Viscosity of 2,2-Dimethylpropane

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Experimental viscosity and density data for 2,2-dimethylpropane are presented for temperatures from 100° to 340° F. and pressures from 100 to 8000 p.s.i.a. The method for correlating the data is discussed, and the data are compared with literature values wherever possible.

THIS investigation is one of several recent efforts by the authors to provide viscosity data for pure hydrocarbons and mixtures (*6, 9, 11-13*).

APPARATUS AND MATERIAL

The instrument used, which has been described in detail (*8, 11*), has an effective pressure range from 14.7 to 10,000 p.s.i.a. and a temperature range from room temperature to 400° F. The design of the viscometer is based on the establishment of a manometric head between two vessels containing the test fluid and a volume of mercury. The reservoirs are connected by a capillary tube through which the test fluid flows and a tube through which mercury flows. A pressure gradient is established by elevating one of the vessels above the other; the resulting flow of mercury displaces the fluid through the capillary.

The schematic diagram of the system (Figure 1) shows the arrangement of the equipment auxiliary to the viscometer. The density cells assembly (*E*, Figure 1), which was not used in some of the previous work because of the availability of reliable data (*17*), was tested with the work reported by Sage and Lacey (*17*) on isobutane (*9*). These density cells are used in this work because no density data are found in the literature for the temperatures and pressures reported here. The principle of these cells is the same as that of a pycnometer. The cell weight and volume are calibrated from time to time. The deviation from the

