

# Calorimetric Properties of Normal Heptane From 0° to 520° K

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Precise measurements of the heat capacity of solid and liquid *n*-heptane from 20° to 523° K are described. An adiabatic calorimeter, with which were determined also the triple point and the heat of fusion, was used from 20° to 370° K, whereas a drop method was used with a Bunsen ice calorimeter from 273° to 523° K. These two series of heat-capacity measurements and three other series of independent values show a maximum difference of approximately 0.25 percent in the range 50° to 370° K. Besides the heat capacity, the enthalpy, entropy, and Gibbs free energy of the solid and liquid at saturation pressures from 0° to 520° K are derived and tabulated. The same properties of the ideal gas from 298° to 470° K also are derived by making use of published precise measurements of gaseous heat capacity, heat of vaporization, and the normal boiling point. Interconsistency in the values of the various thermal properties is shown by the fact that the vapor pressures calculated from these values agree with those precisely measured by other investigators between 299° and 372° K to within  $\pm 0.1$  percent.

## 1. Introduction

Normal heptane is one of the naturally abundant hydrocarbons, and in fact is one of the most abundant components of some fuels for internal-combustion engines. Its thermal properties are, therefore, of corresponding practical importance.

This substance was recommended recently, at the Fourth Conference on Low Temperature Calorimetry<sup>1</sup> [1]<sup>2</sup> as one of several materials suitable as standards for the intercomparison of precision heat-capacity calorimeters. There are at present many laboratories conducting high-precision heat-capacity measurements on various substances. In view of the laborious nature of this work it seems desirable that all work be compatible. At the time of the April 1947 meeting of the American Chemical Society in Atlantic City, N. J., a group of representatives from different laboratories engaged in heat-capacity calorimetry met informally to discuss ways of comparing heat-capacity measurements made in different laboratories and of improving calorimetric techniques. At the time of this meeting the group agreed upon a plan to distribute to participating laboratories identical samples of several substances for comparative measurements. Such substances were to have sufficient purity so that the impurities present would have insignificant effect upon the heat-capacity value. At the Fourth Conference on Low-Temperature Calorimetry *n*-heptane, along with benzoic acid and synthetic sapphire ( $\alpha$ -aluminum oxide) was selected as a standard for the intercomparison of heat-capacity calorimeters. The Bureau undertook and subsequently completed the task of preparing and packaging these materials in suitable quantities for distribution. The results of measurements with the low-temperature adiabatic calorimeter, given in this paper, were obtained on this Calorimetry Conference *n*-heptane sample, whereas the results of the Bunsen ice calorimeter are based on the heat-capacity meas-

urements with a high-purity *n*-heptane sample from a different source. Both samples, however, were of sufficiently high purity that the effect of the impurities on the results is believed to have been negligible. It is hoped that other laboratories will also make heat-capacity measurements on the Calorimetry Conference *n*-heptane, so that calorimeters of various design and the results obtained with them may be compared and a more general agreement may be reached on the heat-capacity values of this substance.

Advantages of using *n*-heptane as a standard include the following: It can be readily purified (especially with respect to nonhydrocarbon impurities), it is chemically stable up to its critical temperature (540° K), and it can be easily distilled into or out of a calorimeter. A discussion of its use as a heat-capacity standard was recently published and values at even temperatures were given [2].<sup>3</sup> The present paper describes the basic experimental measurements in considerably more detail. Although the Calorimetry Conference recommended *n*-heptane as a heat-capacity standard from 10° to 300° K, the results of the measurements presented here indicate that with proper care the substance can be used for this purpose to 400° K.

The heat capacity of *n*-heptane was measured between 20° and 523° K, using two calorimeters widely different in design. An adiabatic method was used from 20° to 370° K, and a "drop" method was used from 273° to 523° K with an accurately thermostated furnace and a Bunsen ice calorimeter. The two methods overlap in the temperature range 273° to 370° K, where they serve to check each other. The triple point and heat of fusion were measured in the adiabatic calorimeter. Vaporization corrections, which become very important in the region of the critical temperature, were derived, using precise measurements of vapor pressure and liquid density made elsewhere.

Several series of precise measurements already published have been combined with the data reported

<sup>1</sup> The Conference on Low Temperature Calorimetry was renamed the Calorimetry Conference at the meeting held on September 5, 1950, in order to include other fields of calorimetry.

<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

<sup>3</sup> Some of the values were later corrected [2a].

here to give critically adjusted values of the thermal properties of the saturated solid and liquid and of the ideal gas. Heat-of-vaporization and vapor-pressure data from 298° to 371° K were used to calculate the second virial coefficient, as well as the entropy, of the real gas at one temperature. Data on gaseous heat capacity and its variation with pressure, at temperatures from 357° to 466° K, were used to evaluate the variation of the second virial coefficient with temperature and the derivation, up to 470° K, of thermal properties of the ideal gas consistent with the best vapor-pressure measurements up to the normal boiling point (372° K).

## 2. Low-Temperature Calorimetry

### 2.1. Apparatus and Method

The low-temperature series of heat-capacity measurements was made from about 20° to 370° K, using an adiabatic calorimeter similar to that described by R. B. Scott, et al. [3]. The readers are referred to this reference for details of the design and operation of the calorimeter. The calorimeter used in this investigation differed only in one respect from that described, in that it did not have a filling tube. The container was suspended within the shield system by means of a linen string. Briefly, the apparatus and the procedure were as follows: The normal-heptane sample, about which details will be given in the next section, was sealed in a copper container and suspended within the adiabatic shield system. The copper container had a volume of about 100 ml and was provided with a central well for a thermometer and heater assembly. Vanes, spaced about 4 mm apart, radiated out from the well to the container wall. A thin layer of pure tin was applied to the inner surface of the container to provide an inert surface to the sample and to solder the vanes in place. The outer surface of the container and the adjacent shield surface were gold plated and polished to minimize the heat transfer by radiation. The space surrounding the container was pumped to a pressure of  $10^{-5}$  mm Hg or less. During the heat-capacity experiments the shield temperature was controlled manually to be the same as that of the container surface by means of shield heaters and constantan—chromel-P differential thermocouples.

The electric power input was measured by means of a Wenner potentiometer in conjunction with a standard cell, volt box, and standard resistor. A precision interval timer, operated on 60-cycle standard, was used to measure the time. The timer was periodically compared with standard second signals and was found to vary not more than 0.02 sec for a heating period, which was never less than 2 min. The temperatures were measured by means of a platinum-resistance thermometer and a high-precision Mueller bridge. The platinum-resistance thermometer was calibrated above 90° K in accordance with the 1948 International Temperature Scale [4], and between 10° and 90° K with a provisional scale [5], which consists of a set of platinum resistance thermometers calibrated against a helium-gas ther-

mometer. The provisional scale is based upon the value 273.16° K for the temperature of the ice point and 90.19° K for the temperature of the oxygen point. All electric instruments and accessory equipment were calibrated at the Bureau.

### 2.2. Sample, Purity, and Triple-Point Temperature

The normal-heptane sample was a part of the high-purity material prepared for the Calorimetry Conference. The material was synthesized and purified by distillation under the direction of F. L. Howard of the Engine Fuels Section of the Bureau [5a]. The distilled product had a purity of 99.98 mole percent. R. T. Leslie of the Pure Substances Section purified this material further by fractional crystallization. The process involved slow crystallization in a vacuum-walled flask immersed in liquid nitrogen. A single-walled flask was attached mouth-to-mouth to the vacuum flask by means of a ground joint. During the freezing process, this assembly was rotated around the axis joining the two flasks with periodic reversal of the direction of rotation to agitate the mixture. When 50 to 75 percent of the liquid was frozen, the assembly was inverted to drain unfrozen liquid into the single-walled flask. This procedure was repeated until the material was found to be sufficiently purified, as determined calorimetrically from its melting curve. The material was passed later through purified silica gel to remove water. In order to obtain the highest possible degree of identity in all samples, the *n*-heptane was subdivided in the liquid state without distillation. The material was siphoned into 800-ml flasks, which in turn were subdivided into 100-ml ampoules. The contents of one (sample O-E) of these ampoules were used in the low-temperature heat-capacity measurements.

All of the sample contained in the break-seal ampoule was transferred under vacuum by distillation into the sample container and sealed. The purity of this material was determined calorimetrically from the equilibrium melting temperatures at various liquid-solid ratios as determined from the energy input, heat of fusion, and heat capacity of the system. The system was assumed to follow Raoult's law of solution and to form no solid solution. The simplified equation,  $N_2 = A\Delta T$ , was used to represent the relation between the mole-fraction impurity,  $N_2$ , and the depression,  $\Delta T$ , of the triple-point temperature of pure *n*-heptane. The cryoscopic constant,  $A$ , was calculated from  $A = L_f/RT_i^2$ , where  $L_f$  is the heat of fusion,  $R$  the gas constant, and  $T_i$  the triple-point temperature. The observed equilibrium temperatures were plotted as the function of  $1/F$ , the reciprocal of the fraction of material melted. The product of the slope of this curve and the cryoscopic constant was taken to be the mole-fraction impurity. As  $N_2$  is proportional to  $1/F$ , the curve extrapolated to  $1/F=0$  was taken to give the triple-point temperature of pure *n*-heptane.

