dadiou and Kohlrausch <sup>a</sup> (1929)	Ganesan and Venkateswaren <sup>b</sup> (1929)	Söderqvist <sup>c</sup> (1929)	Signer and Weiler <sup>d</sup> (1932)	Reitz and Stockmair <sup>e</sup> (1935)	Dupont and Dulou <sup>f</sup> (1936)
153(4br)	153(4) 305(0) 399(0) 447(0)	154(0)		152(6)	149 } (b6) 166 }
482(2)	539(0)		457(0) 490(1) 538(0)	483(2)	488(f3)
555(1/2)				547(1/2)	555(f1)
620(2)	619(0)	620(1)	620(2) 724(0)	619(3)	622(8)
766(4)	770(2)	769(2)	773(0)	766(5) 833(1/2) 900(1/2)	748(2) 769(12) 843(f1) 904(f1) 948(2)
960(2)	972(0)	964(0)	962(0)	965(3)	968(f3)
1001(8)	1005(2)	1002(4)	1000(4)	1002(8)	1004(20)
1028(3)	1031(0)	1030(2) 1064(0)	1032(2) 1057(0) 1106(0)	1029(4) 1063(1/2)	1032(12) 1067(f3)
1156(3br)	1153(0)	1157(0)	1156(1) 1176(1)	1154(1)	1157(3) 1179(f2)
1192(2br)	1203(2)	1203(2)	1204(3) 1260(1)	1199(5)	1203(12)
1386(0br)			1381(0)	1320(0)	1288(b2) 1328(b2)
1444(3br)	1456(0)		1448(1dd) 1465(1dd)	1446(3)	1390(b1) 1439 } (b4) 1460 }
			1587(1)	1587(0)	1585(3)
1603(5)	1609(0)	1605(2)	1608(3)	1604(5)	1608(12)

<sup>a</sup> Dadiou and Kohlrausch, *Monatsh.* **53**–**54**, 282 (1929).<sup>b</sup> Ganesan and Venkateswaren, *Indian J. Phys.* **13**, 195 (1929).<sup>c</sup> Söderqvist, *Zeits. f. Physik* **59**, 446 (1929).<sup>d</sup> Signer and Weiler, *Helv. Chim. Acta* **15**, 649 (1932).<sup>e</sup> Reitz and Stockmair, *Monatsh.* **67**, 92 (1935).<sup>f</sup> Dupont and Dulou, *Bull. soc. chim.* **3**, 1639 (1936).

graph, Fig. 1, of the observed frequencies of the 18B vibration of a benzyl series of compounds  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{X}$  with  $\text{X}=\text{H}$ , SH, Cl, Br, and I, respectively. The vibration 16A which appears only weakly in the Raman spectra of benzene and toluene was not observed in the ethylbenzene spectrum. However, the motion of the 16A vibration of the phenyl group does not appreciably involve the attached group, as may be seen from Fig. 2, and, hence, the toluene and ethylbenzene frequencies are undoubtedly very nearly the same. The frequencies  $486 \text{ cm}^{-1}$  and  $550 \text{ cm}^{-1}$  were assigned to 6A and 16B, respectively, on the basis of the regular variation of the frequencies of the 6A and 16B vibrations found for a series of other benzyl compounds.<sup>5</sup> Differences in frequency between corresponding phenyl

vibrations of toluene and ethylbenzene are small for vibrations greater than  $600 \text{ cm}^{-1}$ .

The ethyl group frequencies could not be as completely determined from the ethylbenzene spectrum as could the phenyl frequencies. The internal C–C stretching frequency is prominent in both the Raman and infra-red absorption spectra. A frequency of  $365 \text{ cm}^{-1}$  was assigned to the  $\text{C}_{\text{ph}}-\text{C}-\text{C}$  angle bending motion on the basis of other compounds. There are lines 1385, 1450 and  $1500 \text{ cm}^{-1}$  in the ethylbenzene spectrum corresponding closely to lines in the toluene spectrum assigned by Pitzer and Scott<sup>3</sup> to the  $\text{CH}_3$  group in toluene. The corresponding assignment was made for ethylbenzene. The frequencies of the other intra-group vibrations of  $\text{C}_2\text{H}_5$  taken from the ethylbenzene spectrum approximate the frequencies of those motions in other compounds. Two of the  $\text{CH}_2$  frequencies coincide with phenyl group frequencies. The

<sup>5</sup> K. W. F. Kohlrausch, *Ramanspektren* (Akademische Verlagsgesellschaft, Leipzig, 1943). Lithoprinted by J. W. Edwards. Section 46.