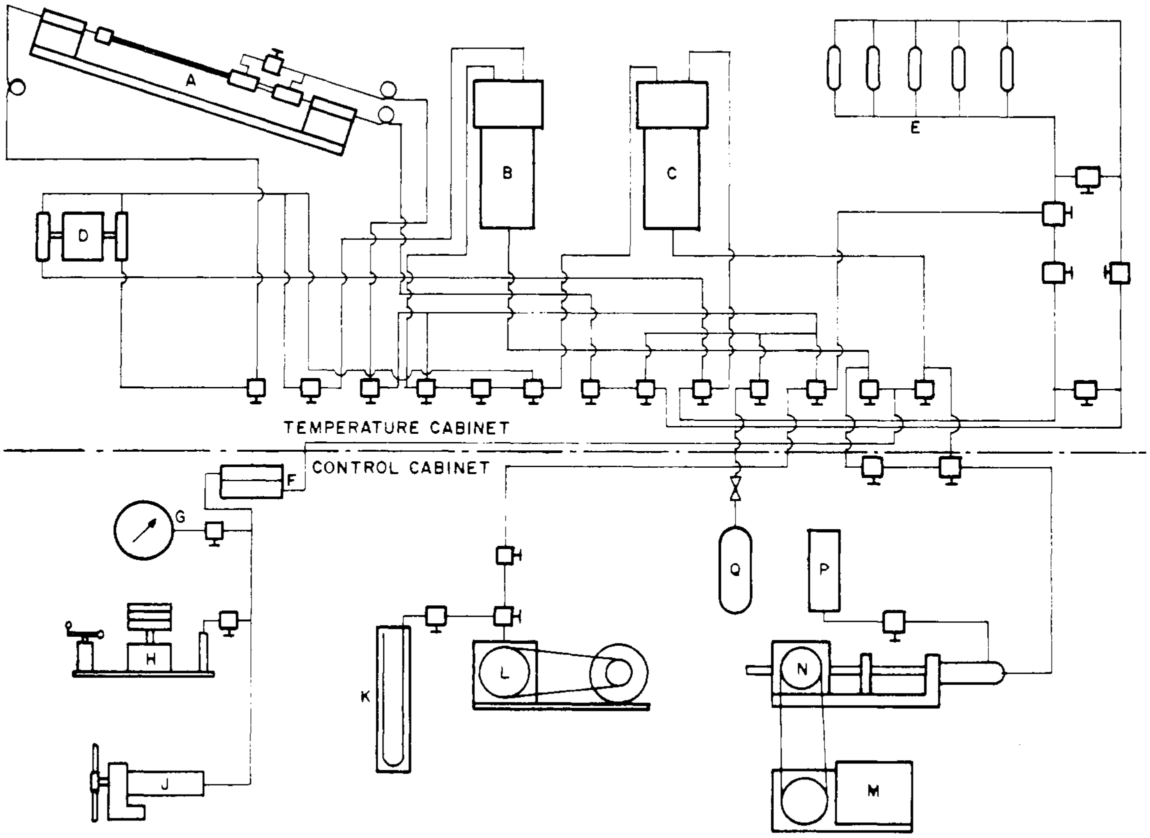

Figure 1. Schematic diagram of the viscometer instrument

A CAPILLARY ASSEMBLY
B STATIONARY VESSEL NO. 1
C STATIONARY VESSEL NO. 2
D MIXING PUMP
E DENSITY CELLS ASSEMBLY
F DIAPHRAGM SEPARATOR
G HEISE GAGE
H DEADWEIGHT TESTER
J HIGH-PRESSURE PUMP
K MANOMETER
L VACUUM PUMP
M MOTOR FOR MERCURY PUMP
N MERCURY INJECTION PUMP
P MERCURY RESERVOIR
Q SAMPLING BOMB

mean of these two parameters is less than 0.7% over a period of 2 years.

The accuracy of the viscometer has been established in previous work (*8*, *18*). Data obtained for nitrogen at ambient temperature and 1000 p.s.i.a. did not differ significantly from the accepted value of Michels and Gibson (*15*) upon application of the t-test at the 95% confidence level. The mean of the calculated values for 31 separate measurements was 192.0 micropoises with a standard deviation of ±0.6 micropoise, well within the 95% confidence range of 192.0 ±1.2 micropoises.

A number of systems reported in the API monograph on viscosity (*11*) were compared with the data reported by Giddings, Kao, and Kobayashi (*7*) and reported by Carmichael, Berry, and Sage (*3-5*). In general, the agreement has been excellent.

The precision of the viscosity measurements has also been established (*8*, *11*, *18*). The errors possibly introduced by errors in measurements of the characteristic dimensions of the instrument were analyzed (*18*). This analysis indicated the maximum error of a calculated value due to errors in these measurements to be near ±0.5%.

Phillips Petroleum Co. research grade 2,2-dimethylpropane, certified 99.92 mole % purity, was used. Mass spectrometric analysis showed no impurities.

EXPERIMENTAL DATA

All of the experimental data reported in this paper are for the liquid phase. They were obtained for pressures up to 6000 p.s.i.a. at 100° F. and up to 8000 p.s.i.a. at 160°, 220°, 280°, and 340° F.

