THERMODYNAMIC PROPERTIES OF SOLID AND LIQUID ETHYLBENZENE FROM 0° TO 300° K

By Russell B. Scott and Ferdinand G. Brickwedde

ABSTRACT

The following properties of a sample of high purity ethylbenzene were measured:
(1) Specific heat of solid and liquid from 15° to 300° K; (2) triple-point tempera-
ture ($-95.005 \pm 0.010°$ C for pure ethylbenzene); (3) heat of fusion (86.47 int.
j g^{-1}); (4) heat of vaporization at 294° K (400.15 int. j g^{-1}); and (5) vapor pres-
sure from 273° to 296° K. With these experimental data, the enthalpy and
entropy of the solid and of the liquid in the range 0° to 300° K were calculated.

CONTENTS

I. INTRODUCTION

The measurements of the thermal properties of solid and liquid
ethylbenzene described in this paper were undertaken as part of a
program to obtain thermodynamic data on ethylbenzene covering the
solid, liquid, and vapor phases and extending from 0° to 1,500° K.
A calorimetric measurement of the specific heat of the vapor at 373.16°
K was reported in an earlier paper [1] [1]; the calculated thermodynamic
functions for the vapor from 300° to 1,500° K are reported in another
paper [2].

---

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

501

Ethylbenzene is important in the manufacture of synthetic rubber as it is converted into styrene by dehydrogenation, styrene being one of the two principal ingredients of GR-S (Government rubber-styrene type). Styrene is also used in making the plastic, polystyrene, a material much used for electrical insulation.

The properties measured and reported in this paper are as follows:
1. specific heat of solid and liquid ethylbenzene from 15° to 300° K,
2. triple-point temperature,
3. heat of fusion,
4. heat of vaporization at 294° K, and
5. vapor pressure in the temperature range 273° to 296° K.

By the use of the experimental data, calculations were made of the enthalpy and entropy of the solid and liquid from 0° to 300° K.

II. PURIFICATION OF THE SAMPLE

The ethylbenzene used for the measurements was part of a sample distilled by M. R. Fenske of The Pennsylvania State College. The physical constants reported for the sample were 50 percent Cottrell boiling point, 136.25° C; index of refraction $n^{20}_d = 1.4958$. The freezing point measured by Alfred Matuszak at the American Petroleum Institute Laboratories of Ohio State University was −95.02° C.

An additional purification by fractional crystallization was carried out at the National Bureau of Standards. Starting with a sample of about 600 ml, four fractionations were made and the unfrozen part of the sample poured off each time until about 150 ml remained. This material was then passed over finely divided silica gel in an 8-mm tube 50 cm long to remove water. It was then placed in a Pyrex bulb which communicated with the sample container of the calorimeter, and the air was removed by pumping until a high vacuum was obtained. The sample was then poured into the sample container of the calorimeter and sealed off while still under vacuum. The effectiveness of silica gel in removing water was verified by the fact that no cloudiness appeared in the sample when it was cooled to −80° C.

The amount of impurity was computed from measurements taken with the calorimeter, which gave the melting, or solid-liquid equilibrium, temperature of the sample as a function of the fraction melted. The temperature at which 50 percent of the sample was melted was found to be 0.002 degree centigrade lower than the temperature at which 99+ percent was melted. This indicates a *liquid soluble, solid insoluble* impurity of about 0.007 mole percent.

III. CALORIMETRIC MEASUREMENTS

1. APPARATUS

Two different calorimeters were used for the measurements on solid and liquid ethylbenzene. They were similar in design to the calorimeter used by Southard and Brickwedde [3] but utilized a pure platinum resistance thermometer for the measurement of temperatures.

Calorimeter D, used for the measurement of the specific heats of solid and liquid ethylbenzene and for the measurement of the heat of fusion, had a capacity of 85 ml and was equipped with 18 vertical, radial vanes for the distribution of heat. The electric heater, which supplied the measured energy to the calorimeter, consisted of about

2 meters of No. 34 American Wire Gage fiber-glass insulated constantan wire wound on the outside of the platinum case of the resistance thermometer. The thermometer and heater were installed by immersing the assembly in molten solder (Sn-Pb eutectic) in the re-entry well of the sample container. An aluminum cap was fastened over the bottom end of the sample container to trap radiation from the exposed ends of the constantan heater and from the thermometer. The heater and thermometer leads made one turn (cemented with Glyptal lacquer) around the sample container before crossing to the radiation shield.

