Low-Temperature Thermal Data for *n*-Pentane, *n*-Heptadecane, and *n*-Octadecane

Revised Thermodynamic Functions for the *n*-Alkanes, C_5-C_{18}

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Low-temperature calorimetric data have been determined for *n*-pentane, *n*-heptadecane, and *n*-octadecane. The quantities measured by adiabatic calorimetry include the heat capacities of the solid and liquid from approximately 12° to 300° or 380° K., heats and temperatures of transition and fusion, and purity of the samples. From these data and previously published data from this laboratory, the following chemical thermodynamic properties were calculated at selected temperatures from 0° to 300° K. for the *n*-paraffins from C_5 to C_{18} in the condensed phase: Gibbs energy function, enthalpy function, enthalpy, entropy, and heat capacity. Polynomials in *N*, the number of carbon atoms, were fitted to the entropies of the 14 *n*-alkanes in the liquid state at 298.15° K., and a quadratic fit significantly better than the linear relationship previously used.

THE REGULARITY in the entropy of the *n*-alkanes with increasing number of carbons has been known and appreciated for over 30 years. In 1932, Parks and Huffman (*11*), working with incomplete data for 12 *n*-alkanes from C_4 through C_{33}, showed that for the *n*-alkanes the entropy at 298° K. could be expressed by the equation

$$S_{298} = 25.0 + 7.7n$$

in which *n* is the number of carbon atoms.

In 1950, low-temperature calorimetric studies of the nine *n*-alkanes, C_8-C_{16}, were completed in this laboratory (*2*). The entropy of each compound in the liquid state at 298.16° K. was calculated from the measured heat capacities and heats of fusion and transition. These entropies fit a linear equation in *N*, the number of carbon atoms.

$$S_{298.16}(\text{liq}) = 24.539 + 7.725N, \text{ cal./deg. mole}$$

When high purity samples became available, low-temperature calorimetric measurements were made on *n*-heptadecane and *n*-octadecane from approximately 11° to 380° K. With these new data, the correlation of the entropy at 298.15° K. could be extended. At this time, it seemed desirable to extend the range of the correlation downward by including unpublished data on *n*-pentane from this laboratory as well as previously published data on *n*-hexane (*1*) and *n*-heptane (*8*). The value for *n*-pentane from this laboratory was chosen over that reported by Messerly and Kennedy (*10*) (from which it differed by 0.20 cal. per deg. per mole) to improve the accuracy of measurement of the entropy increment by the use of data all taken with the same type of equipment and calculated by the same methods. Toward this end the thermodynamic functions for all 14 hydrocarbons were calculated by numerical integration of the smoothed heat capacities using an electronic computer.

EXPERIMENTAL

Apparatus and Physical Constants. The low-temperature calorimetric measurements on *n*-pentane, *n*-heptadecane, and *n*-octadecane, as well as the earlier measurements on the *n*-alkanes from C_8 to C_{16} by Finke *et al.* (*2*), on *n*-hexane by Douslin and Huffman (*1*), and on *n*-heptane by McCullough, and Messerly (*8*), were made with the apparatus as described by Huffman and coworkers (*5, 6, 13*). Briefly, this consisted of an aneroid adiabatic calorimeter utilizing a sealed cylindrical sample container of copper provided with about 30 internal, horizontal, heat-distributing disks spaced about 2 mm. apart. Energy was supplied through a 200-ohm bifilar constantan heater mounted internally on the same mica cross as a 50-ohm platinum resistance thermometer. The adiabatic shields were kept within 0.001° of the temperature of the calorimeter by electronic controls operating automatically to null the output of copper-constantan difference couples between sample container and adiabatic shield.

The measurements were in terms of the 1951 International Atomic Weights (*16*) and fundamental physical constants (*12*). Measurements of temperature were made using platinum resistance thermometers calibrated in terms of the International Temperature Scale of 1948 from 90° to 400° K. (*15*) and the provisional scale of the National Bureau of Standards from 11° to 90° K. (*4*). Celsius temperatures were converted to Kelvin temperatures by the addition of 273.15° (*14*). Energy was measured in terms of joules and converted to thermochemical calories by the relation, 1 cal. = 4.184 (exactly) joules. Measurements of time, electrical potential, resistance, and mass were in terms of standard devices calibrated at the National Bureau of Standards.

Some of the results in this paper were originally calculated with physical constants and temperatures related to the definition, 0° C. = 273.16° K. Temperatures here reported are all in terms of the newer definition (*14*), but only part of the experimental results were recalculated. Some small numerical inconsistencies less than the precision of the data may have been introduced by this procedure.

Materials. The samples used in this reseach were made available through the American Petroleum Institute

Research Project 44 on the "Collection, Analysis, and Calculation of Data on Properties of Hydrocarbons." These samples had been purified by American Petroleum Institute Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons," from materials supplied by the following laboratories: *n*-pentane, *n*-hexane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tetradecane, *n*-hexadecane, and *n*-octadecane by API RP 6 at the Carnegie Institute of Technology, Pittsburgh, Pa.; *n*-tridecane, *n*-pentadecane, and *n*-heptadecane by API RP 42 at the Pennsylvania State College, University Park, Pa. The *n*-pentane was dried before use with P_2O_5 and had a purity of 99.86 mole % from a calorimetric study of temperature and fraction melted (described below). The samples of *n*-heptadecane and *n*-octadecane were not dried but transferred directly to the calorimeter without exposure to air or water. The calorimetric purities of these latter two were 99.89 and 99.98 mole %, respectively.

RESULTS

Heat Capacities in the Solid and Liquid States. The heat capacities of *n*-heptadecane and *n*-octadecane in the condensed phases were measured over the approximate range 12° to 380° K. and that of *n*-pentane over the approximate range 12° to 300° K. The observed values of heat capacity at saturation pressure, C_s, are recorded for these three compounds in Table I. The temperature increments used in the measurements were small enough to obviate corrections for curvature in the C_s *vs.* T plot and are omitted

Table I. Gram-Molal Heat Capacity, Cal./Deg.