The results of the measurements are given in table 1 and are plotted in figure 1. The purity

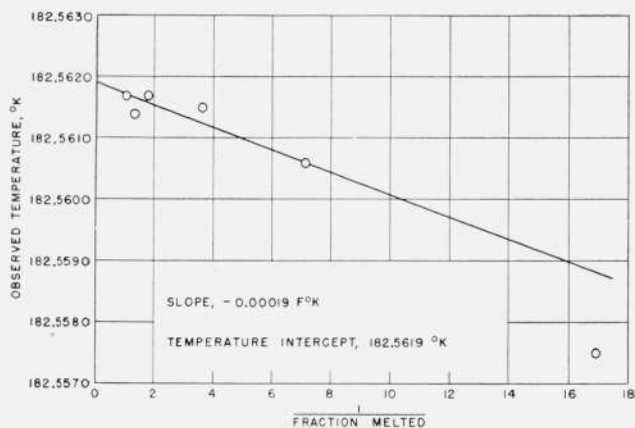


FIGURE 1. Equilibrium melting temperatures of *n*-heptane.

computed from the curve is 99.999 mole percent with an uncertainty of about 0.002 in this figure. The temperature intercept is 182.5619° K on the basis of the value 273.16° K for the temperature of the ice point; and the triple-point temperature, considering calibration uncertainties of the bridge and platinum resistance thermometer and the uncertainty of the temperature scale, is taken to be 182.56 ± 0.01° K.

TABLE 1. Equilibrium melting temperatures of *n*-heptane

$N_2 = 0.0506 \Delta T$

1/F	$T_{\text{obs.}}^a$	$T_{\text{calc.}}$
16.97	182.5575	182.5587
7.15	182.5606	182.5603
3.64	182.5615	182.5612
1.80	182.5617	182.5616
1.32	182.5614	182.5617
1.05	182.5617	182.5617
1.00	-----	182.5617

Temperature intercept, 182.5619° K.  
Purity, 99.999 ± 0.002 mole percent.

<sup>a</sup> These temperatures were obtained from the relation  $^{\circ}\text{K} = ^{\circ}\text{C} + 273.1600^{\circ}$  and are accurate to ± 0.01 deg K. The last two decimal places are significant only in the measurement of small temperature differences.

Column 3 of table 1 gives temperatures calculated from the relation  $T_t - T_{\text{calc.}} = N_2/AF$ , in which  $N_2$  is the mole-fraction impurity as obtained from the experimental data. The comparison of calculated and observed equilibrium temperatures shows that the material followed closely Raoult's law of solution and formed no solid solutions. In all calculations the value used for the cryoscopic constant,  $A$ , was 0.0506 deg<sup>-1</sup>.

### 2.3. Heat of Fusion

The heat of fusion of *n*-heptane was determined in the usual manner, in which electric energy was added continuously from a temperature slightly below the triple point to a temperature above it. The total added energy was corrected for the heat capacity of the container and sample below and above the triple point, and for the premelting of the

sample due to the impurities. In table 2 are given heat-of-fusion measurements made with sample O-E and with another sample, 7-F. Sample 7-F is from another ampoule of *n*-heptane prepared for the Calorimetry Conference. The purity of this sample was found to be 99.997 ± 0.002 mole percent. The heat-of-fusion results with sample 7-F are generally lower, and the difference is considered to arise largely from the uncertainty in the heat-capacity corrections and not from the slight difference in purity. The heat of fusion obtained is probably accurate to about 0.1 percent, and this quantity is taken to be 14,022 ± 14 abs j mole<sup>-1</sup>.

TABLE 2. Heat of fusion of *n*-heptane

Temperature interval	Total energy input	Corrections		$\Delta H_f$ , total	$\Delta H_f$
		Heat capacity	Pre-melting		
<sup>°K</sup>	abs j	abs j	abs j	abs j	abs j mole <sup>-1</sup>
178.7994 to 185.1898 <sup>a</sup> ...	9291.1	844.3	0.8	8447.6	14014.2
177.4223 to 184.2878 <sup>a</sup> ...	9315.9	867.8	.6	8448.7	14016.0
180.4110 to 185.9838 <sup>a</sup> ...	9034.6	586.7	1.5	8449.4	14017.1
179.6455 to 187.5309 <sup>b</sup> ...	9300.8	1,155.3	0.5	8146.0	14034.6
180.8642 to 185.1144 <sup>b</sup> ...	8759.6	616.8	.9	8143.7	14030.7
Mean.....					14022.5
Standard deviation.....					±9.4 <sup>c</sup>

<sup>a</sup> Sample 7-F, mass 60.3984 g.

<sup>b</sup> Sample O-E, mass 58.1570 g.

<sup>c</sup> Standard deviation as used here is defined as  $[\sum d^2/(n-1)]^{1/2}$ , where  $d$  is the difference between a single observation and the mean, and  $n$  is the number of observations.

### 2.4. Heat Capacity

The heat capacity of the *n*-heptane sample was measured from about 20° to 370° K. Both high- and low-filling runs were made under calorimetric conditions as nearly identical as possible. The high-filling experiments contained 58.1570 g and the low-filling, 2.0196 g. In order to minimize the curvature correction in the temperature range where the heat capacity has a large curvature, the temperature change per heating interval was generally smaller than 2 deg below 35° K and from 2 to 5 deg between 35° and 80° K. Above 80° K, the temperature change was made from about 5 to 10 deg. Curvature corrections were applied to those measurements wherever significant, according to the relation given in a different notation by Osborne, et al. [6]:

$$Z_{T_m} = Q/\Delta T - \left( \frac{\partial^2 Z}{\partial T^2} \right)_{T_m} \frac{\Delta T^2}{24} \dots, \quad (1)$$

in which  $Z_{T_m}$  is the corrected heat capacity of the sample container plus its contents (solid or liquid and vapor) at the mean temperature,  $T_m$ , of the heating interval,  $\Delta T$ ;  $Q$  is the electrical energy added; and  $(\partial^2 Z)/(\partial T^2)_{T_m}$  is the second derivative of the heat capacity with respect to temperature at  $T_m$ . The principal data from the high- and low-filling heat-capacity experiments are given in table 3. The heat-capacity data given are "raw" and do not



contain corrections for premelting near the triple-point temperature or for curvature.

In both series of measurement the observed results (corrected for curvature) were plotted on a large scale as deviations from approximate empirical equations, and smooth curves were drawn through the deviation points. The deviation curves and the empirical equations were used to obtain smoothed heat capacities at equally spaced integral temperatures. The deviations of the experimental values from the smoothed heat capacities are shown in figures 2 and 3. The points in the high-filling experiments are in general well within  $\pm 0.1$  percent of the net heat capacity below  $182^\circ$  K and within  $\pm 0.05$  percent in the range  $182^\circ$  to  $370^\circ$  K, whereas those of the low-filling experiments are within  $\pm 0.03$

percent. These give the measure of the respective precision errors introduced into the final heat-capacity values.

The heat capacity of *n*-heptane along the saturation curve,  $C_{\text{sat.}}$ , was computed by the relationship

$$C_{\text{sat.}} = \frac{Z_{\text{hi}} - Z_{\text{lo}}}{M_{\text{hi}} - M_{\text{lo}}} + T \frac{d}{dT} \left( v \frac{dP}{dT} \right) \quad (2)$$

$Z_{\text{hi}}$  and  $Z_{\text{lo}}$  are the smoothed heat capacities at the corresponding temperature,  $T$ , for the high and low fillings, respectively, corresponding to  $M_{\text{hi}}$  and  $M_{\text{lo}}$  grams of *n*-heptane. In the term  $T(d/dT)[v(dP/dT)]$ ,  $v$  is the specific volume of the condensed phase, and  $P$  is the vapor pressure. Below  $235^\circ$  K, the last

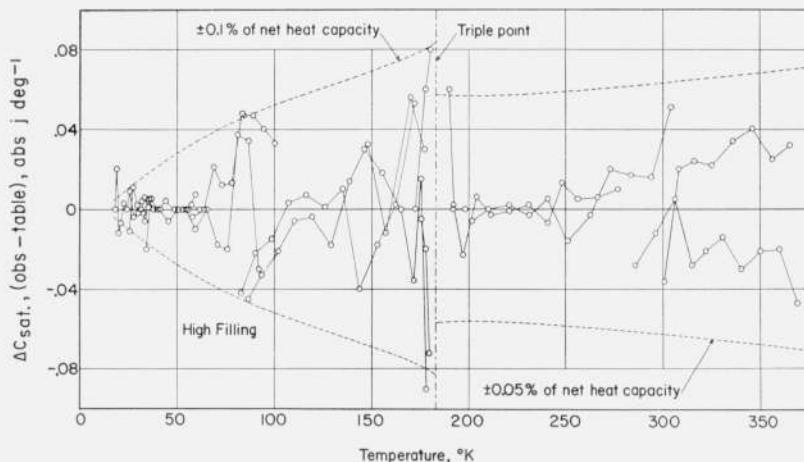


FIGURE 2. Deviations of experimental heat capacities (corrected for curvature) from smoothed values for the container plus *n*-heptane (high filling).