Calorimeter C, used for the measurement of heat of vaporization, was the same calorimeter that had been used for measurements on 1,3-butadiene [4] and cis-2-butene [5]. It was provided with a tube for withdrawing vapor from the sample container. An important difference in the design of the two calorimeters was the disposition of the heaters. In calorimeter C, the heater was in a fine copper tube about 3 meters long wound as a helix inside the sample container, the helix having a radius about two-thirds that of the sample container. One effect of thus distributing the heater was to make the surface temperature of the calorimeter much more uniform while heat was being added.

Both calorimeters utilized three-element thermels for controlling the thermal shields and for exploring the temperature of the surface of the sample container. During operation of the calorimeters the multiple junction couples are used to maintain the thermal shield at the average temperature of the surface of the sample container.

The platinum resistance thermometers used for the temperature measurements were of the type described by Southard and Milner [6]. The calibration of the thermometers has been described by Hoge and Brickwedde [7].

2. SPECIFIC HEAT OF SOLID AND LIQUID

The results of the specific heat measurements are given in column 2 of table 1, tabulated at 5-degree intervals. These are smoothed results obtained by methods described in an earlier paper [4]. Figure 1 shows the deviations of the observed data from the smoothed table. The points shown in figure 1 were obtained by subtracting from the observed specific heat the specific heat obtained by interpolation from table 1.

It will be noted that two sets of points, designated by runs 2 and 3, show a pronounced departure from the table at temperatures below the triple point, the specific heat being considerably lower than that obtained in the other runs. Another peculiarity observed during runs 2 and 3, following the heats which terminated at a temperature a few degrees below the triple point, was that the temperature rose for a long time after adiabatic conditions had been established. This behavior could be explained if it is assumed that a small fraction of the sample remained liquid when the rest was frozen and that this supercooled liquid froze slowly when the temperature again approached the triple point. As heat would be given up by the freezing material it would account for both the temperature rise and the low apparent specific heat. Support for this explanation lies in the fact that ethylbenzene supercools readily.

TABLE 1.—*Specific heat, entropy and enthalpy* [a] *of solid and liquid ethylbenzene at saturated pressure*

[25.3770 cal mole^{-1}=1 int. j g^{-1}. $T°K=t°C+273.16°$.   Atomic weights: C=12.010, H=1.0080.]

T	C_{sat}	S_{sat}	$(H_{sat}-E_0)$	T	C_{sat}	S_{sat}	$(H_{sat}-E_0^s)$
	SOLID				LIQUID		
°K	Int. j g^{-1}°K^{-1}	Int. j g^{-1}°K^{-1}	Int. j g^{-1}	°K	Int. j g^{-1}°K^{-1}	Int. j °K^{-1}	Int. j g^{-1}
0	0	0	0	178.155	1.4813	1.5898	187.67
5	[b]0.00225	0.0007	0.0028	180	1.483	1.6050	190.40
10	[b].01790	.0060	.0450	185	1.488	1.6457	197.83
15	.0553	.0196	.219				
20	.1060	.0423	.621	190	1.494	1.6855	205.28
				195	1.501	1.7244	212.77
25	.1610	.0718	1.286	200	1.508	1.7624	220.29
30	.2184	.1063	2.237	205	1.516	1.7998	227.85
35	.2711	.1440	3.463	210	1.524	1.8364	235.45
40	.3177	.1833	4.936				
45	.3601	.2232	6.633	215	1.534	1.8724	243.10
				220	1.543	1.9077	250.79
50	.3991	.2632	8.532	225	1.554	1.9425	258.53
55	.4342	.3029	10.617	230	1.565	1.9768	266.33
60	.4662	.3420	12.869	235	1.576	2.0106	274.18
65	.4961	.3806	15.276				
70	.5239	.4184	17.826	240	1.588	2.0439	282.09
				245	1.600	2.0767	290.06
75	.5501	.4554	20.512	250	1.612	2.1092	298.09
80	.5760	.4917	23.327	255	1.625	2.1412	306.19
85	.6017	.5274	26.272	260	1.639	2.1729	314.35
90	.6249	.5625	29.339				
95	.6463	.5969	32.518	265	1.652	2.2043	322.57
				270	1.666	2.2353	330.87
100	.6678	.6305	35.803	275	1.681	2.2660	339.23
105	.6896	.6637	39.196	280	1.696	2.2964	347.68
110	.7110	.6962	42.698	285	1.711	2.3266	356.19
115	.7326	.7283	46.306				
120	.7542	.7599	50.024	290	1.726	2.3564	364.79
				295	1.742	2.3861	373.46
125	.7756	.7912	53.848	*298.16*	*1.752*	*2.4047*	*378.98*
130	.7971	.8220	57.780				
135	.8186	.8525	61.819	300	1.759	2.4155	382.21
140	.8401	.8827	65.966				
145	.8618	.9125	70.220				
150	.8836	.9421	74.584				
155	.9056	.9714	79.057				
160	9274	1.0005	83.639				
165	.9490	1.0294	88.330				
170	.9704	1.0580	93.129				
175	.9914	1.0865	98.034				
178.155	1.0052	1.1043	101.18				