T^a	C_s^b	T^a	C_s^b	T^a	C_s^b
		n-Pentane			
		Crystals			
12.29	0.736	28.93	4.883	80.07	15.093
12.49	0.772	33.04	5.953	87.40	16.151
14.25	1.115	34.84	6.412	87.63	16.181
14.49	1.174	40.34	7.748	93.49	16.933
16.19	1.546	45.86	8.986	96.18	17.245
16.45	1.611	51.04	10.095	100.65	17.798[c]
18.70	2.148	54.81	10.849	104.65	18.303[c]
19.64	2.394	56.25	11.125	109.25	18.866[c]
22.01	3.028	60.17	11.840	113.05	19.321[c]
23.72	3.489	62.04	12.183	120.72	20.230[c]
25.13	3.861	66.59	12.948	127.82	21.160[c]
28.79	4.842	73.28	14.035	134.60	22.492[c]
		Liquid			
148.60	33.842	193.93	34.333	276.05	38.350
150.50	33.829	204.41	34.641	281.47	38.731
156.19	33.849	214.76	34.998	285.40	39.005
157.16	33.840	224.98	35.420	290.33	39.382
165.62	33.881	235.50	35.919	294.20	39.665
165.68	33.868	245.87	36.478	298.27	39.969
174.99	33.979	256.09	37.063	302.87	40.329
175.08	33.973	266.15	37.677		
184.28	34.121	273.72	38.183		
		n-Heptadecane			
		Crystals II			
11.54	1.052	41.58	17.134	147.23	58.439
12.20	1.232	45.65	19.640	154.07	60.193
12.90	1.457	50.29	22.438	168.23	63.800
13.43	1.603	51.55	23.166	175.56	65.719
14.29	1.924	55.22	25.264	183.04	67.693
14.73	2.080	57.02	26.237	189.35	69.344
16.01	2.566	62.70	29.331	196.03	71.188
16.19	2.640	68.74	32.313	203.00	73.173
17.84	3.344	75.12	35.214	209.80	75.192
17.96	3.397	81.51	38.031	216.45	77.247
19.70	4.204	83.06	38.694	222.88	79.320
20.05	4.380	88.91	41.041	228.03	81.064
21.89	5.314	95.15	43.206	229.10	81.449
22.30	5.530	101.55	45.351	234.96	83.562[d]
24.49	6.709	107.97	47.417	242.09	86.281[d]
24.82	6.888	114.44	49.417	249.39	89.388[d]
27.35	8.325	120.95	51.340	256.64	92.781[d]
27.77	8.580	121.08	51.339	263.80	96.727[d]
30.46	10.169	127.65	53.221	270.70	101.341[d]
33.97	12.368	134.15	54.978		
37.78	14.754	140.59	56.694		
T^a	C_s^b	T^a	C_s^b	T_a	C_s^b
		n-Heptadecane			
		Crystals I			
286.99	172.987[e]	291.16	209.557[e]	292.31	226.123[e]
289.81	190.949[e]				
		Liquid			
301.87	128.057	322.30	131.069	364.25	138.737
303.93	128.304	333.00	132.898	374.39	140.700
310.96	129.226	343.55	134.832	384.41	142.601
311.80	129.370	353.97	136.786		
		n-Octadecane			
		Crystals			
12.02	1.167	57.68	27.790	178.23	69.048
12.98	1.457	58.17	28.070	185.94	71.114
13.64	1.673	60.01	29.149	189.92	72.203
14.41	1.958	62.24	30.399	193.50	73.177
15.15	2.228	65.30	32.043	197.36	74.252
15.95	2.533	70.85	34.801	205.19	76.451
16.96	2.970	76.78	37.589	212.83	78.744
17.65	3.278	82.69	40.306	214.77	78.866
18.88	3.860	84.28	40.964	220.80	81.199
19.56	4.214	88.58	42.771	221.21	81.161
20.80	4.846	89.76	43.203	228.00	83.416
21.62	5.290	95.70	45.338	235.16	85.867
23.16	6.157	96.99	45.817	242.64	88.451
23.97	6.622	103.35	48.016	250.42	91.365
25.74	7.662	104.76	48.492	258.00	94.349[f]
26.57	8.169	108.50	49.672	265.37	97.440[f]
28.34	9.246	110.12	50.252	270.94	99.713[f]
29.49	9.977	111.47	50.681	271.25	99.798[f]
32.74	12.098	115.85	52.009	272.54	100.832[f]
36.29	14.426	122.87	54.127	275.67	102.318[f]
40.08	16.918	130.04	56.190	277.99	103.613[f]
44.34	19.677	137.76	58.359	278.28	103.626[f]
49.12	22.356	145.61	60.462	284.83	107.523[f]
54.14	25.740	153.53	62.559	285.09	107.536[f]
54.54	25.977	161.53	64.675	291.69	111.958[f]
54.88	26.167	169.76	66.822		
		Liquid			
304.38	136.006	326.22	139.362	358.95	145.558
310.40	136.822	328.25	139.706	368.91	147.537
316.34	137.805	338.62	141.590	378.74	149.499
318.41	138.034	348.85	143.643		

[a] T is the mean temperature (in ° K.) of each heat capacity measurement. [b] C_s is the heat capacity of the condensed phase at saturation pressure. Values of C_s are not corrected for the effects of premelting caused by impurities. [c,d,e,f] The temperature increments of these measurements are in order of increasing T, ° K.: [c] 8.408, 8.202, 8.788, 8.611, 6.710, 7.489, 6.080; [d] 6.853, 7.406, 7.195, 7.283, 7.039, 6.776; [e] 2.954, 2.692, 4.648, 2.318; [f] 7.475, 7.274, 7.178, 7.142, 7.081, 6.865, 6.943, 6.921, 6.739, 6.710, 6.489.

Table II. Gram-Molal Heat Capacity of Liquid

$C_s = A + BT + CT^2 + DT^3$, cal./deg.