The experiments in a single series of measurements are connected by lines.

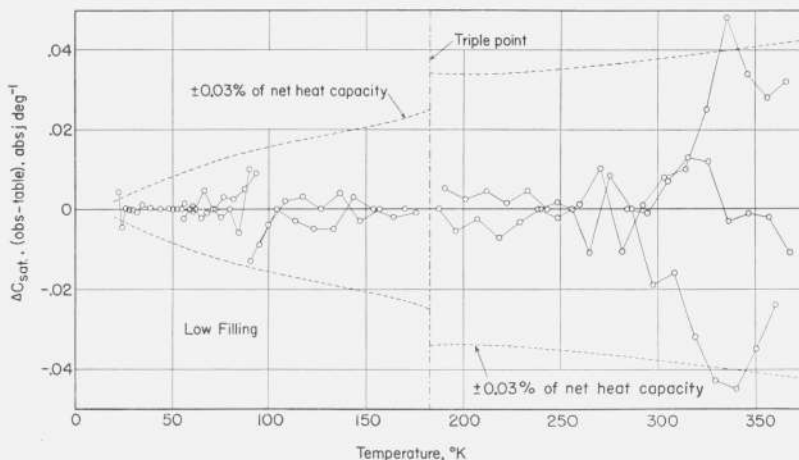


FIGURE 3. Deviations of experimental heat capacities (corrected for curvature) from smoothed values for the container plus *n*-heptane (low filling).

The experiments in a single series of measurements are connected by lines.

term amounts to less than 0.001 percent; consequently, it was not applied below this temperature. In arriving at the final heat-capacity values (table 5), those obtained in the manner outlined above were compared in the range from 270° to 370° K with the results from the high-temperature calorimeter and with previously published values [7]. The discussion concerning the comparison and the final values in this range will be given in section 4.1 of this paper. The heat-capacity values up to 270° K, however, were based entirely upon the results obtained with the low-temperature adiabatic calorimeter. These values are given in table 5 along with those in the range 270° to 370° K and higher. For a considerable range above the triple-point temperature the heat-capacity curve shows a negative slope. The heat-capacity curves of many other substances also exhibit this behavior.

The heat-capacity values below 20° K in the final table (table 5) were obtained by extrapolating the lowest experimental results by means of a Debye function. The equation used was

$$C_{\text{sat.}} = 60 D \left( \frac{138.15}{T} \right), \quad (3)$$

which was obtained by fitting to the experimental values at 20° and 30° K.  $D$  symbolizes the Debye function and  $138.15/T$  its argument.

### 2.5. Reliability of the Heat-Capacity Results Obtained With the Low-Temperature Calorimeter

The precision of the heat-capacity measurements is shown in the deviation plots of figures 2 and 3. The two series of measurements, high and low filling, were made under conditions as nearly identical as possible so that certain systematic additive errors would cancel out. The rate of temperature rise and the positioning of the sample container, of the leads, and of the thermocouples in the two series of experiments were made as nearly identical as possible.

The mass of the sample container was slightly different for the two experiments because of a small difference in the masses of solder used in sealing the container. A correction was applied for this difference from known heat capacities of lead and tin. The heat-capacity correction for the lead-tin solder was made on the assumption of additivity of the heat capacities of lead and tin, and the maximum total correction for the differences in the mass of the container was 0.15 percent of the net heat capacity, which occurred at the lowest temperature of the measurements.

In the test of a similar calorimeter used in the heat-capacity measurements of benzoic acid [8], the heat capacity of water was determined from 274° to 332° K, and the results in general were within 0.02 percent of the very accurate values previously published [9].

Upon consideration of the various sources of error, it is believed that the heat capacities of these meas-

urements have from 50° to 370° K a probable error<sup>4</sup> of 0.1 percent. Below 50° K the probable error is believed to increase to 1 percent largely due to the decrease in the sensitivity of the thermometer, the smaller temperature intervals of the measurements, and smaller energy input.

## 3. High-Temperature Calorimetry

### 3.1. Method and Apparatus

The enthalpy measurements at higher temperatures, which supplement the heat-capacity measurements made from 20° to 370° K, covered the range 273° to 523° K (0° to 250° C), extending to 17 deg below the critical temperature. These were carried out by essentially the same method and with the same apparatus used in recent years for measurements on numerous other substances. The method and revised apparatus have been described in considerable detail [10]. In brief, the method was as follows: The sample, sealed in its container, was suspended in a furnace until it came to the chosen constant temperature, as measured by a platinum resistance thermometer. It was then dropped into a Bunsen ice calorimeter, which measured the heat evolved by the sample plus container in cooling to 0° C. Between 150° and 250° C such measurements were repeated on a much smaller sample in the same container, so as to check the vaporization corrections that are especially important at these higher temperatures. As the same container was used earlier with diphenyl ether [11], no repetition of measurements on the empty container were made. The change in enthalpy of the sample between 0° C and the temperature in the furnace was computed from the difference between the value of heat with the sample present and the earlier value of heat for the empty container. The heat capacity was derived from enthalpy values of the sample so determined for a series of furnace temperatures.

The sample of *n*-heptane used for these high-temperature measurements (NBS Standard Sample 216a), unlike the sample used in the adiabatic calorimeter, had neither been synthesized nor recrystallized, but had been obtained by fractional distillation from natural petroleum. Its content of impurity, as determined at the Bureau by cryoscopic measurements, was  $0.01 \pm 0.01$  mole percent. When the sample was cooled to the temperature of dry ice, there was observed no cloudiness, such as would occur by crystallization of water. This *n*-heptane was boiled to remove all air from the container while the latter was being sealed for the enthalpy measurements. A detailed description of the monel container and of the method of filling and sealing the sample in it were published in connection with the work on diphenyl ether [11].

<sup>4</sup> For these measurements a true probable error cannot be computed statistically. The values given are estimates arrived at by examining various sources of error and they are to be considered (unless stated otherwise) as the authors' best estimate of the error, which is just as likely to be exceeded as not.

### 3.2. Results

The results of the individual measurements are given in columns 1, 2, and 3 of table 4. The measured heats listed were obtained from the masses of mercury drawn into the ice calorimeter, using the calorimeter calibration factor of 270.48 abs j/g of mercury.<sup>5</sup> The values in column 4 were obtained by smoothing the mean values of measured heat for the same empty container determined and reported earlier [11]. The value at 230°C was obtained by an interpolation of the heat divided by the furnace temperature (in deg C). This quotient varies almost linearly with temperature.

In addition to the usual very small corrections for calorimeter heat leak, two additional corrections were necessary in the case of the largest sample (3.7679 g) because of small changes in the mass of material entering the calorimeter. The container proved to be not absolutely tight when this sample was run, and at the higher temperatures the large vapor pressures of the *n*-heptane gave rise to small accumulative losses of mass, aggregating to a few hundredths of 1 percent of the total mass during the

measurements. At the same time it was assumed that the long times of standing at room temperature permitted the originally evacuated gas space of the container to fill with air, and corrections for the contribution of this, amounting to between 0.1 and 0.15 percent of the total heat of each experiment, were applied.

After conversion to a molal basis, the difference between the mean measured heat for the empty container and that for the container with sample is recorded in column 5, taking 100.20 as the molecular weight of *n*-heptane. This difference would be the enthalpy change if the vapor pressure were negligible. Actually, to get the true enthalpy change of the liquid alone, this difference was corrected by an equation given by Osborne [12], modified by substitution from the exact Clapeyron equation for the heat of vaporization. This equation may be written

$$H_0^t = [Q]_0^t - [q]_0^t + M[PV/m]_0^t - M\left\{ \left( \frac{V}{m} \right) - v \right\} T dP/dT \Big|_0^t \quad (4)$$

where  $H_0^t$  is the enthalpy increase from 0° to  $t^\circ$  C per mole of the "saturated" liquid (i. e., maintained at its corresponding vapor pressure  $P$  at each temperature);  $[Q]_0^t$  is the heat evolved, per mole of

<sup>5</sup> This factor, differing slightly from the previously published [10] value of 270.46<sup>7</sup> was arrived at by a correction of the circuit constants applicable in all the numerous calibration experiments.

