Experimental Results for Heat Capacity and Joule-Thomson Coefficient of Ethane at Zero Pressure

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The heat capacity at constant pressure c_p and the differential Joule-Thomson coefficient μ of ethane were measured with a flow apparatus in the temperature range from 25° to 200°C at pressures up to 10 bar. Since the accuracy of the measured values is about 0.1% for c_p and 0.5% for μ, by extrapolating these values to zero pressure, the ideal gas state heat capacity c_p° and the Joule-Thomson coefficient at zero pressure μ° could be determined to about 0.2 and 1.0%, respectively. Whereas the c_p° values differ only slightly from existing literature data, the existing μ° data deviate by about 20% from the new results which are shown to be consistent with precise pvT measurements.

A flow apparatus for the precision measurement of the heat capacity c_p and the differential Joule-Thomson coefficient μ of gaseous hydrocarbons and similar substances at temperatures between 25° and 200°C and pressures up to 120 bar has been described previously, and results for propylene have been reported (*2–4*).

This paper reports results for ethane in the low-pressure range. The methods of measurement and of the evaluation of the direct experimental data were the same as in the previous investigation on propylene.

Experimental Results

The investigated samples of ethane were delivered by Deutsche L'Air Liquide Edelgas GmbH, Düsseldorf. A purity of 99.95 mol % was guaranteed. According to the statement of the supplier, the remaining impurities are higher hydrocarbons ($\leq$0.04 mol %), nitrogen ($\leq$0.004 mol %), carbon dioxide and oxygen (each $\leq$0.001 mol %), and water ($\leq$0.0005 mol %).

Figures 1 and 2 show the experimental c_p and μ values at pressures up to 10 bar. As in the previous investigation on propylene, the uncertainty of these values is about 0.1% for c_p and 0.5% for μ (*2, 4*). By extrapolation of the isotherms to zero pressure, the c_p° and μ° values of Table I were obtained. The uncertainties of these values are assumed as 0.2% for c_p° and 1.0% for μ°.

In Figure 3 the c_p° values of this work are compared with data taken from the literature. In the whole temperature range investigated, the results of this paper are somewhat smaller than those of the earlier investigations. The c_p° value at 15°C measured by Heuse (*11*) with a flow calorimeter agrees with the result of this work within 0.6%, which is within the limits of the experimental errors of both investigations. Eucken and Parts (*9*), using the Lummer-Pringsheim method to determine c_p, obtained c_p° values which are 1.0–1.6% larger than our results; the deviations are to be compared with an estimated experimental error of 0.5–1.0%.

The results of Kistiakowsky and Rice (*13*), determined also with the Lummer-Pringsheim method, deviate from our results from 0.6% at about 30°C to 1.8% at about 90°C, the deviations being somewhat larger than those in the previous investigation on propylene (*2, 4*). The c_p° values of Dailey and Felsing (*6*), determined with the Bennewitz-Schulze method with a claimed accuracy of 1%, surmount our values by about 1.4%. Rossini et al. (*16*) critically reviewed the c_p° data and accepted the calculated values of Pitzer (*15*) as most reliable. These values deviate from the results of this work by 0.4% at 25°C and 1.6% at 100°C. Recently, Chao et al. (*5*) calculated the ideal gas state thermodynamic properties of ethane. In the temperature range between 0° and 200°C, their c_p° values are lower than Pitzer's results by up to 0.3% and exceed the experimental results of this work by a minimum amount of about 0.05% at 25°C and a maximum amount of about 1.4% at 100°C.

The maximum deviation between the literature data and our results occurs in the temperature range above 50°C. At this temperature, our results show a slight decrease in the slope of the c_p° T-curve. Because of this deviation from the literature data, the accuracy of our c_p results was checked: To test the reproducibility of the flow apparatus, the c_p measurements for propylene at 75°C and low pressure were repeated. The results agreed within 0.2% with c_p° data determined two years ago and within 0.1% with values calculated by Kilpatrick and Pitzer (*12*).

Furthermore, a repetition of the ethane measurements at 75°C and 1 bar with a new sample differed by less than 0.15% from the corresponding results obtained two years