Compound	A	B	10^3C	10^6D	Av. Dev., Cal./Deg.	Max. Dev., Cal./Deg.	Range, ° K
n-Pentane	43.994	−0.14067	0.54751	−0.40591	0.01	0.02	150–300
n-Hexane	66.015	−0.33174	1.31138	−1.39453	0.02	0.05	180–290
n-Heptane	56.582	−0.14490	0.57813	−0.41667	0.01	0.04	240–370
n-Octane	147.031	−1.05189	3.83123	−4.27269	0.01	0.05	220–300
n-Nonane	207.014	−1.57603	5.52339	−6.04131	0.03	0.07	225–315
n-Decane	190.004	−1.26634	4.24104	−4.31205	0.01	0.04	245–320
n-Undecane	364.793	−2.98953	10.14208	−11.03895	0.02	0.04	250–300
n-Dodecane	438.377	−3.59983	11.98237	−12.84261	0.02	0.06	270–320
n-Tridecane	855.579	−7.69471	25.61097	−27.95095	0.02	0.04	270–305
n-Tetradecane	−1040.352	+11.72160	−40.36819	+46.74124	0.01	0.03	280–300
n-Pentadecane	309.578	−1.78486	+4.94433	−3.94725	0.01	0.03	285–315
n-Hexadecane	1368.915	−11.96375	37.75152	−39.16098	0.02	0.06	295–320
n-Heptadecane	367.018	−2.28473	6.85283	−6.31643	0.02	0.05	300–385
n-Octadecane	380.871	−2.33384	6.97049	−6.39321	0.02	0.07	310–380

Table III. Triple-Point Temperatures, Gram-Molal Heats of Fusion and Transition

Compound	T_{tp}, ° K.	ΔH, Cal.	A, Deg.$^{-1}$	B, Deg.$^{-1}$
n-Pentane	143.47(m.p.)	2008 ± 0.5[a]	0.04910	0.00348
n-Heptadecane	284.22(trans.)	2615.2 ± 1.4[a]		
	295.14(m.p.)	9599.5 ± 1.0[a]	0.05545	0.00383
n-Octadecane	301.33(m.p.)	14,748 ± 3[a]	0.08173	0.00274

[a] The uncertainty indicated is the maximum deviation from the mean.

except as noted in Table I where ΔT's are given in the premelting region to enable computation of premelting corrections to C_s. The precision uncertainty of the results at temperatures above 30° K. was in general less than 0.1%. Below 30° K., the accuracy uncertainty is estimated to increase to 2% at 12° K. This is due to uncertainty in the temperature scale, insensitivity of the thermometer, and relatively large departures from adiabatic conditions during measurements. Above 30° K., the accuracy uncertainty should not exceed 0.2% except in regions near phase changes; data for the solid state will be less precise and less accurate owing to slow equilibration and uncertainties in the premelting corrections. The additional uncertainty in premelting region will have a negligible effect on the thermodynamic functions because of compensation in the heat of fusion calculation.

Empirical equations were obtained to represent the heat capacity of the 14 *n*-alkanes, C_5 through C_{18}, in the liquid state. The constants for these equations are listed in Table II, together with values of deviations from observed data as an estimate of reliability.

Heats and Temperatures of Phase Transformations. Neither *n*-pentane nor *n*-octadecane showed any solid-solid phase transitions, but *n*-heptadecane undergoes an enantiotropic phase transformation at 284.22° K., 11° below the triple-point temperature. This transition is typical of the odd-numbered paraffins above C_7, and similar transitions have been observed previously (*2*) for *n*-nonane, *n*-undecane, *n*-tridecane, and *n*-pentadecane. The heat capacity of crystals I, the phase which is stable just below the melting point, was substantially higher than that of the liquid even when corrected for heterophase premelting. This, too, was in line with previously reported data (*2*) and is probably connected with some type of "prerotation" in the solid. The heats of transition and melting were determined from the heat capacity and enthalpy measurements over temperature intervals that included the temperatures of transition or fusion. The average of two or more measurements for each compound is listed in Table III.

The triple-point temperature and sample purity for each compound were determined from studies of the equilibrium melting temperature as a function of the fraction of sample melted (*9*). The resulting melting-point summaries are given for the three compounds in Table IV. In each case, the equilibrium temperatures, T_F, were plotted as functions of $1/F$, the reciprocal of the fraction of the sample in the liquid state. The triple-point temperatures, T_{tp}, were determined by linear extrapolations to zero value of $1/F$.

Table IV. Melting-Point Summaries

F	$1/F$	T_F, ° K.	T_{calcd}, ° K.
n-Pentane (impurity = 0.14 mole %)			
0.0644	15.526	143.1010	143.0262
0.2623	3.813	143.3630[a]	143.3630
0.5140	1.946	143.4140	143.4167
0.7356	1.359	143.4354	143.4336
0.9172	1.090	143.4413[a]	143.4413
1.0000	1.000		143.4439
Pure	0		143.4726
n-Heptadecane (impurity = 0.11 mole %)			
0.1283	7.794	294.9922[a]	294.9922
0.2752	3.634	295.0710	295.0735
0.5262	1.900	295.1082	295.1075
0.7212	1.387	295.1165	295.1175
0.9040	1.106	295.1230[a]	295.1230
1.0000	1.000		295.1250
Pure	0		295.1446
n-Octadecane (impurity = 0.02 mole %)			
0.1011	9.892	301.3052	301.3019
0.2412	4.146	301.3163[a]	301.3163
0.4904	2.039	301.3210	301.3215
0.7006	1.427	301.3231[a]	301.3231
0.9029	1.108	301.3252	301.3240
1.0000	1.000		301.3242
Pure	0		301.3268

[a] Straight lines through these points were extrapolated to $1/F = 0$ to calculate triple-point temperatures.

