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Thermal Properties of Cyclopentane and Its Use as a Standard Substance in Low Temperature Thermal Measurements

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The thermal properties of cyclopentane were redetermined in the Penn State isothermal calorimeter and adiabatic calorimeter *B'* and the results compared with other investigations. It is concluded that the heat capacity results of Penn State adiabatic calorimeter *B'*, those of the National Bureau of Standards, and those of the Bureau of Mines Laboratory at Bartlesville, Oklahoma, are in satisfactory agreement, under normal operating conditions, above 30°K.

IN view of the discrepancies observed between the results of various investigators on the thermal properties of simple hydrocarbons,¹⁻⁷ it seemed desirable to test our various calorimeters, using cyclopentane as the "standard" substance. The same sample was used as before.⁴ The hitherto unreported measurements were carried out in our gold calorimeter *C*,⁸ by Dr. E. L.

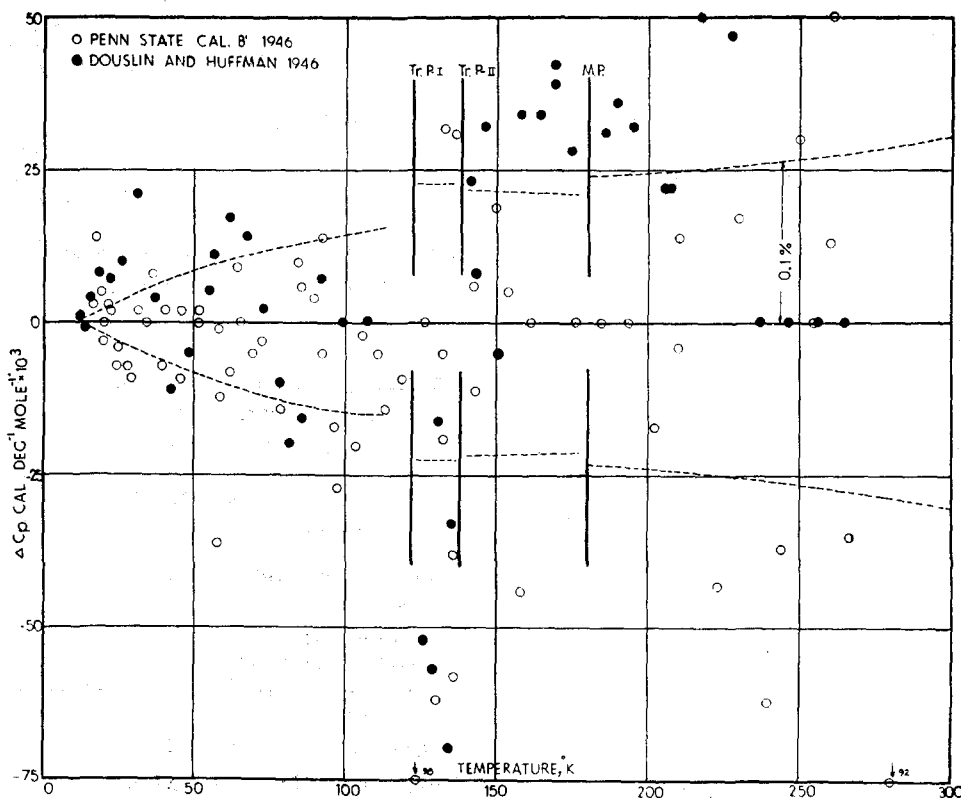


FIG. 1. Comparison plot for cyclopentane. Deviations of experimental points from smooth curve.

* Phillips Petroleum Fellow 1945-47. ** National Research Fellow 1945-46. *** Phillips Petroleum Fellow 1944-46.

¹ Schumann, Aston, and Sagenkahn, *J. Am. Chem. Soc.* **64**, 1039 (1942).

² Guthrie and Huffman, *J. Am. Chem. Soc.* **65**, 1142 (1943).