[a] The enthalpy is referred to $H_0^s=E_0^s$, the internal energy of solid ethylbenzene at 0°K.
[b] Extrapolated by using the Debye function, $0.39983D(120/T)$.

It was thought that the anomolous behavior might be avoided if the sample were cooled slowly, during and after freezing, so this procedure was followed in subsequent runs. The data given in the legend of figure 1 show the thermal treatment of the sample preceding each run. By "fast" cooling is meant the removal of heat at a rate that caused the temperature to fall about 2 degrees per minute after the sample was completely frozen. "Slow" cooling was less than one-tenth this rate.

In preparing the smoothed table of specific heats, the results obtained in runs 2 and 3 below the triple point were not used. The results obtained in run 6 with calorimeter C were given less weight than the other observations because the sample container of calorimeter C was not full, hence the tare heat capacity was a greater part of the gross heat capacity than was the case with calorimeter D. The principal object of the measurements with calorimeter C was to provide an independent check on the accuracy of the measurements.
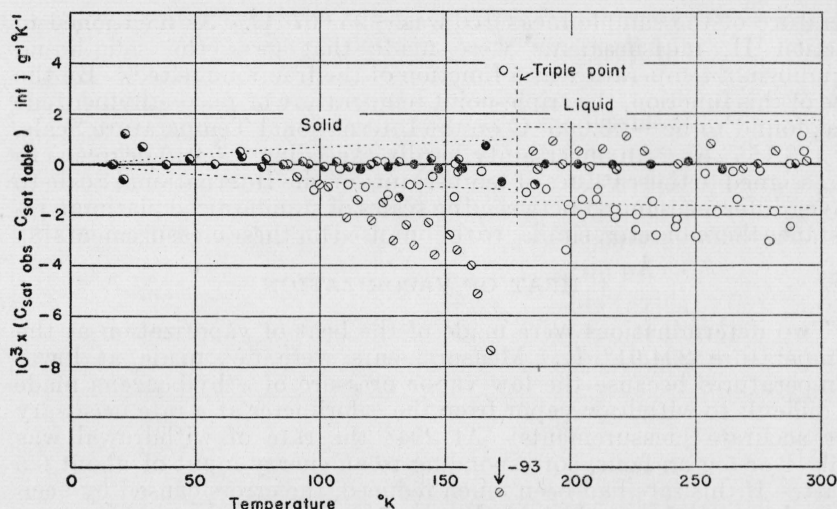
FIGURE 1.—*Deviations of observed specific heats from values obtained by interpolation from table.*

The triple-point temperature is indicated by the vertical dotted line. The dotted curves represent a deviation of ±1 part in 1,000. Symbols and information concerning the thermal treatment of the sample are given in the table below.