Table V. Gram-Molal Thermodynamic Functions for Condensed Phases[a]

T, °K.	$-(G_s - H°_0)/T$, Cal./°K.	$(H_s - H°_0)/T$, Cal./°K.	$H_s - H°_0$, Cal.	S_s, Cal./°K.	C_s, Cal./°K.
n-Pentane Crystal					
10	0.034	0.103	1.028	0.137	0.408
15	0.114	0.333	4.998	0.447	1.279
20	0.259	0.716	14.311	0.975	2.485
25	0.470	1.202	30.060	1.672	3.826
30	0.737	1.751	52.53	2.488	5.155
35	1.050	2.330	81.55	3.380	6.450
40	1.399	2.922	116.87	4.321	7.672
45	1.777	3.513	158.06	5.290	8.790
50	2.178	4.095	204.73	6.273	9.874
60	3.025	5.223	313.35	8.248	11.786
70	3.911	6.284	439.8	10.195	13.502
80	4.816	7.287	582.9	12.103	15.084
90	5.729	8.233	740.9	13.962	16.487
100	6.644	9.120	912.0	15.764	17.721
110	7.553	9.958	1095.3	17.511	18.953
120	8.454	10.757	1290.8	19.211	20.138
130	9.345	11.523	1498.0	20.868	21.290
140	10.226	12.262	1716.6	22.488	22.426
143.47	10.531	12.514	1795.5	23.045	22.827
Liquid					
143.47	10.531	26.510	3803.8	37.041	33.82
150	11.714	26.828	4024	38.54	33.83
160	13.460	27.266	4362	40.72	33.86
170	15.125	27.656	4701	42.78	33.92
180	16.716	28.007	5041	44.72	34.04
190	18.238	28.330	5382	46.56	34.23
200	19.700	28.631	5726	48.33	34.50
210	21.104	28.918	6072	50.02	34.82
220	22.456	29.195	6422	51.65	35.20
230	23.759	29.466	6777	53.22	35.64
240	25.019	29.734	7136	54.75	36.15
250	26.238	30.002	7500	56.24	36.71
260	27.420	30.271	7870	57.69	37.29
270	28.567	30.543	8246	59.11	37.92
273.15	28.923	30.629	8366	59.55	38.13
280	29.683	30.818	8629	60.50	38.61
290	30.769	31.100	9018	61.86	39.34
298.15	31.636	31.334	9342	62.97	39.96
300	31.829	31.387	9416	63.21	40.10
n-Hexane Crystals					
10	0.035	0.102	1.024	0.137	0.410
15	0.117	0.349	5.229	0.466	1.328
20	0.269	0.744	14.889	1.013	2.591
25	0.488	1.254	31.360	1.742	4.003
30	0.767	1.836	55.07	2.603	5.482
35	1.096	2.459	86.06	3.555	6.907
40	1.467	3.101	124.04	4.568	8.274
45	1.869	3.748	168.66	5.617	9.571
50	2.298	4.391	219.57	6.689	10.790
60	3.210	5.648	338.9	8.858	13.030
70	4.171	6.844	479.0	11.015	14.968
80	5.159	7.972	637.7	13.131	16.747
90	6.160	9.039	813.5	15.199	18.378
100	7.165	10.044	1004.4	17.209	19.781
110	8.167	10.990	1208.8	19.157	21.099
120	9.162	11.885	1426.1	21.047	22.363
130	10.147	12.739	1656.0	22.886	23.607
140	11.122	13.558	1898.1	24.680	24.820
150	12.084	14.350	2152.4	26.434	26.049
160	13.035	15.119	2419.0	28.154	27.268
170	13.975	15.869	2697.7	29.844	28.480
177.83	14.703	16.446	2924.7	31.149	29.425
Liquid					
177.83	14.703	34.024	6050.8	48.727	40.62
180	15.11	34.10	6138	49.21	40.64
190	16.96	34.45	6545	51.41	40.76
200	18.74	34.77	6954	53.51	40.97
210	20.44	35.07	7365	55.52	41.26
220	22.08	35.36	7779	57.44	41.63
230	23.66	35.64	8198	59.30	42.09
240	25.18	35.92	8622	61.11	42.66
250	26.65	36.20	9051	62.86	43.27
260	28.08	36.49	9487	64.57	43.91
270	29.46	36.77	9930	66.24	44.59
273.15	29.89	36.87	10071	66.76	44.81
280	30.81	37.07	10379	67.88	45.31
290	32.11	37.36	10836	69.48	46.07
298.15	33.15	37.61	11215	70.77	46.71
300	33.38	37.67	11301	71.05	46.86
n-Heptane Crystals					
10	0.039	0.119	1.189	0.158	0.473
15	0.132	0.386	5.797	0.518	1.464
20	0.299	0.823	16.450	1.122	2.836
25	0.540	1.380	34.493	1.920	4.399
30	0.848	2.017	60.51	2.865	6.014
35	1.210	2.704	94.65	3.914	7.622
40	1.617	3.414	136.56	5.031	9.135
45	2.060	4.131	185.88	6.191	10.583
50	2.533	4.846	242.27	7.379	11.956
60	3.541	6.242	374.51	9.783	14.462
70	4.604	7.581	530.6	12.185	16.694
80	5.700	8.846	707.7	14.546	18.711
90	6.812	10.048	904.3	16.860	20.566
100	7.930	11.181	1118.1	19.111	22.173
110	9.047	12.250	1347.5	21.297	23.700
120	10.156	13.266	1591.9	23.422	25.164
130	11.257	14.235	1850.6	25.492	26.567
140	12.346	15.165	2123.1	27.511	27.945
150	13.423	16.064	2409.5	29.487	29.346
160	14.488	16.940	2710.4	31.428	30.863
170	15.540	17.809	3027.4	33.349	32.599
180	16.584	18.684	3363.1	35.268	34.536
182.55	16.848	18.909	3451.8	35.757	35.037
Liquid					
182.55	16.848	37.288	6806.8	54.136	48.52
190	18.34	37.72	7167	56.07	48.27
200	20.29	38.24	7649	58.54	48.15
210	22.17	38.71	8130	60.89	48.23
220	23.98	39.15	8614	63.14	48.49
230	25.73	39.57	9101	65.30	48.88
240	27.42	39.96	9592	67.39	49.38
250	29.06	40.35	10089	69.42	49.98
260	30.65	40.74	10592	71.39	50.66
270	32.20	41.12	11102	73.32	51.39
273.15	32.68	41.24	11264	73.92	51.64
280	33.70	41.50	11620	75.20	52.19
290	35.16	41.88	12146	77.05	53.04
298.15	36.33	42.19	12581	78.53	53.76
300	36.59	42.27	12681	78.86	53.93
310	37.98	42.66	13225	80.64	54.85
320	39.34	43.05	13778	82.40	55.78
330	40.67	43.45	14340	84.13	56.75
340	41.98	43.86	14913	85.84	57.76
350	43.26	44.27	15495	87.53	58.79
360	44.51	44.69	16089	89.20	59.89
370	45.74	45.11	16694	90.86	61.04
n-Octane Crystals					
10	0.037	0.112	1.122	0.149	0.449
15	0.125	0.371	5.565	0.496	1.446
20	0.288	0.813	16.257	1.101	2.917
25	0.530	1.401	35.02	1.931	4.597
30	0.844	2.081	62.42	2.925	6.357
35	1.220	2.816	98.55	4.036	8.099
40	1.646	3.580	143.20	5.226	9.758
45	2.112	4.356	196.01	6.468	11.344
50	2.611	5.130	256.50	7.741	12.853
60	3.682	6.661	399.6	10.343	15.689
70	4.820	8.127	568.8	12.947	18.105
80	5.997	9.515	761.1	15.512	20.337
90	7.194	10.834	975.0	18.028	22.354
100	8.401	12.073	1207.3	20.474	24.084
110	9.606	13.241	1456.4	22.847	25.737
120	10.807	14.348	1721.7	25.155	27.304