³ Aston, *J. Am. Chem. Soc.* **65**, 2041 (1943).

⁴ Aston, Fink, and Schumann, *J. Am. Chem. Soc.* **65**, 341 (1943).

⁵ Douslin and Huffman, *J. Am. Chem. Soc.* **68**, 173 (1946).

⁶ Aston, Szasz, and Fink, *J. Am. Chem. Soc.* **65**, 1135 (1943).

⁷ Ruehrwein and Huffman, *J. Am. Chem. Soc.* **65**, 1620 (1943).

⁸ Aston and Messerly, *J. Am. Chem. Soc.* **58**, 2354 (1936); **62**, 886 (1940).

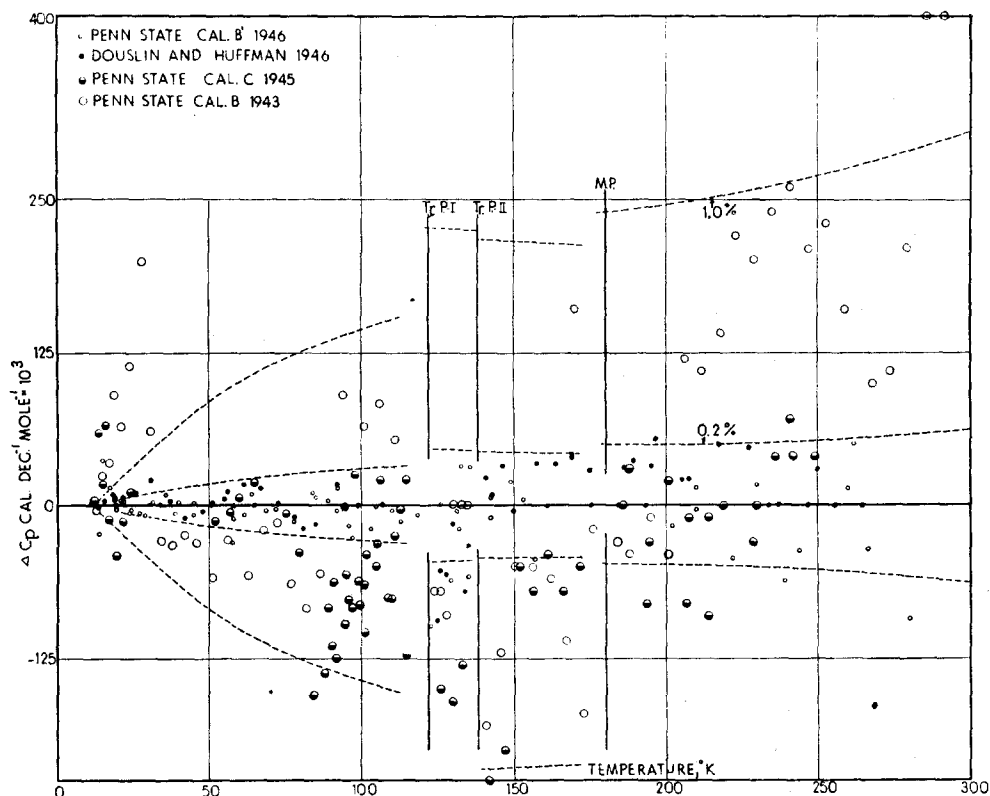


FIG. 2. Comparison plot for cyclopentane. Deviations of experimental points from smooth curve.

Pace,⁹ and in our new adiabatic calorimeter *B'* which is described in detail elsewhere.¹⁰

The results are summarized in Tables I–III and in Figs. 1 and 2. Table I is a summary of the heat capacity results at rounded temperatures of the various investigators obtained from the best curve through the data in each case, together with the percentage deviations from the “best” curve of calorimeter *B'*. Figures 1 and 2 show the deviations of the individual points from our smoothed curve. Except for the data on crystals III the results of the heat capacity measurements indicate a satisfactory agreement between the results in our adiabatic calorimeter *B'* and those of Douslin and Huffman, assuming maximum total errors of 0.10 percent and 0.15 percent, above 30°K, for the Bureau of Mines and our calorimeter, respectively. It should be emphasized that the precision and reproducibility of both calorimeters is better than 0.10 percent at any point. The few deviations in Table I which are larger than 0.25 percent are probably

due to the fact that there is a small uncertainty in the smoothing of the experimental data to obtain values at rounded temperatures.