TABLE III. Frequencies in  $\text{cm}^{-1}$  of centers of infra-red absorption bands in ethylbenzene vapor, 480–1700  $\text{cm}^{-1}$ .

Lambert and Lecomte <sup>a</sup> (1932)	Stair and Coblenz <sup>b</sup> (1935)	Lambert and Lecomte <sup>c</sup> (1938)
		480(f)
		567(F)
		617(f)
682		
704		
	725	
745	742	
780	770	
847	836	
901	903	
969	968	
	985	
1034	1034	
	1085	
	1172	
	1230	
	1282	
	1380	
	1450	
1488		
	1500	
	1592	

<sup>a</sup> Lambert and Lecomte, *Ann. de Physik* **18**, 329 (1932).<sup>b</sup> Stair and Coblenz, *J. Research Nat. Bur. Stand.* **15**, 295 (1935).<sup>c</sup> Lambert and Lecomte, *Ann. de Physik* **10**, 503 (1938).

average of the frequencies 725 and 1230  $\text{cm}^{-1}$  assigned to the two rocking vibrations of the  $\text{CH}_3$  group is in agreement with averages of rocking vibrations of  $\text{CH}_3$  groups in other compounds.<sup>5,6</sup>

The vibration 7A is principally C(phenyl)–C(aliphatic) stretching motion. The high value of its frequency, 1203  $\text{cm}^{-1}$ , compared with the normal value of about 970  $\text{cm}^{-1}$  for a C–C linkage in aliphatic compounds, is attributable to hyperconjugation<sup>7</sup> of the  $\text{C}_{\text{ph}}-\text{C}_{\text{ethyl}}$  bond with the phenyl radical. The energy hyperconjugation of this bond, or the difference in the heats of hydrogenation of benzene<sup>8</sup> and ethylbenzene,<sup>9</sup> is about 0.9 kcal. mole<sup>-1</sup>. The frequencies of the corresponding 7A vibrations in toluene and styrene are 1210 and 1204  $\text{cm}^{-1}$ , respectively.

<sup>6</sup> Gerhard Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

<sup>7</sup> Robert S. Mulliken, Carol A. Rieke, and Weldon G. Brown, "Hyperconjugation," *J. Am. Chem. Soc.* **63**, 41 (1941).

<sup>8</sup> G. B. Kistiakowsky, John R. Ruhoff, Hilton A. Smith, and W. E. Vaughan, "Heats of Organic Reactions. IV. Hydrogenation of Some Dienes and Benzene," *J. Am. Chem. Soc.* **58**, 146 (1936).

<sup>9</sup> M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, "Heats of Organic Reactions. V. Heats of Hydrogenation of Various Hydrocarbons," *J. Am. Chem. Soc.* **59**, 831 (1937).

## 2. Molecular Structure Data and Moments of Inertia

In ethylbenzene the equilibrium positions of the symmetry planes of the phenyl and ethyl groups are perpendicular to each other. Generally

TABLE IV. Frequencies in  $\text{cm}^{-1}$  adopted for the normal modes of intramolecular vibration of ethylbenzene, with the frequencies of benzene and toluene for comparison. [Ethylbenzene frequencies in parentheses were not observed. Benzene and toluene frequencies are from a paper by Pitzer and Scott (see reference 3). Phenyl radical vibrations are for convenience identified with benzene vibrations (Fig. 2), though the motions of the atoms for phenyl radical and benzene vibrations differ in amplitude and direction, and in some cases phenyl and benzene vibrations with the same designation may be quite different, as for example the vibrations Nos. 1 and 12 (see p. 823 in reference 2).]

