

## **Molar Heat Capacity at Constant Volume of *n*-Butane at Temperatures from 141 to 342 K and at Pressures to 33 MPa**

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Molar heat capacities at constant volume ( $C_v$ ) for normal butane are presented. Temperatures ranged from 141 to 342 K for pressures up to 33 MPa. Measurements were conducted on liquid in equilibrium with its vapor and on compressed liquid samples. The high purity of the samples was verified by chemical analysis. For the samples, calorimetric results were obtained for two-phase [ $C_v^{(2)}$ ], saturated liquid ( $C_\sigma$  or  $C'_x$ ), and single-phase ( $C_v$ ) molar heat capacities. The principal sources of uncertainty are the temperature rise measurement and the change-of-volume work adjustment. The expanded uncertainty (i.e., a coverage factor  $k=2$  and thus a two-standard deviation estimate) for values of  $C_v$  is estimated to be 0.7%, for  $C_v^{(2)}$  it is 0.5%, and for  $C_\sigma$  it is 0.7%.

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**KEY WORDS:** butane; compressed liquid; density; heat capacity; isochoric; saturated liquid.

### **1. INTRODUCTION**

One of the long-range objectives of thermophysical property research at the National Institute of Standards and Technology (NIST) is the development of accurate predictive methods for calculating the properties of gaseous and liquid mixtures. These models play a key role in process equipment design, in metering applications, and in the design and operation of transportation systems such as pipelines. The ongoing development and testing of these

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models rely heavily on benchmark experimental measurements. These measurements are conducted on selected pure components and their mixtures to provide a database which is representative of broad classes of fluid types.

Normal butane ( $n\text{-C}_4\text{H}_{10}$ ) is a key component of natural gas. Knowledge of the thermophysical properties for the pure components and their mixtures is vital to the development of predictive models for natural gas mixtures. Previously, our group has measured heat capacities for methane [1], ethane [2], propane [3], (methane + ethane) mixtures [4], and (carbon dioxide + ethane) mixtures [5]. The thermodynamic properties and equation of state for  $n$ -butane have been studied by Haynes and Goodwin [6] and Sychev et al. [7]. As pointed out in both references, no published isochoric heat capacity data were available at the time of their work. Together with published density data, heat capacity measurements will provide a database for developing improved equations of state and testing predictive models for  $n$ -butane and mixtures containing this substance.

## 2. MEASUREMENTS

### 2.1. Procedure

The heat-capacity measurements in this study were performed in the calorimeter described by Goodwin [8] and Magee [9]. Briefly, in this method, a sample of well-established mass (or number of moles;  $n$ ) is confined to a bomb of approximately  $73\text{ cm}^3$  volume; as shown in Ref. 9, the exact volume varies with temperature and pressure. When a precisely measured electrical energy ( $Q$ ) is applied, the resulting temperature rise ( $\Delta T = T_2 - T_1$ ) is measured. When both the energy ( $Q_0$ ) required to heat the empty bomb and the  $pV$  work ( $W_{pV}$ ) are subtracted from the total, the heat capacity is

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v \cong \frac{Q - Q_0 - W_{pV}}{n \Delta T} \quad (1)$$

For this study, a sample was charged to the bomb, then the charge valve was sealed. The bomb and its contents were then cooled to the starting temperature. Then, measurements were begun and continued in the single-phase region until either the upper temperature (about 345 K) or the pressure (35 MPa) was obtained. At the completion of a run, some of the sample was discharged to obtain the next filling density. Difference weighings of a discharge cylinder gave the sample masses. A series of such

runs at different densities ( $\rho$ ) completes the  $C_v(\rho, T)$  surface for the substance under study.

Adjustments must be applied to the raw data for the energy required to heat the empty calorimeter from the initial ( $T_1$ ) to the final ( $T_2$ ) temperature. This is accomplished using the results of previous experiments done with a thoroughly evacuated bomb. These results were fitted to a 12-parameter polynomial  $Q_0(T)$  given previously [9].

Additionally, an adjustment for  $pV$  work done by the fluid on the thin-walled bomb as the pressure rises from  $p_1$  to  $p_2$  is applied for each point. Corrections for  $pV$  work on the bomb were calculated by an equation discussed in a previous publication [10] from this laboratory:

$$W_{pV} = \left( T_2 \left( \frac{\partial p}{\partial T} \right)_{v_2} - \frac{\Delta p}{2} \right) \Delta V \quad (2)$$

where  $\Delta p = p_2 - p_1$  is the pressure rise and  $\Delta V = V_2 - V_1$  is the change of volume. The derivative has been calculated with a published equation of state for *n*-butane by Younglove and Ely [11].

## 2.2. Sample

The samples used in the experimental measurements of heat capacity were obtained from a research-grade supply. The purity of the supply has been verified by chemical analysis, establishing the purity to be 0.9999 mol fraction. The supply liquid was stored over molecular sieves to remove trace quantities of  $H_2O$ .

## 3. RESULTS

During the course of these measurements, pressures and temperatures were measured during each drift interval. The range of measured pressures and temperatures is depicted in the shaded area in Fig. 1. The drift interval is a 20-min period which occurs between heating intervals; it begins after thermal equilibrium has been established. In general, the temperature falls with time at a rate of about  $0.5 \times 10^{-3} \text{ K} \cdot \text{min}^{-1}$ , due to small parasitic heat losses, of the order of  $10^{-3} \text{ W}$ . From these pressures and temperatures, we have calculated the densities of the sample confined to the bomb under dynamic equilibrium conditions. In addition, we have devised a control scheme to hold the bomb at a fixed temperature while the equilibrium pressure is measured. We then measured one or more static points on each isochore and calculated the liquid density under static equilibrium.