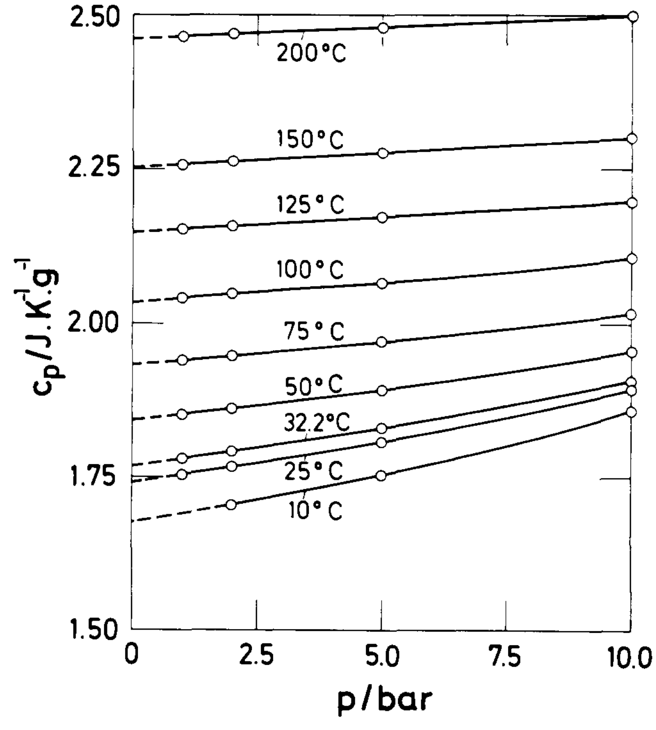

Figure 1. Experimental results for heat capacity at constant pressure of ethane

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ago. Therefore, we think that the change in the slope of the c_p° curve in Figure 3 is correct. The decrease in the slope of the c_p° curve of ethane occurs in the temperature region where the heat capacity contribution of the hindered internal rotation around the C—C bond reaches its maximum (*1*). However, the known statistical calculations do not yield this decrease in the slope of the c_p° *T*-curve.

In Figure 4 the μ° values of this work are compared with the experimental μ° value of ethane determined by Sage et al. (*17*) and Head (*10*). Although the μ° data from these two sources agree within a few tenths of 1%, they are nearly 20% smaller than our results.

To decide which values are correct, the μ° values of the different sources were used, together with c_p° of this work, to calculate the isothermal throttling coefficient at zero pressure

$$\phi^\circ = -\mu^\circ \cdot c_p^\circ$$

which is correlated to the second virial coefficient *B* by

$$\phi^\circ = -T^2 \frac{d}{dT}\left(\frac{B}{T}\right)$$

(T = absolute temperature).

By integrating ϕ°/T^2 over T, the differences $B/T - (B/T)_{25^\circ\mathrm{C}}$ were calculated and compared with independent results from precise *pvT* measurements. For the integration the ϕ° values were represented by the equation $\phi^\circ = A + B \cdot T + C/T^2$. The constants *A*, *B*, and *C* were fitted to the experimental ϕ° values by a least-squares technique. With $A/\mathrm{J{\cdot}bar^{-1}{\cdot}}$