Run	Symbol	Calorimeter	Rate at which sample was cooled after freezing started
1	●	D	Fast
2	◒	D	Do.
3	◍	D	Do.
4	◐	D	Slow
5	◕	D	Do.
6	○	C	Do.

The ratios of the heat capacity of the empty sample containers to that of the container plus sample were as follows:

Temperature (°K)	Ratio	
	Calorimeter D	Calorimeter C
15_____	0. 13	----
90_____	. 41	0. 55
175_____	. 39	. 52
290_____	. 29	. 42

3. HEAT OF FUSION AND TRIPLE-POINT TEMPERATURE

Four determinations of the heat of fusion were made. The methods of measurement and computation of data are described in an earlier paper [4]. The values obtained were 86.46, 86.45, 86.48 and 86.49 int. j g⁻¹, giving a mean value of 86.47 int. j g⁻¹. The triple-point tem-

perature of the sample measured was —95.007° C. As mentioned in section II, measurements were made that 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 ethylbenzene was found to be —95.005° C on the International Temperature Scale, or 178.155° K. An uncertainty hardly exceeding ±0.010 degree is to be assigned to these values of temperature on the International Scale to cover differences found between the scales of standardized platinum resistance thermometers similar to the one used for these measurements [8].

4. HEAT OF VAPORIZATION

Two determinations were made of the heat of vaporization at the temperature 294.01° K. Measurements were not made at lower temperatures because the low vapor pressure of ethylbenzene made it difficult to withdraw vapor from the calorimeter at a rate necessary for accurate measurements. At 294° the rate of withdrawal was only 4 or 5 g an hour, corresponding to an energy input of about 0.5 watt. If this rate had been much reduced, the errors caused by accidental heat leaks would have become more important. A measurement of the heat of vaporization could not be made above room temperature because ethylbenzene vapor would have condensed in the part of the withdrawal tube at room temperature.

The two measurements of the heat of vaporization gave the values 399.81 and 400.49 int. j g $^{-1}$. The difference, 0.17 percent, is larger than the deviations usually obtained, but as the measurements were made under conditions of low vapor pressure the agreement is considered satisfactory.

IV. VAPOR PRESSURE

1. APPARATUS AND METHOD

Figure 2 is a diagram of the apparatus used in measuring the vapor pressure of ethylbenzene. The sample, S, about 0.3 cm ^{3} of ethylbenzene, was contained in one of a pair of holes symmetrically placed in the copper cylinder, C. The other hole contains a platinum resistance thermometer, Th. The copper cylinder is suspended by two thin-walled monel tubes inside the hollow brass cylinder, B. In the present experiment there was air in the space between the cylinders, although, if desired, the space can be evacuated through the tube Tu. The desired temperature of the copper cylinder is maintained by a heating coil wound on the copper cylinder and a cold bath in the Dewar flask, D. The temperature of this bath was kept only 2 or 3 degrees below the temperature of the copper cylinder, so that only a small amount of electric energy was required to maintain the cylinder at a desired temperature. Radiation of heat from the inner or copper cylinder was reduced by covering it with aluminum foil. The temperature was kept constant to within 0.01 degree by manually controlling the current supplied to [the heater, the necessary changes being indicated by the resistance theremometer.

Pressure measurements were made by means of the mercury manometer, M. The short cylinder at the top of the right-hand arm of the manometer has a diameter of about 25 mm and is provided with a glass point with which the mercury makes contact. Contact between the