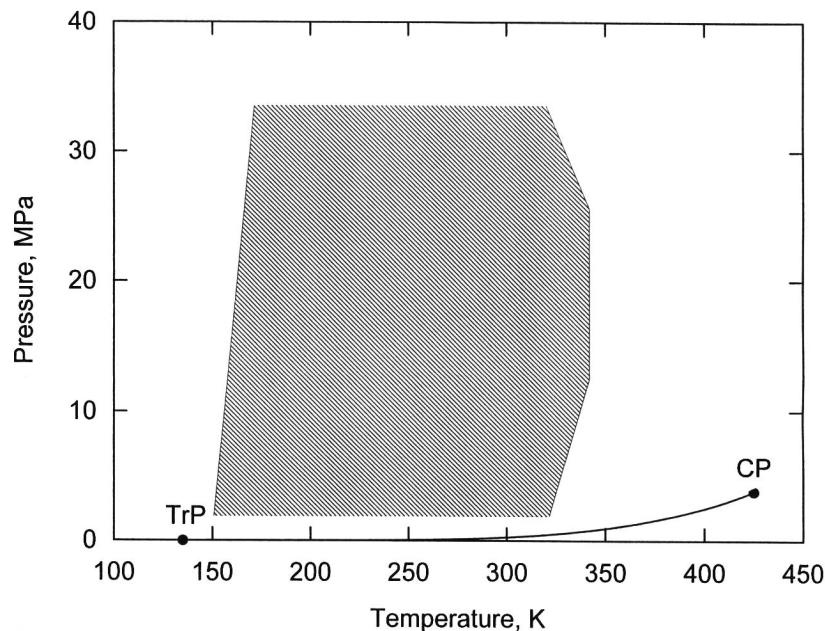


Fig. 1. Range of experimental pressures and temperatures for *n*-butane heat capacity measurements.

There are two purposes for these density tests. The first purpose is to determine the difference between the density obtained under dynamic and that obtained under static equilibrium conditions. The second purpose is to compare these densities to accurate published densities. In Fig. 2, we show how densities from this work and those measured by Haynes [12] and Olds et al. [13] deviate from an equation of state published by Younglove and Ely [11]. This equation of state was developed with the data in Refs. 12 and 13 but not with the present results. The error bars in Fig. 2 signify the 0.1% uncertainty which Haynes estimates for his densities. The data from this study are shown at seven densities. The filled symbols signify static equilibrium measurements, while the open symbols of the same shape are for the dynamic points of the same isochore. Figure 2 shows that the static and dynamic densities on a given isochore differ by less than 0.02%, with the static densities having the larger values. This supports our claim that, since the parasitic heat losses are small, the pressures and temperatures during the drift measurements are reliable enough to extract useful densities which have only slightly higher uncertainties than the static equilibrium measurements. We also note that there is a small systematic

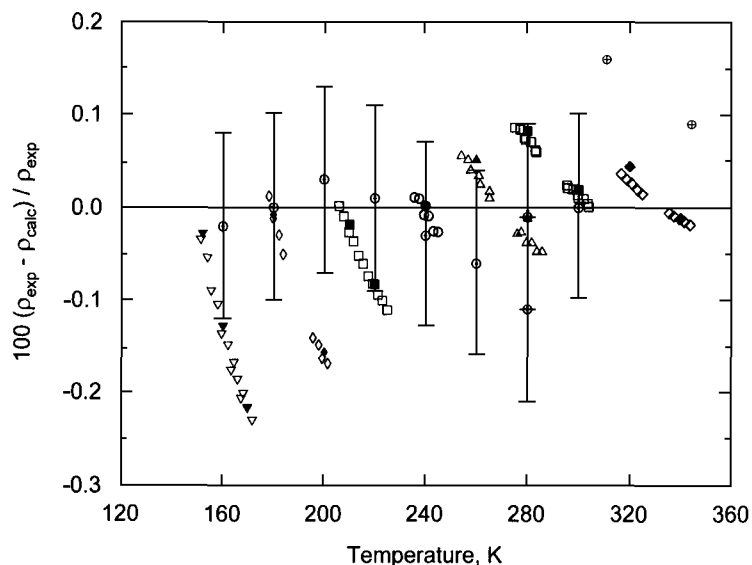


Fig. 2. Comparison of experimental density results for *n*-butane with the values calculated with the equation of state of Ref. 11. Open symbols, dynamic; filled symbols, static. (⊙) Haynes [12]; (⊕) Olds et al. [13].

difference between the densities from the calorimeter and those calculated with the equation in Ref. 11. The trend shows that the calculated densities become larger than the experimental densities by up to 0.23% as the pressure increases to about 35 MPa. Nevertheless, all of these deviations fall within the combined uncertainty of the present densities and those used to develop the equation of state in Ref. 11. The second result is that all of the densities obtained under dynamic equilibrium are within 0.2% of the Haynes [12] data and the Olds et al. [13] data. This result supports our earlier determination, based on propagation of uncertainties, that the densities from this experiment have an uncertainty of 0.2%.