With the exception of the value at 90°K and the data on crystals II and III, the results obtained in our isothermal calorimeter *C* are in agreement with those in *B'* within the error expected from the accuracy claimed for calorimeter *C* (± 0.3 percent above 30°K) and for *B'* (± 0.15 percent). For crystals II and III the data are difficult to reproduce and equilibrium is slow with all calorimeters, and the large differences may be due to this fact. The heat capacity results obtained in our calorimeter *B* do show marked deviations, considerably beyond the accuracy originally claimed for it. Since this calorimeter has been dismantled in 1942 (and most of it used in building calorimeter *B'*) there is no way to recheck its performance at this time. However, the main reason for the large errors was the fact that, to increase the speed of measurements, the blocks were set warm and several heat capacities taken successively with the same setting of the blocks. This produced large drifts.

⁹ For details see Ph.D. dissertation of E. L. Pace, The Pennsylvania State College (1946).

¹⁰ Aston and Szasz, J. Am. Chem. Soc. (to be published).

TABLE I. The heat capacity of cyclopentane at rounded temperatures.

T°K	C _p , cal. deg ⁻¹ mole ⁻¹				Δ% from PSC Cal. B'		
	PSC Cal. B'	Douslin and Huffman	PSC Cal. B	PSC Cal. C	Douslin and Huffman	PSC Cal. C	PSC Cal. B
Crystal I							
14	0.717	.72		0.758	0	+5.7	
15	0.878	.88	0.90	0.908	0	+3.5	+2.2
20	1.880	1.89	1.99	1.855	+0.5	-1.3	+6.1
25	3.080	3.08	3.19	3.107	0	+0.9	+3.7
30	4.310	4.33	4.37		+0.5		+1.4
35	5.523	5.53			+0.11		
40	6.660	6.64	6.68		-0.3		+0.3
45	7.663	7.66			0		
50	8.560	8.56	8.54		0		-0.3
55	9.355	9.37		9.385	+0.2	+0.3	
60	10.080	10.11	10.07	10.035	+0.3	-0.5	-0.1
70	11.37	11.37	11.36	11.31	0	-0.5	-0.1
80	12.46	12.45	12.40	12.42	-0.1	-0.3	-0.5
90	13.43	13.44	13.46	13.34	+0.1	-0.7	+0.2
100	14.32	14.32	14.40	14.27	0	-0.3	+0.5
110	15.19	15.20	15.25	15.17	0	-0.1	+0.4
Crystal II							
125	22.72			22.58		-0.6	
130	22.62	22.58	22.59	22.47	-0.2	-0.7	-0.2
135	22.53			22.42		-0.5	
Crystal III							
140	21.68	21.72	21.49	21.40	+0.2	-1.3	-0.9
150	21.45	21.56	21.38	21.31	+0.5	-0.6	-0.3
160	21.32	21.46	21.30	21.26	+0.7	-0.3	-0.1
170	21.26	21.35	21.20	21.22	+0.4	-0.2	-0.3
Liquid							
180	23.85	23.88	23.79	23.87	+0.1	+0.1	-0.2
190	24.10	24.14	24.06	24.09	+0.2	0	-0.2
200	24.42	24.45	24.42	24.39	+0.1	-0.1	0
210	24.81	24.84	24.90	24.75	+0.1	-0.2	+0.4
220	25.25	25.28	25.38	25.21	+0.1	-0.2	+0.5
230	25.74	25.76	25.94	25.74	0	0	+0.8
240	26.28	26.28	26.53	26.28	0	0	+0.9
250	26.85	26.87	27.07	26.91	+0.1	+0.2	+0.8
260	27.51	27.52	27.66		0		+0.6
270	28.19	28.22	28.31		+0.1		+0.4
280	28.90	28.93	29.10		+0.1		+0.7
290	29.68	29.68	30.05		0		+1.2
300	30.46	30.44	30.96		-0.1		+1.7