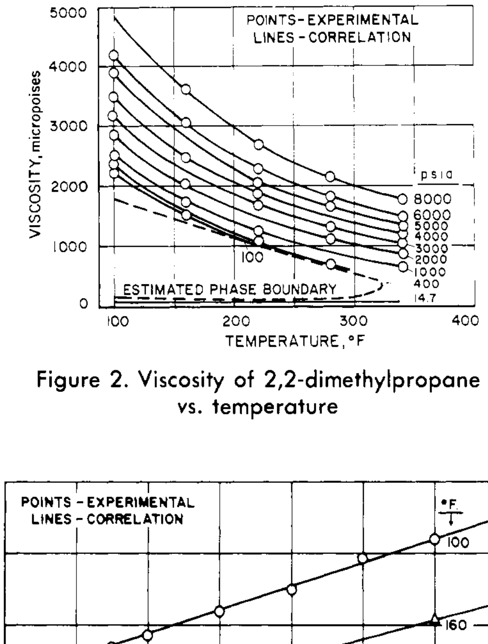

Figure 2. Viscosity of 2,2-dimethylpropane vs. temperature

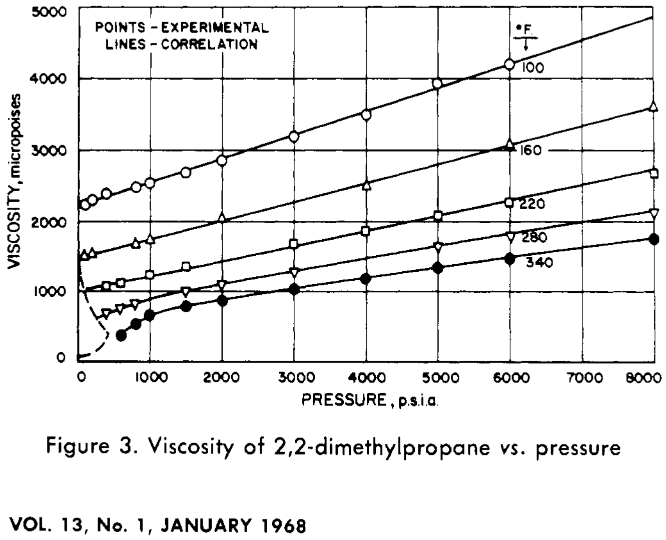

Figure 3. Viscosity of 2,2-dimethylpropane vs. pressure

Isobars of neopentane viscosity are presented in Figure 2; a cross plot of viscosity *vs.* pressure is presented in Figure 3; and density *vs.* pressure is presented in Figure 4. Detailed tables of the experimental data have been prepared and are available from the American Documentation Institute (ADI).

Comparison with Literature. No investigation of the viscosity behavior of 2,2-dimethylpropane has been reported for the range of temperatures and pressures studied in this paper. Atmospheric viscosity values for 2,2-dimethylpropane reported by McCoubrey and Singh (*14*) are used in the residual correlation below.

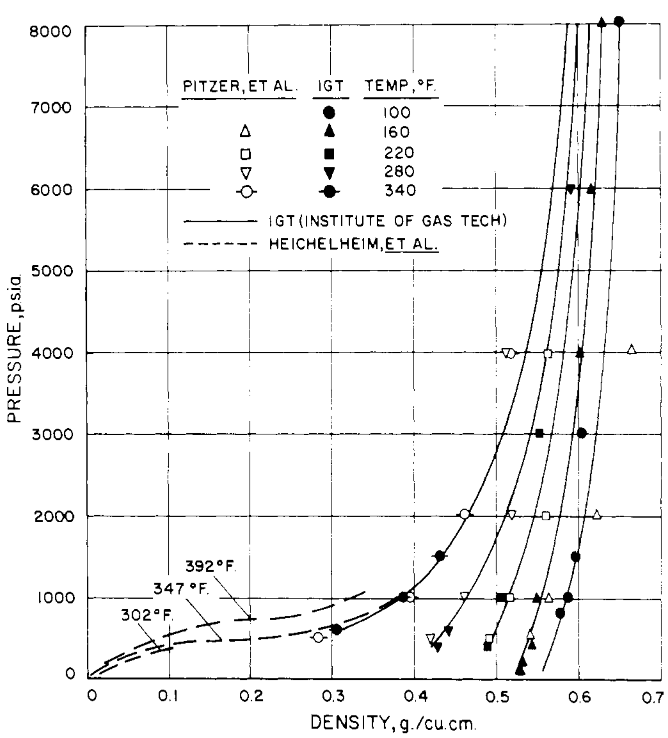

Figure 4. Comparison of density values for 2,2-dimethylpropane

Concerning the density of 2,2-dimethylpropane, Heichelheim *et al.* (*10*) reported the compressibility factor for temperatures from 30° (86° F.) to 200° C. (392° F.) and for pressures from 0.9434 to 73.157 atm. (1075 p.s.i.a.); Beattie, Douslin, and Levine (*1*) reported the compressibility for temperatures from 160° to 275° C. and for pressures from 1 to 7 atm.; and Pitzer *et al.* (*16*) used the data of Beattie, Douslin, and Levine in the comparison of their correlation with the acentric factor of 2,2-dimethylpropane.

Density values from various sources are presented in Figure 4. Low pressure data from the literature are omitted because they do not give a useful comparison. The solid symbols are the values obtained from this study, the open symbols are those calculated based on the work of Pitzer *et al.*, the dashed lines are those of Heichelhein *et al.*, and the solid lines are those obtained from cross plotting the experimental data of this investigation.

Data Treatment. The residual viscosity concept (*2*, *8*, *9*) was used. Residual viscosity is defined as the difference between the viscosity at a given pressure and temperature, and μ_o – the viscosity at the dilute gas phase, which is usually at 1 atm. pressure for most light hydrocarbons and gases at the same temperature. The residual viscosity is then plotted *vs.* density on linear coordinates; usually a smooth continuous curve may be drawn through all the data points. If the density values for a system are known for various temperatures and pressures, the viscosity values at those conditions may be interpolated from this plot. Therefore, to use the residual viscosity correlation, it is essential to know the viscosity values at the dilute gas phase, the density values, and the experimental data. As can be seen (Figure 5) the residual viscosity shows temperature dependence for 2,2-dimethylpropane, especially at lower temperatures. This behavior could be due to the lack of accurate data on μ_o – the gas phase viscosities and that on density.