The heat-capacity data are presented in Table I for two-phase states and in Table II for single-phase liquid states. The average temperature of the heating interval is given under the temperature headings. In the two-phase region, most of the measured vapor pressures are below the range of high-accuracy readings of the pressure gauge (3–70 MPa). Thus the pressures, which were required for corrections, were calculated from a vapor-pressure equation [11] but are not presented in Table I. In the single-phase liquid region, the pressures are calculated from pseudo-isochoric fits of the ( $p, T$ ) data of each isochore. A seven-term equation obtained from the equation of state of Jacobsen and Stewart [14] is used

Table I. Measurements of Heat Capacity  $C_\sigma$  for Saturated Liquid *n*-Butane<sup>a</sup>

| $T_a$<br>(K) | $\rho_a$<br>(mol · dm <sup>-3</sup> ) | $C_v^{(2)}$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) | $C_\sigma$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) |
|--------------|---------------------------------------|---|--|
| 141.736      | 12.420                                | 114.64  | 114.64   |
| 145.858      | 12.419                                | 114.78  | 114.78   |
| 140.506      | 11.239                                | 114.86  | 114.86   |
| 144.361      | 11.237                                | 114.87  | 114.87   |
| 148.185      | 11.235                                | 115.13  | 115.13   |
| 151.978      | 11.234                                | 115.28  | 115.28   |
| 155.744      | 11.232                                | 115.61  | 115.61   |
| 159.480      | 11.231                                | 115.86  | 115.86   |
| 163.186      | 11.229                                | 115.99  | 115.99   |
| 166.868      | 11.227                                | 116.30  | 116.30   |
| 170.524      | 11.226                                | 116.42  | 116.42   |
| 174.155      | 11.224                                | 116.49  | 116.49   |
| 177.758      | 11.222                                | 117.12  | 117.12   |
| 181.345      | 11.221                                | 117.48  | 117.48   |
| 184.906      | 11.219                                | 117.69  | 117.69   |
| 188.441      | 11.218                                | 117.91  | 117.91   |
| 191.953      | 11.216                                | 118.46  | 118.45   |
| 195.449      | 11.214                                | 119.11  | 119.11   |
| 198.917      | 11.213                                | 119.18  | 119.17   |
| 202.365      | 11.211                                | 119.95  | 119.95   |
| 205.793      | 11.210                                | 120.08  | 120.08   |
| 209.196      | 11.208                                | 120.78  | 120.78   |
| 215.951      | 11.205                                | 121.74  | 121.74   |
| 219.297      | 11.203                                | 122.34  | 122.35   |
| 138.610      | 9.512                                 | 114.63  | 114.63   |
| 143.488      | 9.510                                 | 114.80  | 114.80   |
| 148.312      | 9.509                                 | 115.22  | 115.22   |
| 153.088      | 9.507                                 | 115.28  | 115.28   |
| 157.818      | 9.505                                 | 115.51  | 115.51   |
| 162.481      | 9.504                                 | 115.81  | 115.80   |
| 167.077      | 9.502                                 | 116.26  | 116.26   |
| 171.653      | 9.500                                 | 116.48  | 116.47   |
| 176.188      | 9.498                                 | 116.97  | 116.96   |
| 180.686      | 9.497                                 | 117.38  | 117.37   |
| 185.152      | 9.495                                 | 117.70  | 117.68   |
| 189.565      | 9.493                                 | 117.99  | 117.97   |
| 193.941      | 9.492                                 | 118.44  | 118.42   |
| 198.281      | 9.490                                 | 119.36  | 119.33   |
| 202.613      | 9.488                                 | 119.61  | 119.57   |
| 211.142      | 9.485                                 | 120.87  | 120.81   |

<sup>a</sup>  $T_a$ , temperature (ITS-90);  $\rho_a$ , bulk density; and  $C_v^{(2)}$ , two-phase heat capacity. The subscript *a* denotes a condition evaluated at the average of the initial and final temperatures.

Table I. (Continued)