mercury and the point is determined by observing the reflection, from the surface of the mercury, of a grating placed behind the tube, according to a method described by Stillman [9]. The mercury is brought into contact with the point by means of the injector, I, which consists of a stainless-steel piston 10 mm in diameter which displaces mercury in a stainless-steel cylinder of slightly larger diameter. The screw that forces the piston into the cylinder has a pitch of 1 mm, so that very fine adjustment of the mercury level is possible. The total amount of mercury in the manometer and injector can be adjusted by
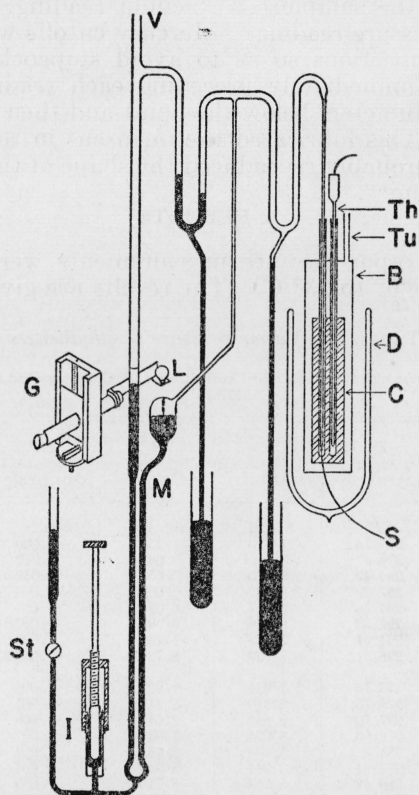

FIGURE 2.—*Apparatus for measuring the vapor pressure of ethylbenzene*

V, Vacuum line; *G*, comparator; *St*, stopcock; *I*, mercury injector; *M*, manometer; *Th*, platinum resistance thermometer; *Tu*, tube; *B*, brass cylinder; *D*, Dewar flask; *C*, copper cylinder; *S*, sample of ethylbenzene.

admitting or withdrawing mercury through the stopcock, *St*. The tubing of small diameter (5 mm) connecting the two sides of the mano-meter was covered with insulation to avoid temperature differences and resulting errors arising from unequal density of mercury in the two sides.

The left, or vacuum, arm of the manometer is 10 mm in diameter, and the mercury meniscus is lubricated with normal butyl phthalate [10] to minimize errors due to capillarity. The position of the mercury meniscus and the depth of the butyl phthalate are determined by the small comparator, *G*, which is mounted so that the microscope traverses a vertical path. An automobile headlight bulb, *L*, mounted

on a bracket attached to the comparator microscope so that the filament is on the axis of the microscope is a source of illumination that always maintains the same position relative to the mercury surface when a measurement is made. A green filter placed in the light path added to the comfort of reading and probably increased the sharpness of the image.

Measurements of vapor pressure were made by determining the positions of the mercury and butyl phthalate surfaces, first with both arms of the manometer evacuated, and then with the right arm communicating with the sample. A vacuum reading was taken before and after each pressure reading. Mercury cutoffs were used to make the necessary connections so as to avoid stopcock grease. It was found necessary, immediately preceding each reading, to lower the mercury a few millimeters below the point and then raise it until contact was made. This lubricated the meniscus in the left arm of the manometer, and probably reproduced the shape of the meniscus in the right arm each time.

2. RESULTS

Two series of vapor-pressure measurements were taken over the temperature range 0° to 23° C. The results are given in table 2.

TABLE 2.—*Vapor pressure of ethylbenzene*

Pressure in millimeters of mercury at standard conditions: 0° C and $g=980.665$ cm sec^{-2}. $T°K=t°C+273.16°$.]

Tª	P Obs.	P Calc.ª	ΔP Obs.−calc.
°K	mm Hg	mm Hg	mm Hg
273.16	1.920	1.926	−0.006
279.53	3.015	3.003	.012
282.49	3.670	3.658	.012
287.39	5.005	5.009	−.004
290.36	6.017	6.024	−.007
292.35	6.786	6.793	−.007
294.61	7.772	7.768	.004
296.61	8.739	8.734	.005
273.16	1.931	1.926	.005
275.73	2.310	2.311	−.001
277.70	2.640	2.649	−.009
279.66	3.024	3.031	−.007
281.63	3.460	3.465	.004
283.64	3.944	3.945	−.001
289.58	5.754	5.745	.009
292.14	6.703	6.711	−.008

ª $\log_{10} P_{(mm\ Hg)} = 13.7540 - 3002.96/T - 0.0090634\,T$.