Vibration type		Ethylbenzene	Toluene	Benzene
Phenyl radical	11	154	216	671
or benzene	18B	(290)	340	1037
vibration.	16A	(405)	405	400
(For identification of vibrations see Fig. 2.)	6A	486	521	606
	16B	550	467	400
	6B	620	622	606
	4	704	695	685
	10B	745	730	849
	12	769	785	1011
	10A	840	842	849
	17B	903	890	985
	5	948	943	1016
	17A	985	(985)	985
	1	1003	1002	992
	18A	1032	1030	1037
	15	1085	1070	1170
	9B	1156	1155	1178
	9A	1177	1175	1178
	7A	1203	1210	3047
	3	1288	1282	1298
	19B	1320	1310	1485
	19A	1488	1483	1485
	8B	1587	1586	1596
	8A	1608	1603	1596
	14	(1630)	1630	1693
	C–H stretching	(3050)	(3050)	(3050)
		(3050)	(3050)	(3050)
		(3050)	(3050)	(3050)
–C <sub>2</sub> H <sub>5</sub> , carbon skeleton vibrations	C <sub>ph</sub> –CH <sub>2</sub> –CH <sub>3</sub> angle	(364)		
	CH <sub>2</sub> –CH <sub>3</sub>	968		
–(CH <sub>2</sub> )-vibrations		1064		
		1156		
		1177		
		1450		
		(2950)		
		(2950)		
–(CH <sub>3</sub> )-vibrations		725	1060	
		1230	1190	
		1385	1380	
		1450	1455	
		1500	1495	
		(2950)		
		(2950)		
		(2950)		

accepted bond lengths<sup>10</sup> were used for ethylbenzene as follows: C—H, 1.09Å; phenyl ring C—C, 1.39Å; and ethyl group C—C, 1.54Å. The C—C bond joining the aromatic and aliphatic groups was assumed to be 1.45Å in keeping with the lengths of C—C bonds shortened by hyperconjugation in other compounds.<sup>11</sup> Generally accepted values were used also for bond angles: 60° and 120° for the phenyl ring and 109°28' for the ethyl group. Using these molecular constants, the product of the principal moments of inertia of the ethylbenzene molecule is  $67.49 \times 10^{-114} \text{ g}^3 \text{ cm}^6$  and the reduced moments of inertia of the methyl and ethyl groups are  $5.24 \times 10^{-40}$  and  $33.5 \times 10^{-40} \text{ g cm}^2$ , respectively.

### 3. Intramolecular Rotation Barriers

Selection of values of 2700 and 1300 cal. mole<sup>-1</sup> for the barriers restricting internal rotations of the methyl and ethyl groups in ethylbenzene resulted in satisfactory agreement between the calorimetric and spectroscopic values for  $S^0$  and  $C_p^0$  of the vapor. Thus the calculated entropy

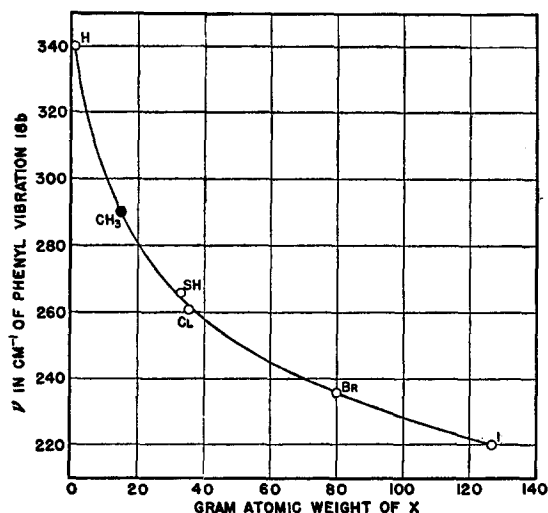


FIG. 1. Dependence on the gram atomic weight of X of the phenyl vibration 18B in the series of compounds  $\text{C}_6\text{H}_5\text{CH}_2\text{X}$ . [Data are from Reitz and Stockmair, *Monatsh.* 67, 92 (1935) and Bacher and Wagner, *Zeits. f. physik Chemie* B43, 191 (1939).]

<sup>10</sup> Linus Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1942). Chapter V.

<sup>11</sup> Linus Pauling, H. D. Springall and K. J. Palmer, "The Electron Diffraction Investigation of Methylacetylene, Dimethylacetylene, Dimethyldiacetylene, Methyl Cyanide, Diacetylene and Cyanogen," *J. Am. Chem. Soc.* 61, 927 (1939).