Experimental data were further analyzed for internal consistency according to a technique discussed in a previous paper (*12*). $\mu/M^{0.25}$ is plotted against P_r/T_r, where μ = viscosity, micropoises; M = molecular weight = 72.146; $P_r = P/P_c$ = reduced pressure; P_c = critical pressure = 489.5 p.s.i.a.; $T_r = T/T_c$ = reduced temperature; T_c = critical temperature = 845.52° R. This plot correlates the data in straight lines, except in the region near the two-phase boundary, with temperatures as parameters. Viscosity values obtained from this correlation agree with experimental data with a maximum deviation of ±1.5% and are presented as solid lines in Figures 2 and 3.

Recommended Values. The recommended values for the viscosity and density of 2,2-dimethylpropane for temperatures from 100° to 340° F. and pressures from 14.7 to 8000 p.s.i.a. are presented in Table I (experimental data in parentheses). These values were based on the combination of values given by smoothed large-scale viscosity-pressure, viscosity-temperature, density-pressure, and density-temperature plots and the correlations mentioned above. The authors believe that the viscosity values presented in Table I are accurate to within ±1% and that the density values are accurate to within ±2%.

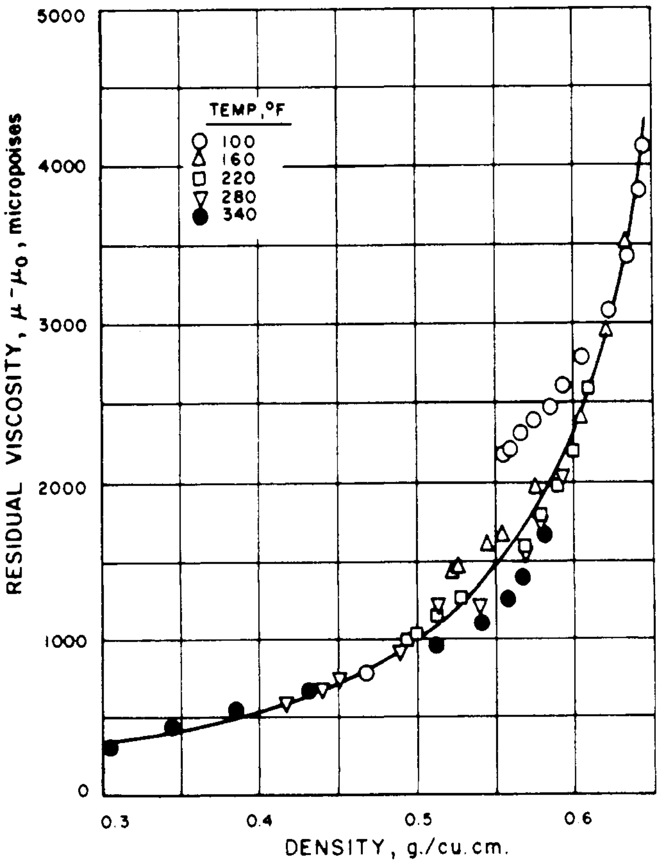

Figure 5. Residual 2,2-dimethylpropane viscosity vs. density

Table I. Viscosity and Density of 2,2-Dimethylpropane

Pressure, P.S.I.A.	100° F. Density g./cc.	100° F. Viscosity, micropoises	160° F. Density, g./cc.	160° F. Viscosity, micropoises	220° F. Density, g./cc.	220° F. Viscosity, micropoises	280° F. Density, g./cc.	280° F. Viscosity, micropoises	340° F. Density, g./cc.	340° F. Viscosity, micropoises
14.7	...	75.3	...	82.0	...	88.9	...	96	...	103
100	0.5550	2240 (2241.3)	0.5248 (0.5304)	1520 (1522.6)	...	...	...	...	...	...
200	0.5602	2270 (2269.2)	0.5280 (0.5326)	1525 (1524.7)	...	1050	...	...	...	...
300	0.5626	2310	0.5325	1551	...	1075	...	...	...	...
400	0.5660	2360 (2378.4)	0.5365 (0.5434)	1578	0.4900 (0.4888)	1090 (1086.4)	0.4175 (0.4290)	685 (690.2)	...	...
500	0.5698	2375	0.5398	1603	0.4975	1115	0.4291	702	...	...
600	0.5732	2398	0.5425	1641	0.5000	1145 (1131.8)	0.4410 (0.4434)	765 (769.9)	0.3060 (0.3059)	365 (362.1)
800	0.5752 (0.5762)	2470 (2465.2)	0.5475	1670 (1667.5)	0.5075	1182	0.4530	845 (843.8)	0.3500	540
1000	0.5851 (0.5869)	2540 (2537.5)	0.5543 (0.5494)	1735 (1736.8)	0.5147 (0.5065)	1235 (1248.1)	0.4662	898	0.3850 (0.3874)	650 (648.4)
1250	0.5897	2622	0.5611	1800	0.5225	1278	0.4800	950	0.4125	725
1500	0.5935	2700 (2698.1)	0.5665	1872	0.5277	1350 (1358.0)	0.4950	1010 (1015.1)	0.4320 (0.4308)	792 (786.6)