TABLE 4. Experimental results with the furnace and ice calorimeter

1 Furnace temperature, $t$	2 Mass of $n\text{-C}_7\text{H}_{16}$ sample	3 Measured heat			4 Corrections			5 Heat change of saturated liquid $n\text{-C}_7\text{H}_{16}$ , 0° to $t^\circ$ C					
		6 With $n\text{-C}_7\text{H}_{16}$	7 Empty container	8 Net for $n\text{-C}_7\text{H}_{16}$	9 $M \left[ P \frac{V}{m} \right]_0^t$	10 $-M \left[ \left( \frac{V}{m} - v \right) T \frac{dP}{dT} \right]_0^t$	11 $-M \int_0^t v \frac{dP}{dT} dt$	12 Observed		13 Calculated from eq (7)	14 Observed minus calculated		
								15 Individual sample	16 Mean for this temperature				
$^\circ\text{C}$	$g$	$abs\ j$	$abs\ j$	$abs\ j\ mole^{-1}$	$abs\ j\ mole^{-1}$	$abs\ j\ mole^{-1}$	$abs\ j\ mole^{-1}$	$abs\ j\ mole^{-1}$	$abs\ j\ mole^{-1}$	$abs\ j\ mole^{-1}$	$abs\ j\ mole^{-1}$	$abs\ j\ mole^{-1}$	
50.00	3.7679	689.7 686.7 692.6 687.6 686.9	264.2	11,289	+5	-30	-3	11,261	11,261	11,250	+11		
100.00	3.7679	1,424.2 1,424.9 1,423.3 2,214.9	534.4	23,661	+30	-139	-17	23,535	23,535	23,522	+13		
150.00	3.7679	2,212.4 2,213.3 2,213.3	809.7	37,330	+107	-368	-62	37,007	37,001	36,989	+12		
	1.1721	1,266.1 1,269.3 1,270.0 1,268.3 3,059.9	809.7	39,214	+343	-2,530	-62	36,965					
200.00	3.7679	3,059.7 3,059.9 1,754.3	1,089.3	52,402	+281	-678	-178	51,827	51,830	51,844	-14		
	1.1721	1,757.1 1,755.2 3,361.0	1,089.3	56,954	+903	-5,735	-178	51,944					
230.00	3.3623	3,360.8 3,355.3 3,359.7 3,980.8 3,975.9	1,259.1	62,586	+514	-1,206	-309	61,585	61,585	61,588	-3		
250.00	3.7679	3,975.0 3,975.8 3,977.3 3,712.1	1,372.8	69,251	+620	-576	-442	68,853	68,801	68,796	+5		
	3.3623	3,708.8 3,712.8 3,707.6 2,288.6	1,372.8	69,658	+695	-1,146	-442	68,765					
	1.1721	2,285.8 2,289.0 2,287.5	1,372.8	78,210	+1,994	-11,041	-442	68,721					

liquid and vapor, in cooling from  $t^\circ$  to  $0^\circ$  the closed container filled with the liquid and vapor maintained in equilibrium;  $[q]_0^t$  is the contribution to  $[Q]_0^t$  made by the empty container, shields, and suspension wire (per mole of liquid and vapor);  $M$  is the molecular weight of the liquid;  $V$  is the volume of the container;  $m$  is the total mass of liquid and vapor;  $v$  is the specific volume of the saturated liquid;  $T$  is the absolute temperature; and the superscript  $t$  and the subscript 0 denote the value at  $t^\circ$  minus that at  $0^\circ$  C.

The enthalpy of the liquid at each furnace temperature relative to that at  $0^\circ$  C was further converted to the heat change of the saturated liquid alone, between the same two temperatures, by use of the thermodynamic relation

$$\int_0^t C_{\text{sat.}} dt = H_0^t - M \int_0^t v(dP/dT) dt, \quad (5)$$

where  $C_{\text{sat.}}$  is the heat capacity of the saturated liquid. The resulting values are recorded in column 9, and their means in column 10, of table 4. In arriving at these from the values of net heat delivered by the whole sample and recorded in column 5, the employed values of the three separate correction terms indicated by eq (4) and (5) are those listed in columns 6, 7, and 8. These various quantities are all given per mole of sample in order that the magnitudes of the corrections relative to the final heat values may be noted, especially to permit an estimate of the relative seriousness of uncertainties in them. It will be noticed that the second correction,  $-M\{(V/m)-v\}TdP/dT|_0^t$ , whose numerical magnitude equals the heat evolved in the condensation of vapor as the temperature changes from  $t^\circ$  to  $0^\circ$  C, is enormously larger for a given furnace temperature in the case of the smallest mass of sample. This is so, partly because the total number of moles of sample is smaller and partly because the fraction of the total container volume not occupied by liquid and hence available to hold vapor is many times greater.

The internal volume,  $V$ , of the container at room temperature was determined by weighing it filled with water, and, from consideration of the thermal expansion and modulus of elasticity of monel, this volume was assumed to vary almost linearly with temperature from a value of  $10.74 \text{ cm}^3$  at  $0^\circ$  to  $10.87 \text{ cm}^3$  at  $250^\circ$  C. The specific volumes  $v$  of liquid *n*-heptane were obtained by extrapolation of the precise values of Smith, Beattie, and Kay [13], measured at several temperatures between  $30^\circ$  and  $250^\circ$  C and at a number of pressures, to the corresponding vapor pressures. The values of vapor pressure and its temperature derivative used in the corrections were computed from the equation

$$\begin{aligned} \log_{10} P(\text{mm Hg}) = & -22.06549 - 1696.682/T \\ & + 14.72529 \log_{10} T - 0.02811435 T \\ & + 1.53130(10^{-5})T^2, \quad (6) \end{aligned}$$

whose coefficients were determined from the vapor pressures given at the five temperatures  $22.352^\circ$ ,  $98.427^\circ$ ,  $123.41^\circ$  [14],  $267.01^\circ$ , and  $250^\circ$  C [15].

Equation (6) undoubtedly does not represent the vapor pressures below the normal boiling point ( $98.427^\circ$  C) as well as precisely measured values cited later in this paper. However, the present corrections are sufficiently small at these lower temperatures to make these errors of negligible consequence. At  $150^\circ$ ,  $200^\circ$ , and  $250^\circ$  C the present calorimetric measurements cover at least two masses of sample (so-called "high" and "low" fillings) at each temperature, and separate corrections were made for each filling. As an alternative procedure, the thermal data for the two sample masses at a given temperature may be substituted separately into eq (4), with elimination of  $dP/dT$  as the least accurately known auxiliary datum. This was tried, and simultaneous solution of these two equations yielded values of  $dP/dT$ , which agreed within 1 or 2 percent with those calculated from eq (6). However, this alternative procedure of treating the data was not adopted. As the values of  $dP/dT$  calculated from eq (6) were believed to be at least as accurate as those calculated from the thermal data alone, the former were used. This permitted the calculation and comparison of separate corrected thermal values from the data on the different sample masses. The mean for each temperature listed in column 10 of table 4 was obtained by applying to the values of column 9 a weighting factor proportional to the sample mass and the number of determinations made on it, and inversely proportional to the average deviation of single measurements from the mean for the set.

### 3.3. Formulated Heat Capacity Based on High-Temperature Results

Undoubtedly the most accurate measurements available of the heat capacity of liquid *n*-heptane between  $280^\circ$  and  $358^\circ$  K are those made at the Bureau by Osborne and Ginnings in 1941, and Osborne, Stimson, and Ginnings in 1939 [7]. The 1939 values were determined in the same large adiabatic calorimeter that had been used in precise measurements on water [9]. The 1941 results, on a different sample, were obtained using a different smaller adiabatic calorimeter. Osborne and Ginnings [7] gave a quadratic function of temperature to represent the 1939 values of the heat capacity ( $C_{\text{sat.}}$ ) from  $280^\circ$  to  $358^\circ$  K. The average deviation of the 1939 observed values from that equation is 0.028 percent, whereas the average deviation of the 1941 observed values from the same equation is 0.037 percent.

Because the present authors wish to give what they believe to be the best values available, they express the heat capacity of the liquid above  $273^\circ$



K by an equation based from 273° to 358° K on only the foregoing adiabatic-calorimeter values of the Bureau, and based above 358° K on only the ice-calorimeter values. This equation, in integrated form and in terms of abs j mole<sup>-1</sup> at T° K, is

$$\int_{273.16}^T C_{\text{sat.}} dt = -50907 + 173.7329T - 0.015729T^2 + 2.2685(10^{-4})T^3 + 10,973(10^{-0.3\sqrt{540.17-T}}). \quad (7)$$

The first four terms are equivalent to the equation of Osborne and Ginnings; the last term, which contributes no more than 0.01 percent below 358° K, was derived by least squares to fit the ice-calorimeter observed values at 423° K (150° C) and above. Values given by this equation are listed in column 11 of table 4. The discrepancies in the results observed with the ice-calorimeter, which are listed in column 12, are within the precision of these measurements.