| $T_a$<br>(K) | $\rho_a$<br>(mol · dm <sup>-3</sup> ) | $C_v^{(2)}$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) | $C_\sigma$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) |
|--------------|---------------------------------------|---|--|
| 215.355      | 9.483                                 | 121.47  | 121.40   |
| 219.550      | 9.481                                 | 122.27  | 122.20   |
| 223.729      | 9.480                                 | 123.17  | 123.08   |
| 227.884      | 9.478                                 | 123.84  | 123.74   |
| 232.009      | 9.476                                 | 124.18  | 124.07   |
| 236.102      | 9.475                                 | 125.01  | 124.89   |
| 240.170      | 9.473                                 | 126.16  | 126.03   |
| 244.213      | 9.471                                 | 126.69  | 126.56   |
| 248.231      | 9.470                                 | 127.58  | 127.43   |
| 252.227      | 9.468                                 | 128.41  | 128.27   |
| 256.177      | 9.466                                 | 129.24  | 129.10   |
| 260.092      | 9.465                                 | 130.31  | 130.17   |
| 263.986      | 9.463                                 | 131.25  | 131.12   |
| 267.856      | 9.461                                 | 132.16  | 132.04   |
| 271.707      | 9.460                                 | 133.20  | 133.09   |
| 275.540      | 9.458                                 | 134.20  | 134.11   |
| 279.353      | 9.456                                 | 135.10  | 135.04   |
| 283.147      | 9.455                                 | 136.09  | 136.08   |
| 286.927      | 9.453                                 | 137.30  | 137.33   |
| 298.207      | 9.448                                 | 140.05  | 140.29   |
| 301.952      | 9.447                                 | 141.44  | 141.77   |
| 305.675      | 9.445                                 | 142.41  | 142.85   |
| 309.400      | 9.443                                 | 143.73  | 144.29   |
| 313.072      | 9.442                                 | 145.03  | 145.72   |
| 316.748      | 9.440                                 | 145.70  | 146.55   |
| 142.674      | 9.913                                 | 114.69  | 114.69   |
| 147.362      | 9.911                                 | 114.92  | 114.92   |
| 152.009      | 9.910                                 | 115.36  | 115.35   |
| 156.619      | 9.908                                 | 115.67  | 115.67   |
| 161.179      | 9.906                                 | 115.98  | 115.98   |
| 165.703      | 9.905                                 | 116.03  | 116.03   |
| 170.185      | 9.903                                 | 116.20  | 116.20   |
| 174.627      | 9.901                                 | 116.59  | 116.59   |
| 179.035      | 9.899                                 | 117.20  | 117.20   |
| 183.410      | 9.898                                 | 117.29  | 117.28   |
| 187.738      | 9.896                                 | 117.82  | 117.80   |
| 192.026      | 9.894                                 | 118.67  | 118.65   |
| 196.288      | 9.892                                 | 119.22  | 119.19   |
| 200.506      | 9.891                                 | 119.56  | 119.53   |
| 204.697      | 9.889                                 | 120.22  | 120.19   |
| 208.880      | 9.887                                 | 120.71  | 120.67   |
| 213.012      | 9.885                                 | 121.28  | 121.23   |
| 217.117      | 9.884                                 | 121.87  | 121.82   |
| 221.204      | 9.882                                 | 122.29  | 122.24   |

Table I. (Continued)

| $T_a$<br>(K) | $\rho_a$<br>(mol · dm <sup>-3</sup> ) | $C_v^{(2)}$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) | $C_\sigma$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) |
|--------------|---------------------------------------|---|--|
| 276.460      | 9.858                                 | 134.29  | 134.37   |
| 280.673      | 9.856                                 | 135.46  | 135.58   |
| 284.858      | 9.854                                 | 136.46  | 136.64   |
| 289.029      | 9.852                                 | 137.19  | 137.45   |
| 293.163      | 9.850                                 | 138.37  | 138.71   |
| 225.258      | 9.880                                 | 123.10  | 123.03   |
| 229.288      | 9.879                                 | 124.07  | 124.00   |
| 233.281      | 9.877                                 | 124.81  | 124.74   |
| 241.193      | 9.873                                 | 126.41  | 126.33   |
| 245.104      | 9.872                                 | 127.03  | 126.95   |
| 249.002      | 9.870                                 | 127.56  | 127.48   |
| 256.729      | 9.867                                 | 129.30  | 129.24   |
| 260.558      | 9.865                                 | 130.61  | 130.57   |
| 264.358      | 9.863                                 | 131.31  | 131.28   |
| 268.135      | 9.862                                 | 132.39  | 132.39   |
| 271.899      | 9.860                                 | 132.87  | 132.90   |

Table II. Measurements of Heat Capacity  $C_v$  for Liquid *n*-Butane<sup>a</sup>

| $T_a$<br>(K) | $\rho_a$<br>(mol · dm <sup>-3</sup> ) | $p$<br>(MPa) | $C_v$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) |
|--------------|---------------------------------------|--------------|---|
| 153.289      | 12.392                                | 5.317        | 84.47   |
| 155.898      | 12.384                                | 9.548        | 84.23   |
| 157.373      | 12.379                                | 11.931       | 85.04   |
| 159.944      | 12.371                                | 16.042       | 84.72   |
| 161.407      | 12.367                                | 18.355       | 85.51   |
| 163.954      | 12.359                                | 22.330       | 85.42   |
| 165.406      | 12.355                                | 24.568       | 85.65   |
| 166.370      | 12.352                                | 26.046       | 85.37   |
| 167.931      | 12.347                                | 28.426       | 85.77   |
| 170.046      | 12.340                                | 31.633       | 85.76   |
| 164.977      | 12.200                                | 4.216        | 84.48   |
| 167.251      | 12.194                                | 7.632        | 84.45   |
| 169.003      | 12.188                                | 10.264       | 84.79   |
| 171.267      | 12.182                                | 13.650       | 84.89   |
| 173.000      | 12.177                                | 16.219       | 85.27   |
| 175.248      | 12.170                                | 19.514       | 85.34   |

<sup>a</sup>  $T_a$ , temperature (ITS-90);  $\rho_a$ , density; and  $p$ , pressure. The subscript  $a$  denotes a condition evaluated at the average of the initial and final temperatures.