1750	0.6001	2790	0.5723	1940	0.5371	1379	0.5025	1050	0.4501	842
2000	0.6060 (0.5960)	2865 (2854.3)	0.5762	2020 (2032.8)	0.5450	1448	0.5140	1120 (1117.3)	0.4665	873 (863.2)
2500	0.6135	3035	0.5858	2125	0.5522	1549	0.5275	1198	0.4887	955
3000	0.6235 (0.6042)	3195 (3172.5)	0.5925	2262	0.5665 (0.5511)	1665 (1675.1)	0.5425	1300 (1302.0)	0.5100	1040 (1043.9)
3500	0.6253	3362	0.5997	2398	0.5749	1760	0.5501	1375	0.5220	1125
4000	0.6320	3515 (3493.5)	0.6050 (0.6026)	2515 (2481.9)	0.5810	1875 (1875.2)	0.5600	1465	0.5355	1200 (1198.2)
4500	0.6349	3700	0.6095	2661	0.5862	1975	0.5683	1555	0.5450	1275
5000	0.6398	3875 (3916.9)	0.6125	2695	0.5915	2070 (2063.3)	0.5730	1645 (1647.5)	0.5560	1345 (1343.6)
6000	0.6445	4200 (4191.3)	0.6192 (0.6166)	3070 (3063.8)	0.6015	2286 (2271.2)	0.5845 (0.5910)	1820 (1813.6)	0.5675	1487 (1479.6)
7000	0.6472	4538	0.6250	3332	0.6100	2515	0.5942	1985	0.5800	1631
8000	0.6503 (0.6509)	4860	0.6300 (0.6291)	3600 (3604.1)	0.6147	2720 (2683.1)	0.5975	2140 (2138.5)	0.5820	1752 (1752.3)

ACKNOWLEDGMENT

Richard Prokopek assisted in the experimental program.

LITERATURE CITED

(1) Beattie, J. A., Douslin, D. R., Levine, S. W., *J. Chem. Phys.* **20**, 1619 (1952).
(2) Breback, W. J., Thodos, G., *Ind. Eng. Chem.* **50**, 1095 (1958).
(3) Carmichael, L. T., Berry, V., Sage, B. H., J. CHEM. ENG. DATA **10**, 57 (1965).
(4) *Ibid.*, **9**, 411 (1964).
(5) Carmichael, L. T., Sage, B. H., *Ibid.*, **8**, 94 (1963).
(6) Dolan, J. P., Starling, K. E., Lee, A. L., Eakin, B. E., Ellington, R. T., *Ibid.*, **8**, 396 (1963).
(7) Giddings, G. G., Kao, J. T., Kobayashi, R., *J. Chem. Phys.* **45**, 578 (1966).
(8) Gonzalez, M. H., M.S. thesis, Institute of Gas Technology, Chicago, Ill., 1966.
(9) Gonzalez, M. H., Lee, A. L., J. CHEM. ENG. DATA **11**, 357 (1966).
(10) Heichelheim, H.R., Kobe, K.A., Silberberg, I.H., McKetta, J.J., *Ibid.*, **7**, 507 (1962).
(11) Lee, A. L., "Viscosity of Light Hydrocarbons," American Petroleum Institute, New York, 1965.
(12) Lee, A. L., Gonzalez, M. H., Eakin, B. E., J. CHEM. ENG. DATA **11**. 281 (1966).
(13) Lee, A.L., Gonzalez, M.H., Eakin, B.E., *J. Petrol. Technol.* **18**, 997 (1966).
(14) McCoubrey, J.C., Singh, N.M., *J. Phys. Chem.* **67**, 517 (1963).
(15) Michels, A., Gibson, R. O., *Proc. Roy. Soc. (London)* **134A**, 288 (1931).
(16) Pitzer, K. S., Lippman, D. Z., Curl, R. F., Huggins, C. M., Petersen, D. E., *J. Am. Chem. Soc.* **77**, 3427 (1955).
(17) Sage, B. H., Lacey, W. N., "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," API Research Project **37**, American Petroleum Institute, New York, 1950.
(18) Starling, K. E., Eakin, B. E., Ellington, R. T., *A.I.Ch.E.J.* **6**, 438 (1960).