Postponing until section 4.1 an inclusion of the measurements reported in section 2, the heat capacity from 273° to 523° K can be obtained by differentiation of eq (7) (abs j mole<sup>-1</sup> deg K<sup>-1</sup>):

$$C_{\text{sat.}} = 173.733 - 0.031458T + 6.8055(10^{-4})T^2 + 3,790(540.17 - T)^{-1}(10^{-0.3\sqrt{540.17-T}}). \quad (8)$$

As the constant 540.17° K in eq (7) and (8) is the critical temperature of *n*-heptane [15], this formulation gives at that temperature a finite value of the enthalpy, but the heat capacity  $C_{\text{sat.}}$  and  $dH_{\text{sat.}}/dT$  become infinite. As the properties of this form of term are believed to hold for all ordinary liquids, the form of the exponential term was in fact selected to possess these trends; although as the temperature exceeds that of the range of the thermal measurements and approaches the critical, the actual values given by eq (7) and (8) rapidly become of little reliability.

### 3.4. Reliability of High-Temperature Results

Evidence as to the probable accuracy of the heat-capacity values given by eq (8) can be obtained from three sources: (a) the reproducibility or precision of the measurements, (b) an examination of the likely systematic errors, and (c) the agreement among the various values of the more precise observers in the temperature regions of overlap.

Considering the precision of the mean heat capacities as determined by heat measurements at intervals of 50 deg, the probable error of the unsmoothed values, determined by measurement with the ice calorimeter of the empty container and of the container with sample, averaged  $\pm 0.2$  percent below 100° C and  $\pm 0.15$  percent above 100° C. The subsequent smoothing of these results with respect

to temperature, which may be considered to have altered the individual unsmoothed heat capacities by amounts averaging 0.2 percent, would normally be expected to increase somewhat the reliability of as smooth a function with temperature as the heat capacity of a liquid.

Various sources of systematic error with the ice calorimeter were examined. Errors may have occurred in temperature measurement, in mass of *n*-heptane, and in the calibration factor of the calorimeter. Also, the heat lost during the drop from the furnace may have been slightly different between runs with the empty container and those with the container plus sample. However, no one of these factors is believed to have contributed to the heat capacity and error of more than  $\pm 0.02$  or  $\pm 0.03$  percent. As for the correction of 0.1 to 0.15 percent necessitated by the assumed presence of air inside the container in one series, this is somewhat uncertain only because the specific heats of air and *n*-heptane are considerably different, for the sum of the masses of the two substances was accurately known. Over-all checks on the accuracy of the ice calorimeter have been described previously [11]. These check runs for the average heat capacity of water between 0° and 25° C, and between 0° and 250° C, gave values lower by only  $0.05 \pm 0.14$  percent and  $0.02 \pm 0.02$  percent, respectively, than earlier precise results with an adiabatic calorimeter [9].

The corrections given by eq (4) and (5) become larger, and, no doubt caused a greater source of error, the higher the temperature. The most uncertain quantity in these corrections is probably  $dP/dT$ . One approach is to investigate the effects of making such changes in this factor in order that the observed mean corrected heat changes of liquid *n*-heptane become identical at each furnace temperature for the series with large and small sample masses. It can be found readily from table 4 that the heat capacity above 400° K would in this way be changed by amounts up to 0.3 percent.

In addition to the foregoing considerations, it can be seen from figure 4 that the heat-capacity values of Osborne and Ginnings, who claimed an accuracy of  $\pm 0.1$  percent and on whose values eq (8) depends almost entirely up to 370° K, do not differ from those of the other investigations by more than 0.2 percent. Some consideration must be given to the deviations below 370° K of the ice-calorimeter values from those of the other investigations, as eq (8) depends almost entirely on the former above 370° K.

Considering these various data on reliability, the estimated accuracy of eq (8) may be considered to correspond to a probable error of  $\pm 0.1$  percent between 280° and 360° K and increasing to  $\pm 0.5$  percent at 500° K. Above the last temperature the uncertainty must be considered still greater in view of the added uncertainty of the course of the heat-capacity curve near the end of the region of measurement.

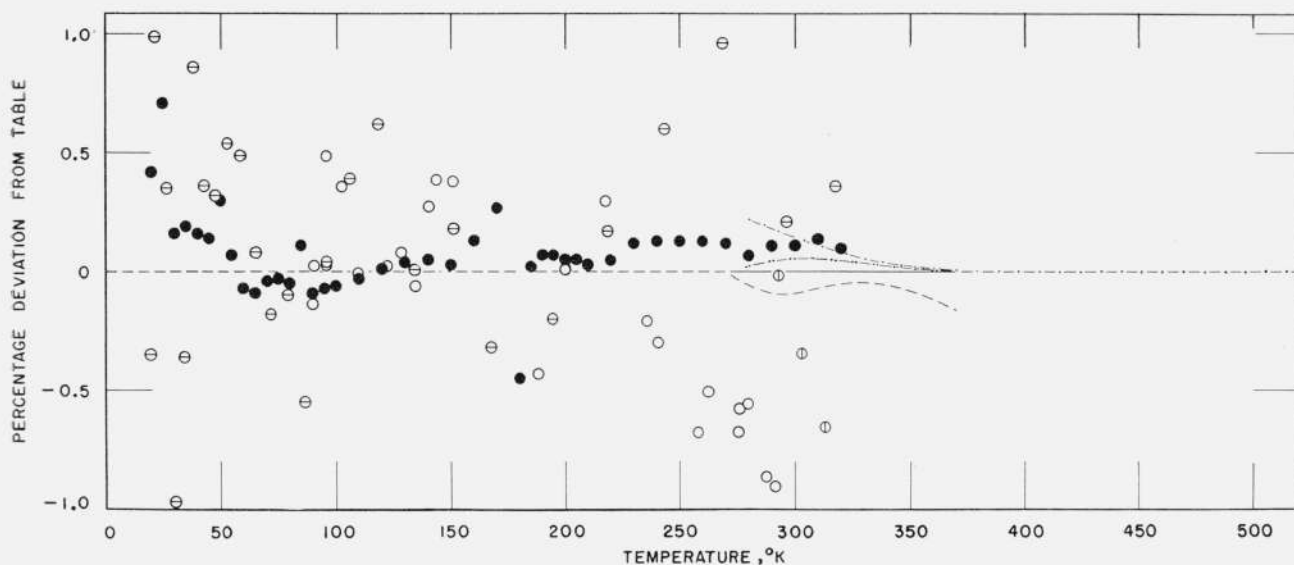


FIGURE 4. Comparison of the heat capacities by various observers with the final values in table 4.

. . . Osborne and Ginnings [7]      ● H. L. Finke, M. E. Gross, and J. F. Messerly [20]  
 - - - Ice calorimeter                ○ K. S. Pitzer [18]  
 ——— Adiabatic calorimeter      ○ G. S. Parks, H. M. Huffman, and S. B. Thomas [17]  
    ○ W. T. Richards and J. H. Wallace [19]

## 4. Derived Thermal Properties of Crystalline and Liquid *n*-Heptane

### 4.1. Tabulated Heat Capacities

In the temperature range 280° to 360° K, three series of heat-capacity values of liquid *n*-heptane measured at the Bureau are available; those obtained with the adiabatic calorimeter that was employed down to 20° K (section 2), those obtained with the ice calorimeter (section 3), and those with two other adiabatic calorimeters (Osborne and Ginnings [7]). Of these three sets of values, the first are consistently the lowest and the second are consistently the highest, the differences being smaller than the estimates of absolute error claimed with the two methods. The "final" tabulated values from these three series of data are given in table 5. These values were arrived at with the following considerations. The values of Osborne and Ginnings (including those of Osborne, Stinson, and Ginnings) are considered the most accurate. The ice-calorimeter method gives less accurate heat capacities as the temperature approaches 273° K, the end of its working range, where the derivative with temperature becomes indeterminate. The shield control in the adiabatic calorimeter becomes a little unwieldy at higher temperatures, and at the same time heat transfer by radiation can be significant if any unknown thermal gradients exist in the calorimeter. From 280° to 360° K the values of Osborne and Ginnings were given greatest weight, with the results of the adiabatic calorimeter used in the present investigation being given increasing weight with

decreasing temperature varying from none at 360° K to about half as much as those of Osborne and Ginnings at temperatures just above 280°, to full weight at and below 270° K. The ice-calorimeter values were given no weight below 350° K but increasing weight above this temperature and full weight where extrapolation of the equation of Osborne and Ginnings is no longer reliable, as discussed earlier in connection with the derivation of eq (8).