(*Continued on page 342*)

Table V. Gram-Molal Thermodynamic Functions for Condensed Phases[a] (*Continued*)

T, °K.	$-(G_s - H^\circ_0)/T$, Cal./°K.	$(H_s - H^\circ_0)/T$, Cal./°K.	$H_s - H^\circ_0$, Cal.	S_s, Cal./°K.	C_s, Cal./°K.
n-Octane					
Crystals					
130	11.997	15.402	2002.2	27.399	28.783
140	13.175	16.409	2297.1	29.584	30.189
150	14.341	17.374	2606.1	31.715	31.577
160	15.493	18.304	2928.6	33.79	32.93
170	16.629	19.206	3264	35.83	34.32
180	17.752	20.086	3615	37.83	35.80
190	18.861	20.955	3981	39.81	37.40
200	19.958	21.821	4364	41.77	39.18
210	21.044	22.695	4765	43.73	41.22
216.37	21.73	23.26	5033	44.99	42.61
Liquid					
216.37	21.73	46.17	9990	67.90	55.48
220	22.49	46.32	10191	68.82	55.53
230	24.56	46.73	10747	71.29	55.78
240	26.56	47.11	11307	73.67	56.19
250	28.49	47.48	11872	75.98	56.74
260	30.36	47.85	12442	78.22	57.44
270	32.17	48.22	13021	80.40	58.22
273.15	32.74	48.34	13205	81.08	58.48
280	33.93	48.59	13607	82.53	59.07
290	35.65	48.97	14202	84.62	59.98
298.15	37.01	49.28	14695	86.30	60.73
300	37.31	49.35	14807	86.67	60.90
n-Nonane					
Crystals II					
10	0.041	0.125	1.247	0.166	0.497
15	0.140	0.413	6.201	0.553	1.601
20	0.320	0.892	17.835	1.212	3.120
25	0.584	1.514	37.85	2.098	4.918
30	0.922	2.235	67.04	3.157	6.785
35	1.325	3.025	105.85	4.350	8.700
40	1.783	3.847	153.88	5.630	10.531
45	2.284	4.690	211.05	6.974	12.293
50	2.822	5.535	276.73	8.357	13.988
60	3.980	7.214	432.8	11.194	17.147
70	5.214	8.831	618.1	14.045	19.862
80	6.495	10.367	829.3	16.862	22.379
90	7.801	11.834	1065.0	19.635	24.676
100	9.121	13.216	1321.6	22.337	26.632
110	10.442	14.520	1597.2	24.962	28.478
120	11.759	15.757	1890.8	27.516	30.222
130	13.067	16.934	2201.4	30.00	31.88
140	14.363	18.060	2528.4	32.42	33.47
150	15.646	19.140	2870.9	34.78	35.02
160	16.915	20.181	3228	37.09	36.57
170	18.168	21.193	3602	39.36	38.19
180	19.408	22.185	3993	41.59	39.95
190	20.634	23.171	4402	43.80	41.89
200	21.848	24.162	4832	46.01	44.18
210	23.051	25.183	5288	48.23	47.16
217.18	23.91	25.95	5636	49.86	49.61
Crystals I					
217.18	23.91	32.86	7137	56.77	63.00
219.65	24.28	33.21	7293	57.49	64.50
Liquid					
219.65	24.28	50.04	10990	74.32	63.44
220	24.363	50.06	11013	74.42	63.43
230	26.601	50.63	11645	77.23	63.19
240	28.767	51.16	12278	79.92	63.36
250	30.86	51.65	12914	82.52	63.81
260	32.90	52.13	13555	85.03	64.47
270	34.87	52.60	14204	87.48	65.26
273.15	35.48	52.75	14410	88.24	65.53
280	36.80	53.07	14861	89.87	66.13
290	38.67	53.54	15527	92.21	67.11
298.15	40.15	53.92	16077	94.08	67.97
300	40.49	54.01	16203	94.50	68.16
310	42.27	54.48	16890	96.75	69.25
320	44.01	54.96	17588	98.97	70.40