RECEIVED for review May 8, 1967. Accepted September 22, 1967. Material supplementary to this article has been deposited as Document number 9676 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. Work supported in part by Institute of Gas Technology members and contributors and in part by the American Petroleum Institute Research Project 65.

Thermodynamic Functions for Methyl Thiocyanate

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Thermodynamic functions of heat capacity, entropy, Gibbs energy function, and enthalpy function have been calculated at selected temperatures between 273.15° and 1000° K. for methyl thiocyanate in the ideal gas state at 1 atm. pressure.

THE recent availability of vapor state far infrared spectroscopic data and the barrier to internal rotation of the methyl group have allowed the calculation of ideal gas thermodynamic functions for methyl thiocyanate. The vapor state frequencies for the low frequency vibrations are necessary, because there is usually a thermodynamically significant liquid-vapor frequency shift for the vibrations below about 250 cm.^{-1}. For example, the liquid state wavenumber for the lowest bending fundamental of methyl thiocyanate is 190.6 cm.^{-1} (*1*), and the vapor state wavenumber is 170 cm.^{-1} (*2*).

Rotational constants and the potential barrier hindering internal rotation for methyl thiocyanate have been determined recently by Nakagawa *et al.* (*3*). The principal moments of inertia used in calculating the contribution of over-all rotation are $I_a = 5.314 \times 10^{-39}$, $I_b = 20.20 \times 10^{-39}$, and $I_c = 25.03 \times 10^{-39}$ gram sq. cm. Nakagawa's value of 1592 cal. per mole for the barrier height was used in calculating the contribution of restricted internal rotation. The reduced moment of inertia for internal rotation of the methyl group was calculated by the method of Pitzer and Gwinn (*4*) to be 5.089×10^{-40} gram sq. cm.

Thermodynamic functions for methyl thiocyanate in the ideal gas state at 1 atm. pressure were calculated at selected temperatures (Table I). The contributions of translation, over-all rotation, and vibration were made with standard formulas of statistical thermodynamics (*5*). These calculations were based on the rigid rotator–harmonic oscillator model. For methyl thiocyanate, the moments of inertia for over-all rotation are independent of internal rotational coordinates, so the treatment of Pitzer and Gwinn (*4*) applies. The contributions of restricted internal rotation were taken from their tables. Vibrational contributions were calculated with the following wavenumbers for the fundamental vibrations: 170, 389, 460, 674, 705, 968, 989, 1328,

Table I. Molal Thermodynamic Properties of Methyl Thiocyanate in the Ideal Gas State

Temp., °K.	$-(G - H_0^\circ)/$ T, Cal./Deg.	$(H^\circ - H_0^\circ)/$ T, Cal./Deg.	$H^\circ - H_0^\circ$ Kcal.	S° Cal./Deg.	C_p°, Cal./Deg.
273.15	57.88	12.24	3.344	70.12	16.70
298.15	58.97	12.64	3.770	71.61	17.37
300	59.05	12.67	3.802	71.72	17.42
400	62.90	14.17	5.669	77.07	19.85
500	66.22	15.51	7.758	81.73	21.92
600	69.15	16.73	10.04	85.88	23.69
700	71.82	17.83	12.48	89.65	25.22
800	74.26	18.85	15.08	93.11	26.54
900	76.54	19.77	17.79	96.31	27.70
1000	78.66	20.62	20.62	99.28	28.70

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