Table II. (Continued)

| $T_a$<br>(K) | $\rho_a$<br>(mol · dm <sup>-3</sup> ) | $p$<br>(MPa) | $C_v$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) |
|--------------|---------------------------------------|--------------|---|
| 176.963      | 12.165                                | 21.998       | 85.70   |
| 179.192      | 12.159                                | 25.187       | 85.76   |
| 180.887      | 12.154                                | 27.584       | 86.11   |
| 183.101      | 12.147                                | 30.689       | 86.19   |
| 180.179      | 11.969                                | 5.214        | 85.00   |
| 181.823      | 11.965                                | 7.504        | 84.89   |
| 184.147      | 11.958                                | 10.705       | 85.07   |
| 185.779      | 11.954                                | 12.931       | 85.30   |
| 188.082      | 11.948                                | 16.050       | 85.73   |
| 189.695      | 11.943                                | 18.219       | 85.94   |
| 191.993      | 11.937                                | 21.288       | 85.75   |
| 193.583      | 11.933                                | 23.396       | 86.52   |
| 195.858      | 11.926                                | 26.386       | 86.35   |
| 197.440      | 11.922                                | 28.444       | 86.86   |
| 199.703      | 11.916                                | 31.354       | 87.19   |
| 203.898      | 11.588                                | 4.688        | 86.20   |
| 205.777      | 11.584                                | 6.945        | 86.33   |
| 207.788      | 11.579                                | 9.348        | 86.70   |
| 209.640      | 11.574                                | 11.546       | 86.88   |
| 211.646      | 11.569                                | 13.911       | 86.85   |
| 213.476      | 11.565                                | 16.054       | 87.59   |
| 215.470      | 11.560                                | 18.373       | 87.46   |
| 217.283      | 11.555                                | 20.466       | 88.12   |
| 219.269      | 11.551                                | 22.740       | 88.67   |
| 221.059      | 11.546                                | 24.775       | 88.52   |
| 223.040      | 11.541                                | 27.012       | 88.82   |
| 224.801      | 11.537                                | 28.983       | 89.39   |
| 226.766      | 11.532                                | 31.168       | 89.57   |
| 228.011      | 11.179                                | 3.113        | 88.23   |
| 229.922      | 11.175                                | 5.087        | 88.66   |
| 231.823      | 11.171                                | 7.039        | 88.96   |
| 233.723      | 11.167                                | 8.980        | 89.32   |
| 235.610      | 11.163                                | 10.897       | 89.69   |
| 237.494      | 11.159                                | 12.800       | 90.05   |
| 239.367      | 11.155                                | 14.680       | 90.38   |
| 241.237      | 11.150                                | 16.547       | 90.86   |
| 243.094      | 11.146                                | 18.389       | 91.18   |
| 244.951      | 11.142                                | 20.220       | 91.58   |
| 246.799      | 11.138                                | 22.031       | 91.95   |
| 248.643      | 11.134                                | 23.827       | 92.23   |
| 250.484      | 11.130                                | 25.608       | 92.63   |
| 252.302      | 11.127                                | 27.356       | 93.17   |
| 254.140      | 11.123                                | 29.111       | 93.20   |
| 255.945      | 11.119                                | 30.823       | 94.05   |

Table II. (Continued)

| $T_a$<br>(K) | $\rho_a$<br>(mol · dm <sup>-3</sup> ) | $p$<br>(MPa) | $C_v$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) |
|--------------|---------------------------------------|--------------|---|
| 257.767      | 11.115                                | 32.539       | 94.59   |
| 254.576      | 10.735                                | 3.343        | 91.82   |
| 255.941      | 10.732                                | 4.537        | 92.03   |
| 258.829      | 10.727                                | 7.051        | 92.63   |
| 259.640      | 10.725                                | 7.754        | 92.76   |
| 263.048      | 10.719                                | 10.691       | 93.30   |
| 263.325      | 10.718                                | 10.928       | 93.51   |
| 266.979      | 10.711                                | 14.044       | 94.26   |
| 267.239      | 10.711                                | 14.265       | 94.41   |
| 270.622      | 10.704                                | 17.119       | 95.19   |
| 271.406      | 10.703                                | 17.777       | 95.59   |
| 274.236      | 10.697                                | 20.139       | 96.00   |
| 275.542      | 10.695                                | 21.223       | 96.33   |
| 277.829      | 10.691                                | 23.112       | 96.56   |
| 279.648      | 10.687                                | 24.606       | 97.18   |
| 281.664      | 10.683                                | 26.254       | 97.65   |
| 283.724      | 10.680                                | 27.926       | 97.85   |
| 285.734      | 10.676                                | 29.550       | 98.74   |
| 287.775      | 10.672                                | 31.187       | 98.62   |
| 289.777      | 10.668                                | 32.782       | 99.51   |
| 277.132      | 10.326                                | 2.725        | 95.80   |
| 279.246      | 10.322                                | 4.304        | 96.54   |
| 280.953      | 10.319                                | 5.576        | 96.63   |
| 281.336      | 10.319                                | 5.860        | 96.64   |
| 283.445      | 10.315                                | 7.424        | 97.18   |
| 285.142      | 10.312                                | 8.677        | 97.48   |
| 285.511      | 10.312                                | 8.949        | 97.67   |
| 287.619      | 10.308                                | 10.499       | 98.37   |
| 289.304      | 10.305                                | 11.733       | 98.29   |
| 289.659      | 10.305                                | 11.993       | 98.57   |
| 291.768      | 10.301                                | 13.530       | 99.07   |
| 293.439      | 10.299                                | 14.742       | 99.56   |
| 293.783      | 10.298                                | 14.991       | 99.69   |
| 295.888      | 10.294                                | 16.511       | 100.11  |
| 297.551      | 10.292                                | 17.706       | 100.32  |
| 297.882      | 10.291                                | 17.943       | 100.52  |
| 299.988      | 10.288                                | 19.449       | 100.88  |
| 301.642      | 10.285                                | 20.626       | 101.13  |
| 301.959      | 10.284                                | 20.851       | 101.44  |
| 304.057      | 10.281                                | 22.337       | 101.76  |
| 305.707      | 10.278                                | 23.499       | 101.99  |
| 306.011      | 10.278                                | 23.713       | 102.47  |
| 308.110      | 10.274                                | 25.184       | 102.88  |
| 310.042      | 10.271                                | 26.532       | 103.39  |