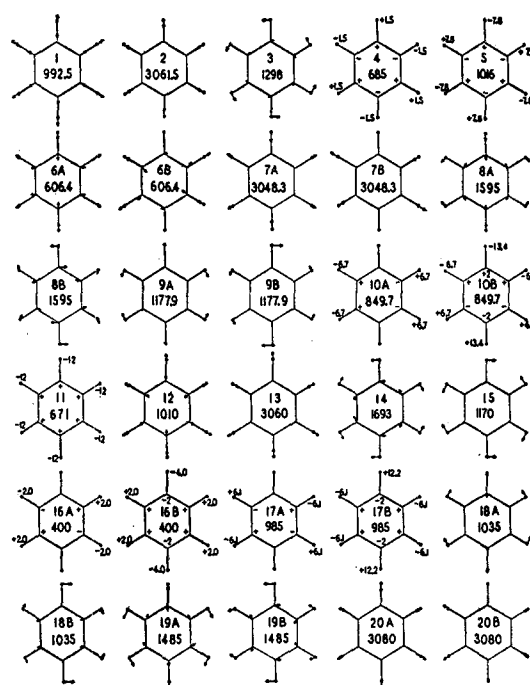


FIG. 2. The frequencies and normal modes of vibration of benzene. + and - refer to motions perpendicular to the plane of the ring. (Reproduced from the paper by Pitzer and D. W. Scott [see reference 3].)

$S^0$  for the ideal gas state at 294°K and 1 atmosphere pressure is 85.81 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, while the calorimetric value for the same conditions is 85.77 cal. mole<sup>-1</sup> deg.<sup>-1</sup>. The calculated specific heat  $C_p^0$  for the ideal gas state at 373.16°K (100°C) is 38.19 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, whereas the calorimetric value is 38.06 cal. mole<sup>-1</sup> deg.<sup>-1</sup>. A low value (1300 cal. mole<sup>-1</sup>) for the barrier restricting rotation of the ethyl group seems reasonable notwithstanding the partial double bond character of the C(aromatic)—C(aliphatic) bond, since a difference in restricting potential around this bond reaches the maximum value for a rotational displacement of only 30° whereas for a normal C(aliphatic)—C(aliphatic) bond the maximum value is reached only for a rotation of 60°. Pitzer and Scott<sup>3</sup> obtained barriers of 500 cal. mole<sup>-1</sup> restricting rotation of the methyl groups of toluene, and meta- and para-xylene.

### 4. Tables of Thermodynamic Properties

In Tables V and VI are tabulated the thermodynamic functions for ethylbenzene in the ideal

TABLE V. Thermodynamic functions of ethylbenzene in the ideal gas state. [ $H^0$  and  $H_0^0 = E_0^0$  are enthalpies at  $T^\circ\text{K}$  and  $0^\circ\text{K}$ , respectively, referred to the enthalpy of the elements in the standard state at  $0^\circ\text{K}$ .  $\Delta H^0$  is the enthalpy change of formation from elements in their standard states at  $T^\circ\text{K}$ .  $H_0^0 = E_0^0 = 13,580$  cal. mole $^{-1}$ , 25.3770 cal. mole $^{-1} = 1$  int j g $^{-1}$ . Atomic weights: C = 12.010, H = 1.0080.]

$T$	$\frac{H^0 - E_0^0}{T}$	$H^0$	$\Delta H^0$	$C_p^0$
$^\circ\text{K}$	cal. $^\circ\text{C}^{-1}$ mole $^{-1}$	cal. mole $^{-1}$	cal. mole $^{-1}$	cal. $^\circ\text{C}^{-1}$ mole $^{-1}$
298.16	18.037	18960	6830	30.80
300.00	18.116	19020	6790	30.98
400	22.562	22610	4930	40.70
500	27.068	27110	3400	49.20
600	31.367	32400	2180	56.26
700	35.354	38330	1240	62.11
800	39.017	44790	530	67.01
900	42.360	51700	10	71.15
1000	45.421	59000	-340	74.68
1100	48.218	66620	-540	77.70
1200	50.786	74520	-610	80.29
1300	53.145	82670	-570	82.52
1400	55.313	91020	-450	84.45
1500	57.316	99550	-280	86.12

gas state calculated on the basis of the preceding frequency assignment, structural data, and rotation barriers. The contributions to the thermodynamic functions arising from hindered rotation were calculated with the aid of the 1942 tables of Pitzer and Gwinn.<sup>12</sup> Values used for the gas constant  $R$ , the radiation constant  $c_2$  (equal to  $hc/k$ ), and the Avogadro number  $N_0$  were 1.98714 cal. mole $^{-1}$  deg. $^{-1}$ , 1.4384 cm deg., and 6.0228  $\times 10^{23}$  mole $^{-1}$ , respectively.