Several additional investigators have measured the heat capacity of solid and liquid *n*-heptane. With the exception of the results of the Petroleum Experiment Station, U. S. Bureau of Mines, there are the following other less precise determinations. Williams and Daniels [16] used an adiabatic calorimeter from 310° to 350° K. Parks, Huffman, and Thomas [17], using an aneroid calorimeter, covered the temperature range from 90° to 299° K. Pitzer's [18] heat capacities were measured at approximately 15° to 318° K; and Richards and Wallace [19] determined the heat capacity from 293° to 313° K from the adiabatic temperature-pressure coefficient. No heat-capacity measurements on the liquid above 358° K, other than those reported in this paper, were found.

A comparison of the results of the various investigations with the adjusted "final" values of table 5 is given in figure 4. Included also in the figure are recent precise values determined on a Calorimetry Conference sample of *n*-heptane in an adiabatic calorimeter by the Petroleum Experiment Station, U. S. Bureau of Mines, Bartlesville, Okla. [20] These values show excellent agreement with those of the present authors.

TABLE 5. Heat capacity, enthalpy, entropy, and free energy of crystalline and liquid *n*-heptane at saturation pressures

<i>T</i>	<i>C</i> <sub>sat.</sub>	( <i>H</i> <sub>sat.</sub> - <i>E</i> <sub>0</sub> <sup>c</sup> )	( <i>S</i> <sub>sat.</sub> - <i>S</i> <sub>0</sub> <sup>c</sup> )	-( <i>F</i> <sub>sat.</sub> - <i>E</i> <sub>0</sub> <sup>c</sup> )
CRYSTALLINE				
° K	abs j deg <sup>-1</sup> mole <sup>-1</sup>	abs j mole <sup>-1</sup>	abs j deg <sup>-1</sup> mole <sup>-1</sup>	abs j mole <sup>-1</sup>
0	0	0	0	0
5	0.222	0.277	0.074	0.092
10	1.770	4.431	0.591	1.478
15	5.718	22.06	1.967	7.445
20	11.80	65.25	4.410	22.95
25	18.30	140.4	7.737	53.01
30	25.08	248.8	11.67	101.3
35	31.82	391.1	16.05	170.4
40	38.17	566.2	20.71	262.3
45	44.17	772.2	25.56	377.9
50	49.84	1,007.3	30.51	518.0
55	55.27	1,270.2	35.52	683.1
60	60.48	1,559.7	40.55	873.2
65	65.37	1,874.4	45.59	1,088.6
70	69.83	2,212.6	50.60	1,329.1
75	74.09	2,572.4	55.56	1,594.5
80	78.28	2,953.4	60.48	1,884.6
85	82.21	3,354.7	65.34	2,199.1
90	86.03	3,775.4	70.15	2,537.9
95	89.44	4,214.2	74.89	2,900.5
100	92.77	4,669.7	79.56	3,286.7
105	95.98	5,141.6	84.17	3,696.0
110	99.12	5,629.4	88.71	4,128.3
115	102.19	6,132.7	93.18	4,583.0
120	105.20	6,651.2	97.59	5,060.0
125	108.17	7,184.6	101.95	5,558.8
130	111.10	7,732.8	106.25	6,079.4
135	113.99	8,295.5	110.50	6,621.2
140	116.83	8,872.6	114.69	7,184.2
145	119.73	9,464.0	118.84	7,768.1
150	122.72	10,070	122.95	8,372.6
155	125.78	10,691	127.02	8,997.5
160	129.03	11,328	131.07	9,642.8
165	132.46	11,982	135.09	10,308
170	136.03	12,653	139.10	10,994
175	139.82	13,342	143.09	11,699
180	145.13	14,054	147.10	12,425
182.562	* 148.58	14,430	149.18	12,804
LIQUID				
182.562	* 203.15	28,452	225.98	12,804
185	202.58	28,946	228.67	13,358
190	201.86	29,957	234.06	14,515
195	201.45	30,965	239.30	15,699
200	201.31	31,972	244.40	16,908
205	201.39	32,979	249.37	18,142
210	201.68	33,986	254.23	19,402
215	202.13	34,996	258.98	20,685
220	202.74	36,008	263.63	21,991
225	203.47	37,024	268.20	23,321
230	204.36	38,043	272.68	24,673
235	205.37	39,067	277.08	26,048
240	206.47	40,097	281.42	27,444
245	207.64	41,132	285.69	28,862
250	208.93	42,174	289.90	30,301
255	210.30	43,222	294.05	31,760
260	211.73	44,277	298.15	33,241
265	213.23	45,339	302.19	34,742
270	214.81	46,409	306.19	36,263
275	216.51	47,487	310.15	37,804
280	218.23	48,574	314.07	39,364
285	219.97	49,670	317.94	40,944
290	221.75	50,774	321.78	42,543
295	223.57	51,888	325.59	44,161
298.16	224.74	52,996	327.95	45,195
300	225.44	53,010	329.37	45,801
310	229.27	55,285	336.82	49,129
320	233.25	57,598	344.16	52,533
330	237.38	59,952	351.41	56,013
340	241.67	62,349	358.56	59,561

TABLE 5. Heat capacity, enthalpy, entropy, and free energy of crystalline and liquid *n*-heptane at saturation pressures—Con.

<i>T</i>	<i>C</i> <sub>sat.</sub>	( <i>H</i> <sub>sat.</sub> - <i>E</i> <sub>0</sub> <sup>c</sup> )	( <i>S</i> <sub>sat.</sub> - <i>S</i> <sub>0</sub> <sup>c</sup> )	-( <i>F</i> <sub>sat.</sub> - <i>E</i> <sub>0</sub> <sup>c</sup> )
LIQUID—Continued				
° K	abs j deg <sup>-1</sup> mole <sup>-1</sup>	abs j mole <sup>-1</sup>	abs j deg <sup>-1</sup> mole <sup>-1</sup>	abs j mole <sup>-1</sup>
350	246.09	64,790	365.63	63,180
360	250.63	67,276	372.62	66,867
370	255.30	69,810	379.55	70,624
380	260.10	72,392	386.42	74,448
390	265.04	75,024	393.24	78,340
400	270.13	77,708	400.02	82,300
410	275.36	80,445	406.75	86,323
420	280.75	83,238	413.45	90,411
430	286.30	86,088	420.12	94,564
440	292.02	88,998	426.77	98,781
450	297.95	91,969	433.40	103,061
460	304.14	95,005	440.01	107,400
470	310.67	98,109	446.62	111,802
480	317.73	101,286	453.24	116,269
490	325.74	104,544	459.87	120,792
500	335.65	107,898	466.54	125,372
510	350.24	111,379	473.32	130,014
520	379.36	115,073	480.36	134,714

\* Extrapolated.

## 4.2. Enthalpy, Entropy, and Gibbs Free Energy

In table 5, columns 3, 4, and 5, the values of relative enthalpy, entropy, and relative Gibbs free energy of crystalline and liquid *n*-heptane are tabulated at saturation pressures and at round temperatures from 0° to 520° K. For most purposes intermediate values can be obtained by linear interpolation or more accurately by quadratic interpolation. These properties were obtained by evaluating the thermodynamic relations

$$H_{\text{sat.}} - E_0^c = \int_0^T C_{\text{sat.}} dT + L_f + \int_0^T V_{\text{sat.}} (dP/dT) dT; \quad (9)$$

$$(S_{\text{sat.}} - S_0^c) = \int_0^T (C_{\text{sat.}}/T) dT + L_f/T_i; \quad (10)$$

$$-(F_{\text{sat.}} - E_0^c) = TS_{\text{sat.}} - (H_{\text{sat.}} - E_0^c). \quad (11)$$

*E*<sub>0</sub><sup>c</sup> is the internal energy of crystalline *n*-heptane at 0° K, and *T*<sub>i</sub> is the absolute temperature of the triple-point. The entropy of crystalline *n*-heptane is assumed to be zero at 0° K. The terms containing *L*<sub>f</sub>, the heat of fusion, are obviously to be omitted below the triple point.

Below 20° K the above three equations were evaluated analytically, using the Debye heat-capacity function. Between 20° and 270° K the evaluation was by tabular integration, using Lagrangian four-point integration coefficients [21]. No attempt was made to fit the tabulated values of these properties between 20° and 270° K to equations. Between 270° and 520° K the evaluations were carried out analytically by using for the heat capacity eq (8), making in

the enthalpy, entropy, and free energy the proper small adjustments graphically arrived at by use of the differences between the tabulated heat capacities and those represented by eq (8) in the temperature range from 270° to 370° K.