It was found that the observations were well represented by the equation

$$\log_{10} P_{(mm\ Hg)} = 13.7540 - \frac{3002.96}{T} - 0.0090634\,T, \qquad (1)$$

where P is the vapor pressure in millimeters of Hg reduced to standard conditions (0° C and $g=980.665$ cm sec^{-2}), and T is the Kelvin temperature ($T°$ K$=273.16°+t°$ C). Column 3 of table 2 gives the values of the vapor pressure calculated from this equation and column 4 gives the difference between the observed and calculated pressures. The average deviation of the observations from the equation is 0.006 mm Hg.

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

1. ENTROPY AND ENTHALPY OF SOLID AND LIQUID

In table 1, column 3, values of the entropy, $S_{sat,}$, of solid and liquid ethylbenzene at saturation pressure are given at 5-degree intervals. These were obtained by evaluating $\int_0^T (C_{sat,}/T)dT$, using tabular integration and Simpson's rule and adding at the triple point the entropy of fusion, L_f/T_f. Column 4 of table 1 gives values of the enthalpy $(H_{sat,}-E_0^s)$ at saturation pressure, referred to the internal energy of solid ethylbenzene at 0° K. The values of the enthalpy were obtained by evaluating $\int_0^T C_{sat,}dT$ and adding at the triple point the enthalpy of fusion, L_f. Strictly, the value of $(H_{sat,}-E_0^s)$ should include a term $\int_0^T v(dp/dT)_{sat,}dT$, but for the temperatures of the present investigation this term was negligible.

2. HEAT OF VAPORIZATION CALCULATED FROM THE VAPOR-PRESSURE EQUATION

The vapor-pressure equation, 1, was used with the Clausius-Clapeyron relation

$$L_v = T(V-v)\,\frac{dp}{dT} \tag{2}$$

to calculate the heat of vaporization of 294.01° K and thus provide a check on the accuracy of the measurements. In equation 2, L_v is the heat of vaporization, V is the specific volume of the saturated vapor, v is the specific volume of the liquid, and dp/dT is the derivative of the vapor-pressure–temperature relation. The specific volume of the saturated vapor at 294.01° K was computed by using the Berthelot equation of state with the critical constants $T_c=619.6^\circ$ K and $p_c=38.1$ atm, as determined by Altschul [11], and by using the vapor pressure 7.507 mm Hg calculated from equation 1. The value obtained was 22984 ml g^{-1}. The density of liquid ethylbenzene at 20° C is 0.868 g ml^{-1} [12], which corresponds to a specific volume, v, of 1.15 ml g^{-1}. From equation 1, dp/dT was found to be 0.44384 mm Hg $^\circ$K^{-1} at 294.01 $^\circ$K. Substituting these values into equation 2, L_v is found to be 2.9991×10^6 mm Hg ml g^{-1}, which, upon conversion, becomes 399.78 int. j g^{-1}. This is in good agreement with the directly measured heats of vaporization, being only 0.09 percent lower than the mean of the two calorimetric values.

VI. ESTIMATE OF ERRORS

1. CALORIMETRIC MEASUREMENTS

Two tests were made to obtain evidence concerning the accuracy of the calorimetric measurements. In the first test the specific heat of air-free water, from 0° to 20° C, and its heat of vaporization at 20° C, were measured with calorimeter C. The results were in good agreement with the values reported by Osborne, Stimson, and Ginnings [13], the differences being of the order of 0.03 percent.

In the second test, calorimeter C was used to make some measurements between 90° and 295° K, on the same sample of ethylbenzene that had been investigated with calorimeter D. The average deviation between the values obtained with the two calorimeters was 0.10 percent.

The authors estimate that there is an even chance that the errors in the values of specific heat above 40° K given in table 1 and of the heat of vaporization reported in section III–5 do not exceed 0.1 percent. Below 40° K the errors in the specific heat measurements are larger, perhaps reaching 1 percent at 20° K. The value given for the heat of fusion, section III–4, may be somewhat more accurate than 0.1 percent because errors in measurement of temperature differences are less important.

2. VAPOR PRESSURE

An examination of the vapor-pressure data shows that about half of the observations deviate from the mean by more than 0.006 mm Hg. If systematic errors are negligible, this would indicate that the probable error of a single observation is 0.006 mm Hg. However, as errors caused by impurities or by prismatic effects in the manometer tube may well be systematic, too much confidence should not be attached to the figure indicated by the scattering of the observations.