Table II. (Continued)

| $T_a$<br>(K) | $\rho_a$<br>(mol · dm <sup>-3</sup> ) | $P$<br>(MPa) | $C_v$<br>(J · mol <sup>-1</sup> · K <sup>-1</sup> ) |
|--------------|---------------------------------------|--------------|---|
| 312.138      | 10.267                                | 27.987       | 103.24  |
| 314.052      | 10.264                                | 29.310       | 104.14  |
| 316.141      | 10.261                                | 30.747       | 104.45  |
| 318.047      | 10.258                                | 32.053       | 104.67  |
| 320.133      | 10.254                                | 33.476       | 105.82  |
| 302.143      | 9.830                                 | 1.903        | 100.78  |
| 304.202      | 9.827                                 | 3.178        | 101.00  |
| 306.326      | 9.824                                 | 4.489        | 101.72  |
| 308.426      | 9.820                                 | 5.781        | 101.89  |
| 310.496      | 9.818                                 | 7.051        | 102.86  |
| 312.632      | 9.814                                 | 8.357        | 102.94  |
| 314.644      | 9.812                                 | 9.583        | 103.60  |
| 316.825      | 9.808                                 | 10.908       | 103.58  |
| 318.784      | 9.806                                 | 12.093       | 103.82  |
| 320.996      | 9.803                                 | 13.427       | 104.88  |
| 322.900      | 9.800                                 | 14.570       | 105.19  |
| 325.153      | 9.797                                 | 15.919       | 105.60  |
| 327.010      | 9.794                                 | 17.026       | 106.16  |
| 329.288      | 9.791                                 | 18.380       | 106.86  |
| 331.112      | 9.788                                 | 19.459       | 107.30  |
| 333.419      | 9.785                                 | 20.820       | 107.63  |
| 335.207      | 9.782                                 | 21.869       | 107.92  |
| 337.527      | 9.779                                 | 23.226       | 108.05  |
| 339.283      | 9.776                                 | 24.249       | 109.35  |
| 341.620      | 9.773                                 | 25.606       | 109.37  |
| 322.540      | 9.421                                 | 2.228        | 105.03  |
| 324.767      | 9.418                                 | 3.402        | 105.42  |
| 324.940      | 9.418                                 | 3.493        | 105.29  |
| 325.884      | 9.416                                 | 3.990        | 105.87  |
| 326.758      | 9.415                                 | 4.450        | 106.21  |
| 328.987      | 9.412                                 | 5.620        | 106.31  |
| 329.229      | 9.412                                 | 5.747        | 105.98  |
| 330.156      | 9.411                                 | 6.233        | 106.00  |
| 330.964      | 9.410                                 | 6.655        | 106.84  |
| 333.208      | 9.407                                 | 7.828        | 107.22  |
| 333.499      | 9.407                                 | 7.980        | 107.40  |
| 334.401      | 9.406                                 | 8.450        | 107.27  |
| 335.153      | 9.405                                 | 8.842        | 107.06  |
| 337.424      | 9.402                                 | 10.023       | 107.59  |
| 337.770      | 9.401                                 | 10.202       | 108.15  |
| 338.649      | 9.400                                 | 10.658       | 108.46  |
| 339.331      | 9.399                                 | 11.012       | 108.42  |
| 341.611      | 9.397                                 | 12.192       | 108.23  |
| 342.004      | 9.396                                 | 12.395       | 109.35  |

to fit the  $(p, T)$  data of each isochore within the uncertainty of the measurements. The density, given in Table II for single-phase liquid states, is calculated from the number of moles and the bomb volume. A detailed discussion of the uncertainties of measured quantities is available in a previous work [15]. We have determined that the expanded uncertainty (i.e., a coverage factor  $k=2$  and thus a two-standard deviation estimate) of  $C_V$  is 0.7%, for  $C_V^{(2)}$  it is 0.5%, and for  $C_\sigma$  it is 0.7%.

In Table I, values of the two-phase heat capacity at constant volume [ $C_V^{(2)}$ ] are presented, as well as the saturated liquid heat capacity  $C_\sigma$  [also known as  $C'_x = T(dS'/dT)$ ]. Values of  $C_\sigma$  are obtained by adjusting the  $C_V^{(2)}$  data with the equation given by Rowlinson [16],

$$C_\sigma = C_V^{(2)} - \frac{T}{\rho^2} \frac{d\rho_\sigma}{dT} \frac{dp_\sigma}{dT} + T \left( \frac{1}{\rho_\sigma} - \frac{1}{\rho} \right) \frac{d^2 p_\sigma}{dT^2} \quad (3)$$

where  $\rho_\sigma$  and  $p_\sigma$  are the density and the pressure of the saturated liquid and  $\rho$  is the bulk density of the sample residing in the bomb. The derivative quantities were calculated with the ancillary equations of Younglove and Ely [11].