Because of its small magnitude the term  $\int_0^T V_{\text{sat.}} (dP/dT) dT$  was not applied up to 255° K. Above 273.16° K the following empirical equation (in terms of abs j per mole) was used:

$$\log_{10} \int_{273.16}^T v (dP/dT) dT = 0.0074729T - 1.2633 - 7.049 (10^{-8}) (540.17 - T)^3, \quad (12)$$

in each case, of course, adding the value of the integral from 0° to 273.16° K. This equation reproduces the values directly calculated from the data within 2 j per mole. In the substitution of eq (8) into eq (10) to evaluate the greater part of each entropy value above 270° K, the exponential term was replaced according to the following identity:

$$\begin{aligned} & \int (3,790/T) (540.17 - T)^{-\frac{1}{2}} (10^{-0.3\sqrt{540.17-T}}) dT \\ & \equiv 21.102 (10^{-0.3\sqrt{540.17-T}}) + \int 3,790 (1/T - 1/520) \\ & \quad \times (540.17 - T)^{-\frac{1}{2}} (10^{-0.3\sqrt{540.17-T}}) dT. \quad (13) \end{aligned}$$

In this way the part requiring graphical integration was reduced to the last term of eq (13), which is very small at all the temperatures involved.

## 5. Derived Thermal Properties of Gaseous *n*-Heptane

### 5.1. Equation of State

A number of observers<sup>6</sup> have measured the heat of vaporization of *n*-heptane at various temperatures. For the comparison of these values, an equation of state of the real gas is needed. At low pressures the form involving so-called virial coefficients no higher than the second (*B*) may be used,

$$PV = RT + BP, \quad (14)$$

where *B*, which is assumed to be approximately independent of pressure, may be taken to have a temperature dependence of the form [22]

$$B = b - ce^{a/T}, \quad (15)$$

*a*, *b*, and *c* being empirical constants.

Waddington, Todd, and Huffman [23] have made precise measurements, in a flow calorimeter, of the heat capacity of *n*-heptane vapor at different pressures below 1 atm and at temperatures from 357° to 466° K. On the basis of eq (14) and (15), the vari-

ation of heat capacity with pressure is given by the relation

$$(\partial C_p / \partial P)_T = c(a^2/T^3 + 2a/T^2)e^{a/T}. \quad (16)$$

The best approximation arrived at to a fit of their data to eq (16) [24] gave *a* = 1,400° K and *c* = 18.71 cm<sup>3</sup> mole<sup>-1</sup>. The agreement is shown in table 6. Equation (15) now becomes (in cm<sup>3</sup> mole<sup>-1</sup>)

$$B = b - 18.71e^{1,400/T}. \quad (17)$$

TABLE 6. Variation of heat capacity of *n*-heptane gas with pressure

Temperature	$(\partial C_p / \partial P)_T$	
	Observed	Calculated (eq 15, 16, 17)
° K	abs j deg <sup>-1</sup> atm <sup>-1</sup> mole <sup>-1</sup>	abs j deg <sup>-1</sup> atm <sup>-1</sup> mole <sup>-1</sup>
357.10	6.07	6.21
373.15	4.81	4.67
400.40	2.97	3.00
434.35	1.88	1.84
466.10	1.13	1.23

The constant *b* in eq (17) was evaluated by calculating values of *B* from the exact equation

$$B = [L_v/T(dP/dT)] - RT/P + V_l, \quad (18)$$

obtained by substituting eq (14) into the Clapeyron equation. The molal volume of the liquid *V<sub>l</sub>*, at the vapor pressure *P*, was interpolated from the values of Smith, Beattie, and Kay [13]. The necessary values of vapor pressure and its temperature derivative were computed from the equation (with *P* in atmospheres and *t* in degrees C) [14]

$$\log_{10} P = 4.02159 - 1,268.115/(t + 216.900), \quad (19)$$

which appears to be based on precise measurements from 299° to 372° K at the Bureau [25]. Table 7 lists the employed observed values of *L<sub>v</sub>*, the heat of vaporization, as well as the resulting values of *b* obtained by use of eq (17), (18), and (19).

TABLE 7. Observed heats of vaporization, and values of the second virial coefficient of *n*-heptane calculated from heat-of-vaporization and vapor-pressure data

Temperature	Heat of vaporization			<i>b</i> (from eq 17, 18, and 19)
	Mean observed value	Number of measurements	Reference	
° K	abs j mole <sup>-1</sup>			cm <sup>3</sup> mole <sup>-1</sup>
288.16	37,164	1	[7]	-3,138
298.16	36,547 ± 2	8	[7]	-1,511
308.16	35,941	1	[7]	-904
331.22	34,493 ± 8	4	[23]	-776
350.49	33,213 ± 21	3	[23]	-534
363.64	32,280 ± 8	3	[23]	-855
370.39	32,009 ± 17	8	[26]	-648
371.51	32,030 ± 85	2	[18]	-537

<sup>6</sup>See table 7.

At small vapor pressures this method of determining the second virial coefficient becomes much less accurate owing to the large magnitudes of the first two terms in the second member of eq (18) and the ordinarily smaller percentage accuracy of low vapor pressures. Assigning to each value of the last column of table 7 a weight inversely proportional to the standard deviation <sup>7</sup> as determined statistically from the factors in eq (18), and directly proportional to the square root of the number of determinations of the heat of vaporization at that temperature, a mean value of  $-776 \text{ cm}^3 \text{ mole}^{-1}$  was found for  $b$ . The final equation for the second virial coefficient thus becomes (in  $\text{cm}^3 \text{ mole}^{-1}$ )

$$B = -776 - 18.71e^{1.400/T} \quad (20)$$

Smith, Beattie, and Kay [13] measured the densities of *n*-heptane gas at temperatures of  $548^\circ$ ,  $573^\circ$ ,  $598^\circ$ , and  $623^\circ \text{ K}$  and at densities of from 1 to 5 moles per liter (pressures above 25 atm). Hirschfelder, McClure, and Weeks [22] extrapolated these data to zero pressure and gave the equation of state (in  $\text{cm}^3 \text{ mole}^{-1}$ )

$$B = 749 - 418.69e^{629/T} \quad (21)$$

A comparison of the values of the second virial coefficient at several temperatures as calculated by eq (20) and (21) is afforded by table 8. Considering the widely different temperatures and pressures under which the data determining the two equations were measured, the agreement at the lower temperatures is good. At the higher temperatures eq (21) undoubtedly gives much better values. However, the constants of eq (21) in eq (16) give very poor agreement with the observed variation of heat capacity with pressure below  $400^\circ \text{ K}$ , the disagreement being decidedly outside the experimental error. It seems likely that at the lower temperatures eq (20) is considerably more reliable, not only because the use of eq (21) would involve extrapolation over wide temperature and pressure ranges from those in which the supporting *PVT* data were measured, but also

TABLE 8. Second virial coefficient of *n*-heptane gas calculated from eq (20) and (21)

Temperature	<i>B</i>	
	Calculated from eq (20)	Calculated from eq (21)
$^\circ \text{K}$	$\text{cm}^3 \text{ mole}^{-1}$	$\text{cm}^3 \text{ mole}^{-1}$
300	-2,765	-2,659
350	-1,797	-1,777
400	-1,395	-1,268
500	-1,196	-945
550	-1,083	-724
600	-1,014	-565
650	-969	-445
	-937	-353

<sup>7</sup> It was subsequently pointed out to the authors that the square of the standard deviation should have been used in arriving at the weighting factors. The resulting value of  $b$  would then have been  $-789 \text{ cm}^3 \text{ mole}^{-1}$ , with which the value actually used agrees well within its uncertainty.

because of the likely appreciable variation with temperature of the "constants" of eq (15), as pointed out by Hirschfelder, McClure, and Weeks [22].

## 5.2. Heat Capacity

Waddington, Todd, and Huffman [23] extrapolated their values of the heat capacity of the gas ( $357^\circ$  to  $466^\circ \text{ K}$ ) to zero pressure. Their equation, when converted to  $\text{abs j deg}^{-1} \text{ mole}^{-1}$  (taking  $1 \text{ cal} = 4.1840 \text{ abs j}$ ) and expressed as a function of the absolute temperature, is

$$C_p^\circ = -0.987 + 0.62191T - 2.3256(10^{-4})T^2 \quad (22)$$

All their experimentally derived points are fitted by this equation to  $\pm 0.05$  percent, the precision of the measurements themselves being given as  $\pm 0.1$  percent.

In order to compare the values of heat of vaporization in table 7 at some one temperature, it is desirable to have heat capacities of the gas between  $288^\circ$  and  $357^\circ \text{ K}$  as well. The use of eq (22) extrapolated over this temperature region was found to lead to vapor-pressure-temperature coefficients between  $298^\circ$  and  $370^\circ \text{ K}$  that are rather consistently about 0.4 percent less than indicated by eq (19). As the latter equation is thought to be considerably more accurate than this, much better agreement with it was secured by assuming slightly higher heat-capacity values below  $370^\circ \text{ K}$  than given by eq (22). The equation adopted between  $288^\circ$  and  $370^\circ \text{ K}$  (in  $\text{abs j deg}^{-1} \text{ mole}^{-1}$ ) is

$$C_p^\circ = 197.28 + 0.4498(T - 370) \quad (23)$$

This gives the same value at  $370^\circ \text{ K}$  as eq (22), but eliminates the small curvature of that equation by assuming as a constant temperature coefficient that of eq (22) at  $370^\circ \text{ K}$ .