3. CALCULATED VALUES OF ENTROPY AND ENTHALPY

As the calculated values of the entropy and enthalpy of the solid and liquid at saturation conditions involve only the errors of the calorimetric measurements, the probable error assigned to the reported values is 0.1 percent at the higher temperatures. Below 100° K errors in the entropy and enthalpy of the solid are probably larger because of the contributions of the less accurate specific-heat values below 40° K.

VII. COMPARISONS WITH THE RESULTS OF OTHER OBSERVERS

In figure 3 the results of measurements by other observers of the specific heat of ethylbenzene are compared with the values obtained in this investigation. The ordinates of the graph are reported values of specific heat minus values obtained from table 1. The dotted curve represents a difference of 1 percent. The values reported by Guthrie, Spitzer, and Huffman [14] appeared while this paper was being prepared for publication. The agreement is good. Except in the region just below the triple point and at temperatures below 60° K, the differences seldom exceed 0.15 percent. The values given by Huffman, Parks, and Daniels [15] are, on the average, about 1 percent lower than those given in table 1. The values given by Blacet, Leighton, and Bartlett [16] are in fair agreement with the present values in the neighborhood of 300° K but are much lower at lower temperatures.

The heat of fusion as measured by Guthrie, Spitzer, and Huffman [14] was 86.31 int. j g^{-1}. Huffman, Parks, and Daniels [15] reported 86.32 int. j g^{-1}. These values are somewhat lower than the value 86.47 obtained in the present investigation. It is possible that the differences are the results of impurities in the samples. The purer

sample used in the present measurements permitted a more accurate determination of the specific heat of the solid in the region just below the triple point because there was less premelting. This results in an improved value of the heat of fusion because the actual measurement consists of heating the sample from a temperature below the triple point to a temperature above the triple point, and the heat required to raise the temperatures of the solid and liquid must be subtracted from the total energy supplied.

Osborne and Ginnings [17] measured the heat of vaporization of ethylbenzene at 25° C. They obtained the value 397.89 int. j g⁻¹. The mean value obtained in the present investigation was 400.15 int. j g⁻¹ at 294° K. In order to compare these values, the latter was
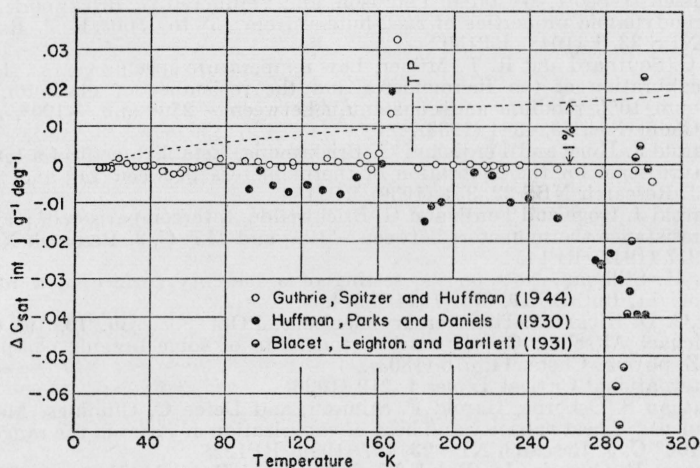

FIGURE 3.—*Comparison of the values of specific heat given in table 1 with the results of other observers.*

Ordinates represent the differences (observed values minus the values obtained from table 1). The distance between the dotted curve and the axis of zero ordinate represents a difference of 1 percent. The triple-point temperature is indicated by the vertical line labeled *TP*.

adjusted to correspond to the temperature 25° C (298.16° K) by means of the relation

$$dL/dT = C_p^\circ - C_{sat.\ liq.} - d/dT(H^\circ - H_{sat.\ vap.}).$$ (3)

The heat of vaporization at 298.16° K was found to be 397.92 int. j g⁻¹. This is in excellent agreement with the value of Osborne and Ginnings.