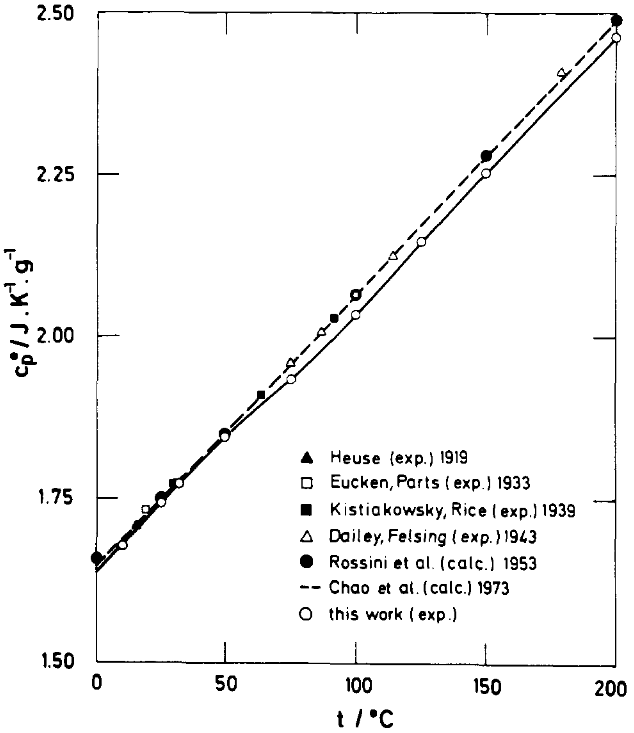

Figure 3. Ideal gas state heat capacity at constant pressure of ethane

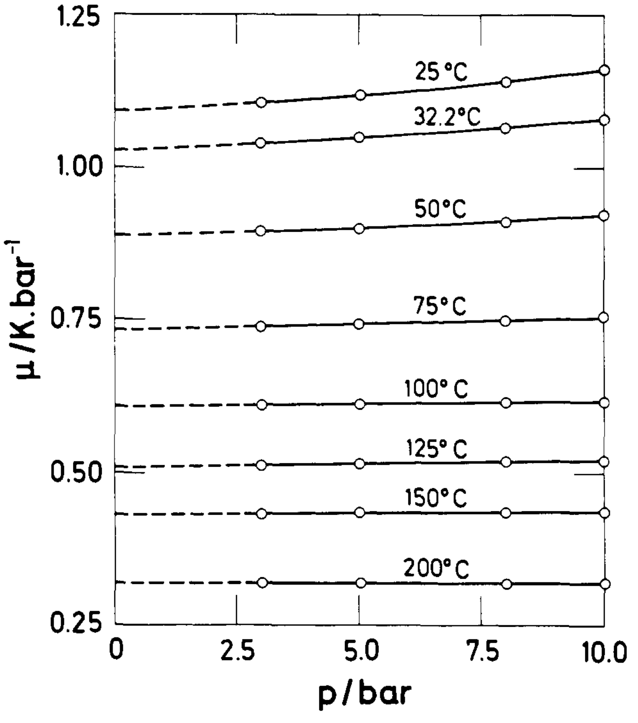

Figure 2. Experimental results for differential Joule-Thomson coefficient of ethane

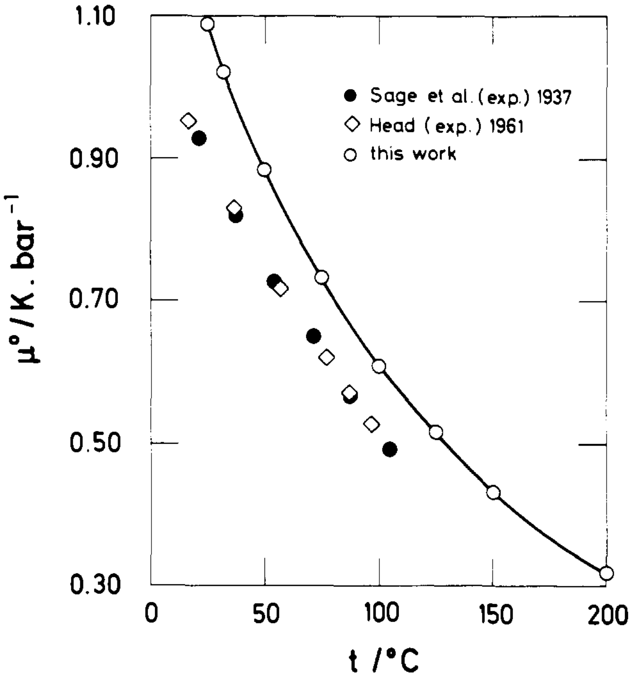

Figure 4. Differential Joule-Thomson coefficient at zero pressure of ethane

Table I. Ideal Gas State Heat Capacity at Constant Pressure c_p° and Differential Joule-Thomson Coefficient at Zero Pressure μ° of Ethane

t, °C[a]	10	25	32.2	50	75	100	125	150	200
c_p°, J·K^{-1}·g^{-1}	1.679	1.745	1.772	1.845	1.934	2.034	2.148	2.254	2.464
μ°, K·bar^{-1}	. . .	1.088	1.019	0.883	0.733	0.606	0.509	0.432	0.318

[a] Corresponding to IPTS-68.

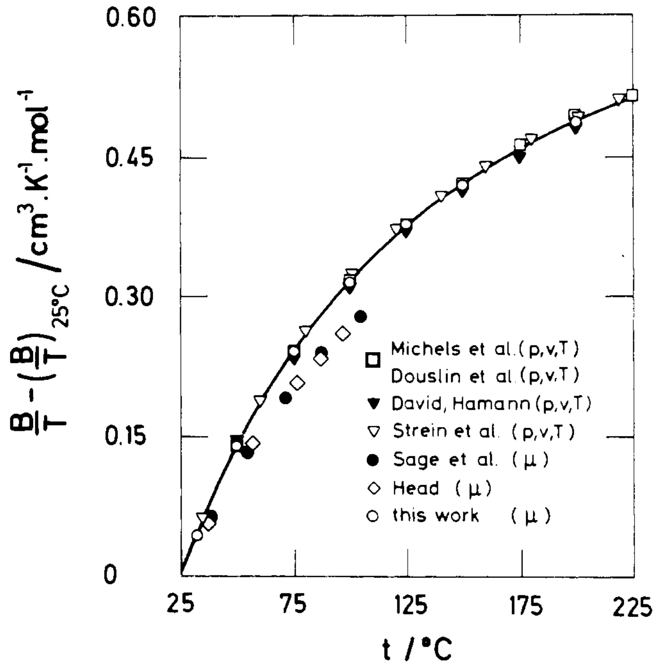

Figure 5. Differences of B/T for ethane from pvT and μ measurements. B = second virial coefficient; T = absolute temperature

$g^{-1} = -0.23083$, $B/J{\cdot}K^{-1}{\cdot}bar^{-1}{\cdot}g^{-1} = +3.0636{\cdot}10^{-4}$ and $C/J{\cdot}K^{2}{\cdot}bar^{-1}{\cdot}g^{1} = -1.5612{\cdot}10^{5}$, this equation represents the ϕ° values of this work within a maximum deviation of 0.42%.