## 5.3. Standard Enthalpy and Entropy at $298.16^\circ \text{ K}$

In preparation for calculating the thermal properties of gaseous *n*-heptane at various temperatures in its hypothetical standard state (the ideal gas at a pressure of 1 atm), the values of enthalpy and entropy at some one temperature, relative to the crystalline solid at  $0^\circ \text{ K}$ , may now be calculated from the values for the liquid at this same temperature, the heat of vaporization, and the equation of state.

From considerations of both the accuracy and the precision of the values of heats of vaporization in table 7, the most reliable value is probably that of Osborne and Ginnings measured at  $298.16^\circ \text{ K}$ . They claimed an accuracy of  $\pm 0.1$  percent. A direct comparison of the other seven values in the table with this value was made after calculating from each of them the heat of vaporization at  $298.16^\circ \text{ K}$  by means of the following steps:

(a) Saturated liquid at  $298.16^\circ \text{ K} \rightarrow$  saturated liquid at  $T$ .

- (b) Saturated liquid at  $T \rightarrow$  saturated gas at  $T$ .  
 (c) Saturated gas at  $T \rightarrow$  gas at  $T$ , zero pressure.  
 (d) Gas at  $T$ , zero pressure  $\rightarrow$  gas at  $298.16^\circ \text{K}$ , zero pressure.  
 (e) Gas at  $298.16^\circ \text{K}$ , zero pressure  $\rightarrow$  saturated gas at  $298.16^\circ \text{K}$ .

The enthalpy change of step (a) was obtained from table 5. That of step (b) is the heat of vaporization measured at  $T$ , and that of step (d) was calculated from eq (23). The enthalpy changes of steps (c) and (e) were found after substitution of eq (19) and (20) into the thermodynamic relation

$$\int_0^P dH = (B - TdB/dT)P. \quad (24)$$

The resulting values are given in table 9. The deviations, also listed, are within the uncertainties claimed by the various investigators.

TABLE 9. Comparison of experimental values of heats of vaporization of *n*-heptane extrapolated to  $298.16^\circ \text{K}$

Temperature of measurement	Experimental heat of vaporization from table 7 corrected to $298.16^\circ \text{K}$	Deviation from value measured at $298.16^\circ \text{K}$
$^\circ \text{K}$	<i>abs j mole<sup>-1</sup></i>	<i>%</i>
288.16	36,541	-0.02
298.16	36,547	.00
308.16	36,562	+0.04
331.22	36,555	+0.02
350.49	36,504	-0.12
363.64	36,432	-0.32
376.39	36,612	+0.18
371.51	36,728	+0.50

The enthalpy of the saturated liquid at  $298.16^\circ \text{K}$  (relative to the crystalline form at  $0^\circ \text{K}$ ), from table 5, is  $52,596 \text{ abs j mole}^{-1}$ . The value  $36,547 \text{ abs j mole}^{-1}$  was adopted as the heat of vaporization, and the increase in the enthalpy in converting the saturated vapor to zero pressure was calculated from eq (19), (20), and (24) to be  $76 \text{ abs j mole}^{-1}$ . Hence, the enthalpy of the ideal gas at  $298.16^\circ \text{K}$ , relative to the crystalline form at  $0^\circ \text{K}$ , is  $89,219 \text{ abs j mole}^{-1}$ .

The absolute entropy of the saturated liquid at  $298.16^\circ \text{K}$ , from table 5, is  $327.98 \text{ abs j deg}^{-1} \text{ mole}^{-1}$ . From the adopted value for the heat of vaporization the entropy of vaporization is  $122.57 \text{ abs j deg}^{-1} \text{ mole}^{-1}$ . The entropy of the ideal gas at 1-atm pressure is less than that of the saturated vapor at the same temperature by  $-R \ln P - PdB/dT$ , where  $R$  is the gas constant, and  $P$  is the vapor pressure in atmospheres.  $dB/dT$  was evaluated from eq (20), and for the vapor pressure a value 0.15 percent higher than given by eq (19) was used, in order to secure better agreement between that equation and vapor pressures calculated from the thermal functions near the normal boiling point ( $372^\circ \text{K}$ ), where eq (19) is probably more accurate. The last correction to the standard state thus becomes  $-23.16 \text{ abs j deg}^{-1} \text{ mole}^{-1}$ , giving for the standard entropy of the gas at  $298.16^\circ \text{K}$  the value  $427.39 \text{ abs j deg}^{-1} \text{ mole}^{-1}$ .

## 5.4. Enthalpy, Entropy, and Gibbs Free Energy

In column 2 of table 10 are tabulated the values of heat capacity of *n*-heptane in the ideal-gas state calculated over the range  $298.16^\circ$  to  $370^\circ \text{K}$  from eq (23) and above  $370^\circ$  from eq (22). In columns 3, 4, and 5 appear the values of relative enthalpy, entropy, and relative Gibbs free energy, respectively, calculated from the equations

$$H^\circ - E_0^\circ = \int C_p^\circ dT; \quad (25)$$

$$S^\circ = \int (C_p^\circ/T) dT; \quad (26)$$

$$-(F^\circ - E_0^\circ) = TS^\circ - (H^\circ - E_0^\circ). \quad (27)$$

For the heat capacity, eq (22) and (23) were substituted over the temperature ranges of applicability indicated above, with determination of the integration constants of eq (25) and (26) from the values at  $298.16^\circ \text{K}$  of enthalpy and entropy, respectively, derived in the preceding section. The values of entropy and free energy are those at the standard pressure, one atmosphere.

## 5.5. Comparison With Observed Vapor Pressures

By equating the Gibbs free energies of saturated liquid and vapor, the thermal functions for the two states may be used to derive values of vapor pressure, which may be compared with the directly determined values. With vapor pressure  $P$  in atmospheres, the resulting equation is

$$RT \ln P = [F_{\text{sat.}}(\text{liq}) - H_0^\circ] - [F^\circ(\text{gas}) - H_0^\circ] - PB. \quad (28)$$

Substituting values of relative free energy from tables 5 and 10 and values of  $B$  from eq (20), eq (28) was solved between  $300^\circ$  and  $370^\circ \text{K}$ , approximately the temperature range of the direct measurements.

TABLE 10. Standard heat capacity, enthalpy, entropy, and free energy of *n*-heptane in the ideal-gas state at 1-atm pressure

$T$	$C_p^\circ$	$(H^\circ - E_0^\circ)$	$(S^\circ - S_0^\circ)$	$-(F^\circ - E_0^\circ)$
$^\circ \text{K}$	<i>abs j deg<sup>-1</sup> mole<sup>-1</sup></i>	<i>abs j mole<sup>-1</sup></i>	<i>abs j deg<sup>-1</sup> mole<sup>-1</sup></i>	<i>abs j mole<sup>-1</sup></i>
298.16	164.97	89,219	427.39	38,213
300	165.80	89,523	428.41	39,000
310	170.29	91,204	433.92	43,312
320	174.79	92,929	439.40	47,679
330	179.29	94,699	444.85	52,100
340	183.79	96,515	450.27	56,576
350	188.29	98,375	455.66	61,105
360	192.78	100,280	461.03	65,689
370	197.28	102,231	466.37	70,326
380	201.76	104,226	471.69	75,016
390	206.19	106,266	476.99	79,759
400	210.57	108,350	482.26	84,556
410	214.90	110,477	487.52	89,404
420	219.19	112,648	492.75	94,306
430	223.43	114,861	497.95	99,259
440	227.63	117,116	503.14	104,265
450	231.78	119,413	508.30	109,322
460	235.88	121,752	513.44	114,431
470	239.94	124,131	518.56	119,591

The deviations from eq (19), which are within 0.1 percent and near 370° K become much smaller, are probably within the accuracy of the directly measured values.

In the derivation of the thermodynamic properties of the gas relative to those of the solid and the liquid, the observed precise vapor pressures were actually used. However, greatest weight was given to the highest observed vapor pressures, those near the normal boiling point. Thus the results are practically the same as if only the normal boiling point had been used, it being necessary to assume at least one vapor pressure value. Consequently, the close agreement between eq (19) and (28), noted above, is essentially a test of the compatibility between the observed thermal properties and the variation with temperature of the observed vapor pressures.

Though eq (28) may be used to calculate from the tabulated thermal properties of this paper reasonably accurate values of vapor pressure from 370° to 470° K as well, these are not listed here. The increasing magnitude of the vapor pressure as the temperature rises rapidly increases the contribution of the last term in eq (28), with the result that the uncertainties in the values of the second virial coefficient rapidly become more important.

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