The vapor pressure of ethylbenzene was measured by Guttman, Westrum, and Pitzer [18] at temperatures between 0° and 60° C. They represented the results by the equation

$$\log_{10} P_{mm\ Hg} = -2959.08 T^{-1} - 5.8 \log_{10} T + 25.25883.$$ (4)

This equation yields vapor pressures about 0.04 mm Hg higher than those obtained from equation 1 in the temperature range 273° to 297° K.

The authors are indebted to M. R. Fenske, of The Pennsylvania State College, for the preparation of a pure sample of ethylbenzene for these measurements.

VIII. REFERENCES

[1] Russell B. Scott and Jane W. Mellors, Specific heats of gaseous 1,3-butadiene, isobutene, styrene and ethylbenzene, J. Research NBS **34**, 243 (1945) RP1640.

[2] Ferdinand G. Brickwedde, Morris Moskow, and Russell B. Scott, Thermodynamic properties of ethylbenzene vapor from 300° to 1500° K, J. Chem. Phys. **13**, 547 (1945).

[3] J. C. Southard and F. G. Brickwedde, Low temperature specific heats. I. An improved calorimeter for use from 14° to 300° K. The heat capacity and entropy of naphthalene, J. Am. Chem. Soc. **55**, 4378 (1933).

[4] Russell B. Scott, Cyril H. Myers, Robert D. Rands, Jr., Ferdinand G. Brickwedde, and Norman Bekkedahl, Thermodynamic properties of 1,3-butadiene in the solid, liquid, and vapor states, J. Research NBS **35**, 39 (1945) RP1661.

[5] Russell B. Scott, W. Julian Ferguson, and Ferdinand G. Brickwedde, Thermodynamic properties of cis-2-butene from 15° to 1500° K, J. Research NBS **33**, 1 (1944) RP1592.

[6] J. C. Southard and R. T. Milner, Low temperature specific heats. II. The calibration of the thermometer and the resistance of platinum, platinum–10% rhodium and constantan between −259° and −190°, J. Am. Chem. Soc. **55**, 4384 (1933).

[7] Harold J. Hoge and Ferdinand G. Brickwedde, Establishment of a temperature scale for the calibration of thermometers between 14° and 83° K, J. Research NBS **22**, 351 (1939) RP1188.

[8] Harold J. Hoge and Ferdinand G. Brickwedde, Intercomparison of platimum resistance thermometers between −190° and 445° C, J. Research NBS **28**, 217 (1942) RP1454.

[9] M. H. Stillman, Note on the setting of a mercury surface to a required height, Bul. BS **10**, 371 (1914) S214.

[10] K .C. D. Hickman, The mercury meniscus, J.Opt. Soc. Am. **19**, 190 (1929).

[11] Michael Altschul, On the critical constants of some organic compounds, Z. physik. Chem. **11**, 576 (1893).

[12] International Critical Tables **1**, 219 (1926).

[13] Nathan S. Osborne, Harold F. Stimson, and Defoe C. Ginnings, Measurements of heat capacity and heat of vaporization of water in the range 0° to 100° C, J. Research NBS **23**, 197 (1939) RP1228.

[14] George B. Guthrie, Jr., Ralph W. Spitzer, and Hugh M. Huffman, Thermal data. XVIII. The heat capacity, heat of fusion, entropy and free energy of ethylbenzene, J. Am. Chem. Soc. **66**, 2120 (1944).

[15] H. M. Huffman, George S. Parks, and Albert C. Daniels, Thermal data on organic compounds. VII. The heat capacities, entropies, and free energies of twelve aromatic hydrocarbons, J. Am. Chem. Soc. **52**, 1547 (1930).

[16] Francis E. Blacet, Philip A. Leighton, and Edward P. Bartlett, The specific heats of five pure organic liquids and of ethyl alcohol-water mixtures, J. Phys. Chem. **35**, 1935 (1931).

[17] Nathan S. Osborne and Defoe C. Ginnings, Private communication.

[18] Lester Gussman, Edgar F. Westrum, Jr., and Kenneth S. Pitzer, The thermodynamics of styrene (phenylethylene), including equilibrium of formation from ethylbenzene, J. Am. Chem. Soc. **65**, 1246 (1943).

WASHINGTON, AUGUST 25, 1945.