$H^0$  and  $F^0$  are the enthalpy and free energy of ethylbenzene in the ideal gas state relative to the enthalpy of its elements at  $0^\circ\text{K}$  in their standard states, that is the graphitic state for C and the (ideal) gaseous state for  $\text{H}_2$ .  $S^0$  is the entropy in the ideal gas state, relative to the solid at  $0^\circ\text{K}$ . Table values of  $S^0$  and  $F^0$  are for a pressure of one atmosphere.

The internal energy and enthalpy of ethylbenzene in the ideal gas state at  $0^\circ\text{K}$ , that is  $E_0^0$  or  $H_0^0$ , were calculated using: (1) the value +35,106 cal. mole $^{-1}$  of Prosen and Rossini<sup>13</sup> for  $\Delta H_{298.16^\circ\text{K}}^0$ , the heat of the formation of gaseous styrene from its elements in their standard states

at  $25^\circ\text{C}$ ; (2) the values of Dolliver, Gresham, Kistiakowsky, and Vaughan,<sup>9</sup> -48,931 and -77,498 cal. mole $^{-1}$ , for  $\Delta H_{355.16^\circ\text{K}}^0$ , the heats of hydrogenation of ethylbenzene and styrene, respectively, to ethylcyclohexane at  $355.16^\circ\text{K}$  corrected to the new atomic weight of carbon; (3) 1812 cal. mole $^{-1}$  for the difference between the enthalpies of gaseous styrene at  $355.16^\circ$  and  $298.16^\circ\text{K}$ , based on National Bureau of Standards measurements and calculations on styrene; (4) enthalpy differences for ethylbenzene from Table V; and (5) enthalpies of C and  $\text{H}_2$  from Woolley *et al.*<sup>14</sup> The value obtained for  $E_0^0$  of ethylbenzene was 13,580 cal. mole $^{-1}$ .

For the convenience of those desiring values of the enthalpy and free energy of ethylbenzene relative to the enthalpy,  $E_0^0$  or  $H_0^0$ , of crystalline ethylbenzene at  $0^\circ\text{K}$ , Table VII was included. Table VII values of  $(H^0 - E_0^0)$  and  $(F^0 - E_0^0)$  like Table V and Table VI values of  $(H^0 - E_0^0)/T$  and  $-(F^0 - E_0^0)/T$  may be combined with other values of  $E_0^0$  based on different heats of

TABLE VI. Thermodynamic functions of ethylbenzene in the ideal gas state at 1-atmosphere pressure. [ $F^0$  and  $E_0^0$  are the free energy at  $T^\circ\text{K}$  and the internal energy at  $0^\circ\text{K}$ , respectively, referred to the internal energy of the elements in their standard states at  $0^\circ\text{K}$ .  $\Delta F^0$  and  $K$  are the free-energy changes and equilibrium constants, respectively, for the reaction forming ethylbenzene from its elements at  $T^\circ\text{K}$ .  $E_0^0 = 13,580$  cal. mole $^{-1}$ , 25.3770 cal. mole $^{-1} = 1$  int j g $^{-1}$ . Atomic weights: C = 12.010, H = 1.0080.]

$T$	$-\left(\frac{F^0 - E_0^0}{T}\right)$	$S^0$	$-F^0$	$\Delta F^0$	$\log_{10} K$
$^\circ\text{K}$	cal. $^\circ\text{C}^{-1}$ mole $^{-1}$	cal $^\circ\text{C}^{-1}$ mole $^{-1}$	cal. mole $^{-1}$	cal. mole $^{-1}$	$-\Delta F^0/RT$
298.16	68.20	86.24	6760	30910	-22.654
300.00	68.32	86.43	6920	31050	-22.622
400	74.14	96.70	16080	39420	-21.539
500	79.65	106.72	26250	48240	-21.086
600	84.97	116.33	37400	57320	-20.879
700	90.11	125.46	49500	66590	-20.791
800	95.07	134.08	62470	75990	-20.759
900	99.86	142.22	76300	85450	-20.749
1000	104.48	149.90	90900	94960	-20.755
1100	108.95	157.17	106260	104490	-20.761
1200	113.26	164.04	122330	114050	-20.772
1300	117.41	170.56	139060	123600	-20.779
1400	121.43	176.74	156420	133140	-20.785
1500	125.31	182.63	174390	142700	-20.792