Table II, which records the transition and melting temperatures, shows a good agreement between the temperature scales used here and at the Bureau of Mines in Bartlesville. Table III shows the results on the heats of transition and fusion. The poor agreement of the heats of fusion is hard to explain as also is the unsatisfactory agreement of the heats of the upper transition. This is true for the comparison between any two sets of data and may be connected with the nature of crystals II and III.

For the low temperature extrapolation to 0°K, the following characteristic Debye Temperatures (θ) were found from the low temperature heat capacities (all assuming six degrees of freedom).

Penn State Calorimeter B ¹¹	151.6
Douslin and Huffman ⁵	151.6
Penn State Calorimeter B ¹	149.7

It should be noted that the discrepancies mentioned do not seriously affect the entropy

¹¹ Ph.D. Dissertation of G. J. Szasz, The Pennsylvania State College (1947).

TABLE II. Transition temperatures of cyclopentane.

Lower transition temperature of cyclopentane	
Aston, Fink, and Schumann	122.39 ± 0.05°K
Douslin and Huffman	122.39 ± 0.05°K
This research	122.36 ± 0.005°K
Upper transition temperature of cyclopentane	
Aston, Fink, and Schumann	138.07 ± 0.05°K
Douslin and Huffman	138.08 ± 0.05°K
Triple point temperature of cyclopentane	
Aston, Fink, and Schumann	179.69 ± 0.05°K
Douslin and Huffman	179.71 ± 0.05°K

TABLE III. Heats of transition of cyclopentane.

Molal heat of lower transition of cyclopentane	
Aston, Fink, and Schumann	1165.1 ± 0.8
Douslin and Huffman	1167.3 ± 1.0
This research	1167.4 ± 1.0
Molal heat of upper transition of cyclopentane	
Aston, Fink, and Schumann	82.80 ± 0.08
Douslin and Huffman	82.32 ± 0.19
This research	81.91 ± 0.07
Molal heat of fusion of cyclopentane	
Aston, Fink, and Schumann	144.05 ± 0.30
Douslin and Huffman	145.54 ± 0.34
This research	144.31 ± 0.30

results. Aston *et al.*⁴ obtained 48.97 ± 0.05 e.u. for $S(l)_{298.16}$, while Douslin and Huffman⁵ obtained 48.79 e.u. ± 0.10.

Figure 2 includes all results and gives a good indication of the relative accuracy of the various measurements. The actual heat capacity values used in constructing this plot can all be found elsewhere.^{4, 5, 9, 11}

Other recent comparisons between precise thermodynamic measurements performed in different laboratories are those on ethyl benzene and naphthalene. Ethylbenzene was studied by Guthrie, Spitzer, and Huffman¹², and by Scott and Brickwedde.¹³ The agreement in the heat capacities was satisfactory above 60°K, while the heats of fusion differed by 0.19 percent. Naphthalene was studied by Southard and Brickwedde,¹⁴ and by Hicks.¹⁵ The agreement was satisfactory—within the limits of the somewhat less accurate isothermal calorimeter used by Hicks.

ACKNOWLEDGMENT

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¹² Guthrie, Spitzer, and Huffman, J. Am. Chem. Soc. **66**, 2120 (1944).

¹³ Scott and Brickwedde, J. Research Nat. Bur. of Stand. **55**, 501 (1945).

¹⁴ Southard and Brickwedde, J. Am. Chem. Soc. **55**, 4378 (1933).

¹⁵ Hicks, J. Am. Chem. Soc. **60**, 1000 (1938).