The saturated liquid heat capacity  $C_\sigma$ , as a saturation quantity, depends on a single variable—temperature. If the data are internally consistent, then the values from different isochores must fall on a single curve. Though the  $C_\sigma$  values were evaluated from experiments with different amounts of sample in the calorimeter, the results should demonstrate consistency of all isochores. The saturated-liquid heat capacities for all of the filling densities are depicted graphically in Fig. 3. To intercompare the data sets from different isochores, we fitted an equation to the  $C_\sigma$  data. This equation accurately describes the whole data set at temperatures from 139 to 317 K.

For *n*-butane, the three-parameter expression,

$$(C_\sigma/C_0) = a_1 T_r^{1/4} + a_2 T_r^{1/2} + a_3 T_r^{9/4} \quad (4)$$

where  $C_0 = 1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ,  $T_r = T/T_c$ ,  $T_c = 425.16 \text{ K}$ ,  $a_1 = 3.8251447 \times 10^2$ ,  $a_2 = -3.2492719 \times 10^2$ , and  $a_3 = 1.3907469 \times 10^2$ , was fit by applying software based on the Wagner method of structural optimization [17]. The deviations of the present results and the published  $C_p$  data of Aston and Messerly [18], Dana et al. [19], and Huffman et al. [20] from Eq. (4) are shown in Fig. 4. Only the present results were used to obtain the fit. Deviations of our results are distributed randomly over the entire temperature range, with a standard deviation of the fit of 0.13%, indicating that there is a good internal consistency. The data of Aston and Messerly have

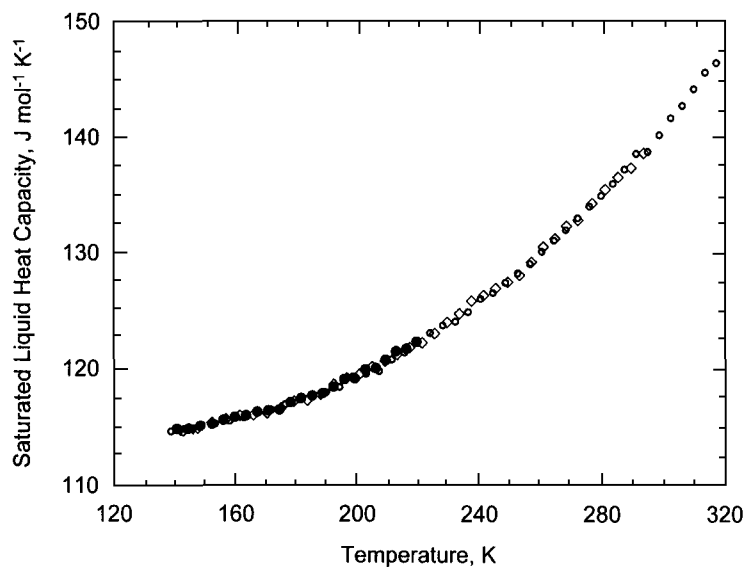


Fig. 3. Experimental saturated liquid heat-capacity ( $C_\sigma$ ) values for *n*-butane: symbols signify different filling masses.

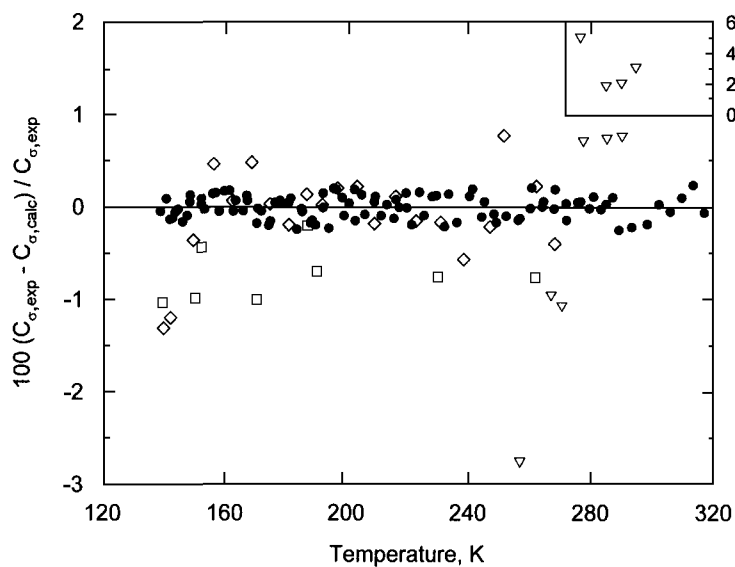


Fig. 4. Comparison of experimental  $C_\sigma$  results for *n*-butane with the values calculated with Eq. (4). (●) this work; (◇) Aston and Messerly [18]; (▽) Dana et al. [19]; (□) Huffman et al. [20].