<sup>12</sup> Kenneth S. Pitzer and William D. Gwinn, "Energy Levels and Thermodynamic Functions for Molecules with Internal Rotation. I. Rigid Frame with Attached Tops," J. Chem. Phys. 10, 428 (1942).

<sup>13</sup> Edward J. Prosen and Frederick D. Rossini, "Heats of Formation and Combustion of 1,3-Butadiene and Styrene," J. Research Nat. Bur. Stand. 34, 59 (1945).

<sup>14</sup> Harold W. Woolley, Morris Moskow, Ferdinand G. Brickwedde, and John G. Aston, "Thermodynamics of Synthetic Rubber and Related Substances. VI. Equilibrium Constants of Some Reactions Involved in the Production of 1,3-Butadiene." A report submitted to the Office of the Rubber Director, War Production Board, March 24, 1944.

reaction to obtain other values of  $H^0$  and  $F^0$  for the investigation of thermodynamic equilibria with other compounds. The Table VII value for  $(H^0 - E_0^s)$  at 298.16°K was taken from Table I; other Table VII values were obtained by adding 760 cal. mole<sup>-1</sup> to values of  $H^0$  and  $F^0$  in Tables V and VI.

The heat of vaporization of solid ethylbenzene at 0°K, that is  $(E_0^0 - E_0^s)$ , is 14,340 cal. mole<sup>-1</sup>.

Stull and Mayfield<sup>15,16</sup> calculated the specific heats  $C_p^0$  of a number of hydrocarbon gases, including ethylbenzene, assuming unrestricted internal rotations around single C—C bonds and summing specific heat contributions for independent vibrations of all the valence bonds of the compound using frequencies whose values are averages for these bonds in a number of compounds. Their values of  $C_p^0$  for ethylbenzene

TABLE VII. Enthalpy and free energy of ethylbenzene in the ideal gas state relative to the enthalpy,  $H_0^s = E_0^s$ , of crystalline ethylbenzene at 0°K. [25.3770 cal. mole<sup>-1</sup> = 1 int j g<sup>-1</sup>. Atomic weights: C = 12.010, H = 1.0080.]

$T$	$H^0 - E_0^s$	$-(F^0 - E_0^s)$
°K	cal. mole <sup>-1</sup>	cal. mole <sup>-1</sup>
298.16	19720	6000
300.00	19780	6160
400	23370	15320
500	27870	25490
600	33160	36640
700	39090	48740
800	45550	61710
900	52460	75540
1000	59760	90140
1100	67380	105500
1200	75280	121570
1300	83430	138300
1400	91780	155660
1500	100310	173630

are lower than the  $C_p^0$  values found in Table V, the differences being 1.9 cal. mole<sup>-1</sup> deg.<sup>-1</sup> or about 6 percent at 300°K, 1.6 cal. mole<sup>-1</sup> deg.<sup>-1</sup> or 3 percent at 500°, 0.50 cal. mole<sup>-1</sup> deg.<sup>-1</sup> or 0.6 percent at 1000°K and 0.17 cal. mole<sup>-1</sup> deg.<sup>-1</sup> or 0.2 percent at 1500°K. Stull and Mayfield found that for a number of substances the deviations of their values from calorimetric data and more precisely calculated values averaged 4 percent.

<sup>15</sup> Daniel R. Stull and F. Drew Mayfield, "Heat Capacities of Hydrocarbon Gases," Ind. and Eng. Chem. **35**, 639 (1943).

<sup>16</sup> For principles and methods of calculations see John G. Aston, "The Third Law of Thermodynamics and Statistical Mechanics," Chapter IV in *Treatise on Physical Chemistry*, by H. S. Taylor and Samuel Glasstone (D. Van Nostrand Company, Inc., New York, 1942). Also reference 6, Chapter V, 1.