T, °K.	$-(G_s - H^\circ_0)/T$, Cal./°K.	$(H_s - H^\circ_0)/T$, Cal./°K.	$H_s - H^\circ_0$, Cal.	S_s, Cal./°K.	C_s, Cal./°K.
n-Decane					
Crystals					
10	0.040	0.120	1.20	0.160	0.480
15	0.134	0.398	5.96	0.532	1.557
20	0.311	0.881	17.62	1.192	3.186
25	0.574	1.531	38.26	2.105	5.086
30	0.919	2.292	68.76	3.211	7.141
35	1.335	3.133	109.65	4.468	9.202
40	1.811	4.016	160.64	5.827	11.182
45	2.336	4.921	221.44	7.257	13.104
50	2.902	5.834	291.71	8.736	14.978
60	4.127	7.645	458.7	11.772	18.375
70	5.437	9.398	657.8	14.835	21.375
80	6.802	11.067	885.3	17.869	24.082
90	8.198	12.650	1138.5	20.848	26.485
100	9.608	14.142	1414.2	23.750	28.598
110	11.023	15.545	1709.9	26.568	30.542
120	12.433	16.874	2024.8	29.307	32.420
130	13.834	18.138	2357.9	31.97	34.17
140	15.223	19.344	2708.1	34.56	35.85
150	16.596	20.499	3074	37.09	37.46
160	17.955	21.609	3457	39.56	39.05
170	19.298	22.681	3855	41.97	40.65
180	20.624	23.725	4270	44.34	42.30
190	21.934	24.749	4702	46.68	44.05
200	23.230	25.758	5151	48.98	45.85
210	24.511	26.761	5619	51.27	47.81
220	25.779	27.768	6109	53.54	50.06
230	27.036	28.791	6621	55.82	52.57
240	28.283	29.839	7161	58.12	55.32
243.50	28.72	30.21	7356	58.93	56.28
Liquid					
243.50	28.72	58.39	14219	87.11	70.83
250	30.26	58.72	14680	88.98	71.10
260	32.57	59.21	15394	91.78	71.66
270	34.81	59.68	16114	94.50	72.38
273.15	35.51	59.83	16343	95.34	72.64
280	36.99	60.15	16842	97.14	73.24
290	39.11	60.62	17580	99.73	74.26
298.15	40.80	61.00	18189	101.80	75.16
300	41.17	61.09	18328	102.27	75.37
310	43.18	61.57	19087	104.76	76.52
320	45.15	62.06	19859	107.21	77.75
n-Undecane					
Crystals II					
10	0.046	0.139	1.389	0.185	0.554
15	0.154	0.454	6.804	0.608	1.732
20	0.352	0.976	19.515	1.328	3.429
25	0.641	1.662	41.54	2.303	5.412
30	1.014	2.462	73.86	3.476	7.527
35	1.458	3.342	116.97	4.800	9.716
40	1.964	4.273	170.90	6.237	11.839
45	2.522	5.231	235.37	7.753	13.954
50	3.124	6.205	310.2	9.329	15.973
60	4.428	8.150	488.9	12.578	19.737
70	5.828	10.049	703.4	15.877	23.089
80	7.289	11.869	949.5	19.158	26.092
90	8.788	13.606	1224.4	22.394	28.822
100	10.308	15.246	1524.6	25.554	31.166
110	11.833	16.793	1847.1	28.626	33.335
120	13.358	18.256	2190.7	31.61	35.35
130	14.875	19.646	2553.9	34.52	37.27
140	16.380	20.971	2935.9	37.35	39.10
150	17.870	22.240	3336	40.11	40.90
160	19.344	23.462	3753	42.80	42.68
170	20.802	24.647	4189	45.44	44.53
180	22.245	25.804	4644	48.04	46.44
190	23.670	26.943	5119	50.61	48.46
200	25.080	28.074	5614	53.15	50.66
210	26.478	29.206	6133	55.68	53.10
220	27.863	30.353	6677	58.21	55.81
230	29.237	31.52	7249	60.75	58.55
236.60	30.14	32.29	7641	62.43	60.36

(*Continued on page 343*)

Table V. Gram-Molal Thermodynamic Functions for Condensed Phases[a] (*Continued*)