Figure 5 shows that the difference $B/T - (B/T)_{25°C}$ calculated from the μ° values of this work agrees excellently with the results from pvT measurements by Michels et al. (*14*), David and Hamann (*7*), Strein et al. (*18*), and Douslin and Harrison (*8*). For example, the deviations in $\Delta(B/T)$ from Michels and Douslin's results are only 0.7–7.4%. On the other hand, the B/T differences obtained from the μ° values of Sage et al. (*17*) and Head (*10*) deviated by up to 20% from the results of the pvT measurements. This comparison indicates that the Joule-Thomson coefficients determined by these authors are inconsistent with the accepted thermodynamic properties of ethane.

Literature Cited

(1) Barho, W., dissertation, Universität Karlsruhe, Karlsruhe, Germany, 1966, and unpublished calculations.
(2) Bier, K., Ernst, G., Kunze, J., Maurer, G., *Verfahrenstechnik*, **6**, 261 (1972).
(3) Bier, K., Ernst, G., Maurer, G., *J. Chem. Thermodyn.*, **6**, 1027 (1974).
(4) Bier, K., Ernst, G., Kunze, J., Maurer, G., *ibid.*, p 1039.
(5) Chao, J., Wilhoit, R. C., Zwolinski, B. J., *J. Phys. Chem. Ref. Data*, **2**, 427 (1973).
(6) Dailey, B. P., Felsing, W. A., *J. Am. Chem. Soc.*, **65**, 42 (1943).
(7) David, H. G., Hamann, S. D., Proc. Conf. Thermodyn. Transport Properties Fluids, p 74, London, England, 1958.
(8) Douslin, D. R., Harrison, R. H., *J. Chem. Thermodyn.*, **5**, 491 (1973).
(9) Eucken, A., Parts, A., *Z. Phys. Chem.*, **20B**, 184 (1933).
(10) Head, J. F., PhD thesis, Imperial College of Science and Technology, London, England, 1961.
(11) Heuse, W., *Ann. Phys.*, **59**, 86 (1919).
(12) Kilpatrick, J. E., Pitzer, K. S., *J. Res. Nat. Bur. Stand.*, **38**, 191 (1974).
(13) Kistiakowsky, G. B., Rice, W. W., *J. Chem. Phys.*, **7**, 281 (1939).
(14) Michels, A., Van Straaten, W., Dawson, J., **Physica, 20**, 17 (1954).
(15) Pitzer, K. S., *Ind. Eng. Chem.*, **36**, 829 (1944).
(16) Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M., Pimentel, G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," p 633, Carnegie Press, Pittsburgh, Pa., 1953.
(17) Sage, B. H., Webster, D. C., Lacey, W. N., *Ind. Eng. Chem.*, **29**, 658 (1937).
(18) Strein, K., Lichtenthaler, R. N., Schramm, B., Schäfer, Kl., *Ber. Bunsenges. Phys. Chem.*, **75**, 1308 (1971).

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Density and Crystallinity Measurements of Liquid and Solid *n*-Undecane, *n*-Tridecane, and *o*-Xylene from 200 to 350K

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Densities of solid and liquid *n*-undecane, *n*-tridecane, and *o*-xylene are reported for temperatures from 200 to 350K. Density increases upon freezing by 13, 13, and 12%, respectively, for these hydrocarbons. The data are presented graphically and are also represented by equations to within the scatter of the data. The uncertainties of the data are 0.2% for the liquid and 1% for the solid state. X-ray examinations revealed that these materials have complex crystalline structures when frozen. Near 200K the main crystal structure is orthorhombic, but several phase transformations occur for each of these materials between 200K and the melting point.

As part of the Skylab program, the Marshall Space Flight Center of the National Aeronautics and Space Administration (MSFC-NASA) required a temperature stabilizing device at several temperatures below ambient. The resulting device, referred to as a thermal capacitor, is simply a container filled with hydrocarbon. Temperature stability is achieved at the freezing point of the hydrocarbon because of the reversible heat reservoir created by its latent heat of fusion. To obtain stability over a range of temperatures, several hydrocarbons, *n*-undecane, *n*-tridecane, and *o*-xylene, have been used. During operation the hydrocarbon container experiences large strains resulting from the volume changes of the hydrocarbon as it cycles between the liquid and solid state. In the past the container has broken after repeated thermal cycles. Therefore, MSFC requested that NBS determine the liquid and solid volume changes of these hydrocarbons at temperatures from 200 to 350K. NBS was also asked to examine the crystallinity of these materials from 200K to their freezing points by X-ray methods.

The following sections present descriptions of the materials, methods of density and specific volume measurements, and X-ray examination. Finally, the results of both density and

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