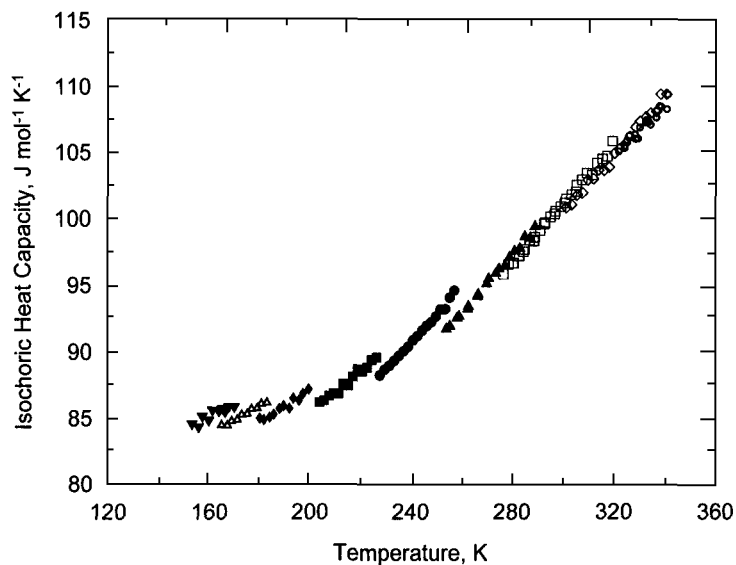


Fig. 5. Experimental liquid-phase heat-capacity ( $C_v$ ) data for  $n$ -butane.

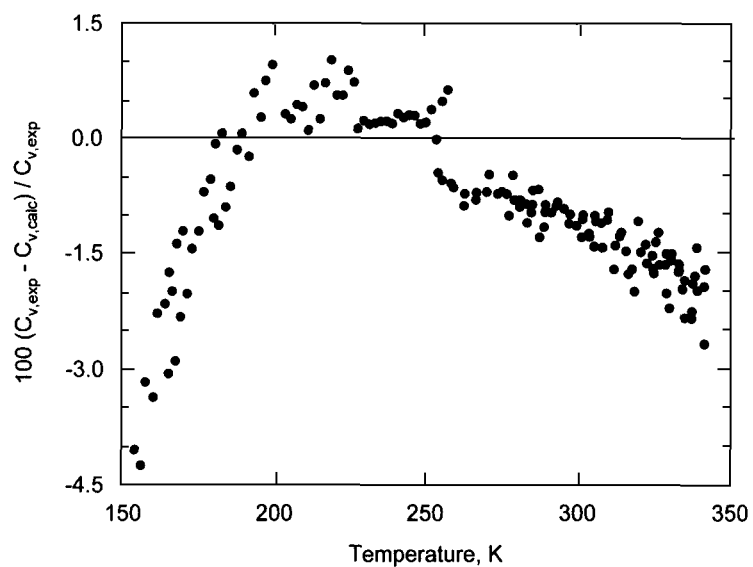


Fig. 6. Comparison of experimental  $C_v$  data for  $n$ -butane from this work with the values calculated using an equation of state [11].

a claimed uncertainty of 0.5% and show excellent agreement with our results. The data of Huffman et al. have an uncertainty of 1% and agree with our results to within this claim. The data of Dana et al. have a claimed uncertainty of 2% but show discrepancies from Eq. (4) of as much as 5%. However, a closer examination of the  $C_p$  data of Dana et al. reveals a scatter of approximately 7% in their measurements, which leads us to conclude that the uncertainty of their data cannot be less than this quantity.

Values of the single-phase liquid heat capacity are shown in Fig. 5. The data are presented on isochores in a  $C_v$ - $T$  diagram. Most isochores overlap in their temperature ranges. Figure 5 shows that for *n*-butane, the slope of each  $C_v$ - $T$  isochore is nearly independent of the density of the isochore. Thus, almost all of the *n*-butane data fall on a simple curve.

Often, when equations of state based solely on  $(p, \rho, T)$  data are used for predicting heat capacities of liquids, they give predictions that have considerable uncertainty. Since the equation of state of Younglove and Ely [11] is one of the most accurate models available for *n*-butane, we decided to test it with the measured values of this study. Younglove and Ely estimated that calculated heat capacities have an uncertainty of  $\pm 2\%$  at temperatures below  $T_c$  in the liquid phase. Figure 6 shows the results of this comparison. The calculated  $C_v$  values used for Fig. 6 were derived from this equation of state using the relation,

$$C_v(T, \rho) = C_v^0(T) - T \int_0^\rho (\partial^2 p / \partial T^2)_\rho d\rho / \rho^2 \quad (5)$$

where  $C_v^0$  is the heat capacity for the ideal gas. Figure 6 shows that most of the predicted values are within  $\pm 2\%$  of the measurements, except for those at temperatures below 180 and above 320 K. There are strong systematic deviations between the data and the predicted heat capacities. Most of the predicted values are larger than our experimental results. Overall, the root-mean-square deviation of the experimental  $C_v$  results from the calculated values is 1.38%, which is good agreement. However, if experimental  $C_v$  data had been available when Younglove and Ely optimized their equation of state, this agreement would have been much better.

#### 4. CONCLUSIONS

For *n*-butane, we have reported 148  $C_v$  and 100  $C_\sigma$  values. Examination of both dynamically and statically measured liquid densities from this study shows that the agreement with published data is within 0.2%. Agreement was within 1% for reliable published heat capacities at constant

pressure  $C_p$  for the saturated liquid. No published liquid  $C_v$  data were found for comparison. Comparisons with  $C_v$  values calculated with a published equation of state show that systematic deviations exist which are larger than our claimed uncertainty. We recommend the formulation of a new equation of state for *n*-butane which incorporates recently published experimental data.

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