T, °K.	$-(G_s - H^\circ_0)/T$, Cal./°K.	$(H_s - H^\circ_0)/T$, Cal./°K.	$H_s - H^\circ_0$, Cal.	S_s, Cal./°K.	C_s, Cal./°K.
n-Undecane					
Crystals I					
236.60	30.14	39.22	9280	69.36	81.58
240	30.70	39.83	9559	70.53	82.60
247.58	31.97	41.24	10211	73.21	90.44
Liquid					
247.58	31.97	62.65	15512	94.62	78.68
250	32.57	62.81	15703	95.38	78.75
260	35.05	63.43	16492	98.48	79.14
270	37.45	64.02	17286	101.48	79.72
273.15	38.19	64.20	17538	102.40	79.94
280	39.79	64.59	18087	104.39	80.52
290	42.07	65.16	18897	107.23	81.55
298.15	43.88	65.62	19566	109.50	82.47
300	44.28	65.73	19718	110.01	82.68
310	46.45	66.29	20551	112.75	83.90
n-Dodecane					
Crystals					
10	0.044	0.134	1.336	0.178	0.533
15	0.149	0.440	6.603	0.589	1.707
20	0.343	0.968	19.356	1.311	3.485
25	0.632	1.680	41.99	2.312	5.600
30	1.012	2.526	75.77	3.538	7.901
35	1.470	3.464	121.23	4.934	10.257
40	1.998	4.458	178.33	6.456	12.583
45	2.581	5.485	246.81	8.066	14.829
50	3.213	6.530	326.4	9.743	17.015
60	4.589	8.618	517.0	13.207	21.078
70	6.071	10.658	746.0	16.729	24.636
80	7.623	12.607	1008.5	20.230	27.850
90	9.217	14.466	1301.9	23.683	30.730
100	10.832	16.216	1621.6	27.048	33.163
110	12.455	17.862	1964.7	30.31	35.45
120	14.077	19.418	2330.1	33.49	37.61
130	15.690	20.896	2716.4	36.58	39.64
140	17.290	22.306	3122	39.59	41.60
150	18.876	23.654	3548	42.53	43.45
160	20.444	24.949	3991	45.39	45.28
170	21.995	26.198	4453	48.19	47.12
180	23.526	27.414	4934	50.94	49.04
190	25.041	28.602	5434	53.64	50.97
200	26.538	29.771	5954	56.30	53.01
210	28.017	30.92	6495	58.94	55.16
220	29.483	32.08	7058	61.56	57.46
230	30.93	33.24	7645	64.17	60.01
240	32.37	34.41	8259	66.78	62.86
250	33.80	35.61	8903	69.41	66.20
260	35.22	36.86	9584	72.08	69.99
263.58	35.73	37.32	9837	73.05	71.35
Liquid					
263.58	35.73	70.72	18641	106.45	86.80
270	37.43	71.11	19200	108.55	87.18
273.15	38.26	71.29	19475	109.56	87.39
280	40.03	71.69	20075	111.73	87.92
290	42.56	72.27	20959	114.83	88.91
298.15	44.57	72.74	21687	117.31	89.86
300	45.02	72.84	21854	117.86	90.09
310	47.41	73.42	22761	120.84	91.32
320	49.76	74.00	23681	123.76	92.62
n-Tridecane					
Crystals II					
10	0.050	0.149	1.489	0.199	0.594
15	0.167	0.494	7.403	0.661	1.883
20	0.382	1.059	21.180	1.441	3.717
25	0.696	1.802	45.05	2.498	5.893
30	1.100	2.684	80.51	3.784	8.290
35	1.586	3.664	128.22	5.250	10.795
40	2.144	4.710	188.40	6.854	13.265
45	2.761	5.798	260.92	8.559	15.707
50	3.429	6.906	345.3	10.335	18.055
60	4.885	9.140	548.3	14.025	22.482
70	6.460	11.334	793.3	17.794	26.407
80	8.112	13.439	1075.1	21.551	29.927
90	9.812	15.452	1390.6	25.264	33.040
100	11.540	17.351	1735.1	28.891	35.793
110	13.278	19.142	2105.6	32.42	38.28
120	15.017	20.838	2500.5	35.85	40.68
130	16.749	22.450	2918.5	39.19	42.90
140	18.470	23.988	3358	42.45	45.04
150	20.175	25.461	3819	45.63	47.10
160	21.863	26.877	4300	48.74	49.12
170	23.535	28.244	4801	51.77	51.13
180	25.187	29.573	5323	54.76	53.23
190	26.821	30.87	5866	57.69	55.45
200	28.437	32.16	6432	60.60	57.78
210	30.03	33.44	7022	63.48	60.31
220	31.62	34.72	7640	66.35	63.18
230	33.19	36.03	8288	69.23	66.50
240	34.75	37.38	8973	72.14	70.79
250	36.31	38.84	9710	75.15	77.12
255.00	37.08	39.63	10105	76.71	80.87
Crystals I					
255.00	37.08	46.81	11936	83.89	100.10
260	38.00	47.89	12451	85.90	106.58
267.78	39.45	49.81	13339	89.26	121.52
Liquid					
267.78	39.45	75.25	20151	114.70	94.90
270	40.07	75.41	20362	115.48	94.93
273.15	40.94	75.64	20661	116.58	94.98
280	42.82	76.11	21313	118.94	95.37
290	45.50	76.79	22271	122.30	96.31
298.15	47.64	77.34	23060	124.98	97.25
300	48.12	77.46	23240	125.59	97.47
310	50.67	78.13	24221	128.80	98.72
n-Tetradecane					
Crystals					
10	0.049	0.146	1.459	0.195	0.582
15	0.163	0.479	7.184	0.642	1.860
20	0.375	1.053	21.068	1.428	3.792
25	0.689	1.830	45.74	2.519	6.130
30	1.103	2.758	82.74	3.861	8.708
35	1.606	3.798	132.94	5.404	11.360
40	2.184	4.909	196.34	7.093	13.980
45	2.829	6.062	272.78	8.891	16.584
50	3.528	7.240	361.9	10.768	19.084
60	5.057	9.607	576.4	14.664	23.750
70	6.714	11.930	835.0	18.644	27.896
80	8.454	14.161	1132.8	22.615	31.614
90	10.245	16.288	1465.8	26.533	34.876
100	12.067	18.291	1829.1	30.35	37.71
110	13.899	20.178	2219.5	34.07	40.36
120	15.732	21.964	2635	37.69	42.82
130	17.558	23.658	3075	41.21	45.13
140	19.371	25.271	3537	44.64	47.34
150	21.167	26.815	4022	47.98	49.51
160	22.945	28.299	4527	51.24	51.60
170	24.704	29.732	5054	54.43	53.73
180	26.443	31.12	5602	57.56	55.87
190	28.163	32.48	6172	60.64	58.04
200	29.863	33.81	6763	63.68	60.29
210	31.54	35.13	7378	66.67	62.66
220	33.20	36.44	8017	69.65	65.16
230	34.85	37.74	8682	72.60	67.90
240	36.49	39.06	9376	75.55	70.89
250	38.11	40.40	10101	78.51	74.14
260	39.72	41.77	10860	81.49	77.86
270	41.32	43.18	11659	84.51	82.02
273.15	41.83	43.64	11920	85.47	83.35
279.02	42.77	44.50	12416	87.27	85.82
Liquid					
279.02	42.77	83.10	23188	125.87	102.83
280	43.06	83.17	23289	126.23	102.92
290	45.99	83.87	24323	129.86	103.91
298.15	48.32	84.43	25174	132.75	104.80
300	48.84	84.56	25368	133.40	105.01

(*Continued on page 344*)

Table V. Gram-Molal Thermodynamic Functions for Condensed Phases[a] (*Continued*)

T, °K.	$-(G_s - H^\circ_0)/T$, Cal./°K.	$(H_s - H^\circ_0)/T$, Cal./°K.	$H_s - H^\circ_0$, Cal.	S_s, Cal./°K.	C_s, Cal./°K.
n-Pentadecane					
Crystals II					
10	0.052	0.158	1.577	0.210	0.629
15	0.176	0.524	7.854	0.700	2.015
20	0.406	1.139	22.785	1.545	4.029
25	0.744	1.951	48.76	2.695	6.438
30	1.184	2.916	87.48	4.100	9.068
35	1.712	3.998	139.91	5.710	11.913
40	2.321	5.164	206.54	7.485	14.715
45	3.000	6.375	286.88	9.375	17.463
50	3.736	7.619	380.9	11.355	20.154
60	5.347	10.130	607.8	15.477	25.149
70	7.095	12.603	882.2	19.698	29.586
80	8.934	14.980	1198.3	23.914	33.606
90	10.831	17.254	1552.8	28.085	37.188
100	12.761	19.404	1940.4	32.16	40.26
110	14.707	21.432	2357.5	36.13	43.14
120	16.655	23.355	2802.6	40.01	45.82
130	18.596	25.182	3273	43.77	48.36
140	20.527	26.924	3769	47.45	50.77
150	22.442	28.592	4288	51.03	53.09
160	24.339	30.19	4831	54.53	55.39
170	26.216	31.74	5396	57.96	57.69
180	28.074	33.25	5985	61.32	60.02
190	29.911	34.72	6597	64.63	62.41
200	31.72	36.17	7233	67.89	64.94
210	33.52	37.60	7896	71.13	67.56
220	35.31	39.02	8586	74.33	70.47
230	37.07	40.46	9307	77.54	73.80
240	38.83	41.93	10063	80.76	77.49
250	40.57	43.43	10859	84.01	81.92
260	42.30	45.02	11706	87.33	87.68
270	44.03	46.77	12630	90.81	98.73
270.90	44.19	46.95	12719	91.14	100.22
Crystals I					
270.90	44.19	55.04	14910	99.23	124.40
273.15	44.65	55.63	15197	100.29	130.43
280	46.05	57.69	16153	103.74	148.78
283.10	46.69	58.74	16628	105.43	157.16
Liquid					
283.10	46.69	87.94	24896	134.63	110.96
290	48.81	88.49	25663	137.31	111.50
298.15	51.28	89.13	26575	140.41	112.32
300	51.83	89.27	26783	141.11	112.53
310	54.77	90.04	27915	144.82	113.82
n-Hexadecane					
Crystals					
10	0.053	0.160	1.599	0.213	0.638
15	0.179	0.527	7.912	0.706	2.029
20	0.410	1.150	22.998	1.560	4.110
25	0.754	1.993	49.83	2.747	6.653
30	1.205	3.005	90.15	4.210	9.492
35	1.751	4.138	144.83	5.889	12.415
40	2.383	5.360	214.41	7.743	15.404
45	3.088	6.638	298.72	9.726	18.313
50	3.855	7.946	397.3	11.801	21.126
60	5.538	10.598	635.8	16.136	26.473
70	7.368	13.202	924.1	20.570	31.070
80	9.296	15.704	1256.3	25.000	35.300
90	11.284	18.099	1628.8	29.383	39.084
100	13.310	20.358	2035.8	33.66	42.25
110	15.351	22.485	2473.3	37.83	45.22
120	17.395	24.496	2939.5	41.89	48.00
130	19.431	26.406	3432	45.83	50.62
140	21.455	28.225	3951	49.68	53.10
150	23.462	29.963	4494	53.42	55.49
160	25.449	31.63	5061	57.08	57.84
170	27.416	33.24	5651	60.65	60.19
180	29.360	34.80	6265	64.16	62.63
190	31.28	36.33	6903	67.62	65.11
200	33.18	37.83	7567	71.02	67.63
210	35.06	39.32	8257	74.38	70.29
220	36.93	40.79	8973	77.72	73.10
230	38.77	42.25	9719	81.03	76.05
240	40.60	43.73	10495	84.33	79.19
250	42.42	45.21	11304	87.63	82.57
260	44.22	46.72	12148	90.95	86.41
270	46.01	48.27	13034	94.29	90.70
273.15	46.57	48.77	13322	95.35	92.16
280	47.80	49.87	13965	97.67	95.60
290	49.57	51.54	14947	101.12	100.82
291.33	49.81	51.77	15081	101.58	101.51
Liquid					
291.33	49.81	95.54	27834	145.35	119.09
298.15	52.03	96.09	28649	148.12	119.85
300	52.62	96.23	28871	148.86	120.07
310	55.79	97.02	30078	152.82	121.43
320	58.88	97.81	31300	156.70	123.05
n-Heptadecane					
Crystals II					
10	0.057	0.173	1.73	0.230	0.689
12	0.099	0.297	3.56	0.396	1.176
14	0.157	0.466	6.53	0.623	1.804
16	0.232	0.681	10.89	0.913	2.565
18	0.328	0.936	16.85	1.264	3.417
20	0.440	1.231	24.61	1.671	4.353
25	0.807	2.114	52.85	2.921	6.995
30	1.283	3.166	94.97	4.449	9.895
35	1.858	4.349	152.21	6.207	13.016
40	2.522	5.628	225.13	8.150	16.151
45	3.261	6.971	313.7	10.232	19.247
50	4.067	8.350	417.5	12.417	22.265
60	5.837	11.145	668.7	16.982	27.904
70	7.762	13.906	973.4	21.668	32.90
80	9.794	16.563	1325.0	26.357	37.38
90	11.893	19.108	1719.7	31.00	41.43
100	14.033	21.512	2151.2	35.55	44.84
110	16.190	23.781	2615.9	39.97	48.06
120	18.350	25.933	3112	44.28	51.06
130	20.513	27.969	3636	48.48	53.86
140	22.651	29.921	4189	52.57	56.54
150	24.782	31.78	4767	56.56	59.15
160	26.891	33.57	5371	60.46	61.70
170	28.979	35.30	6001	64.28	64.26
180	31.05	36.98	6657	68.03	66.89
190	33.08	38.63	7339	71.71	69.52
200	35.11	40.24	8048	75.35	72.31
210	37.11	41.84	8786	78.95	75.25
220	39.09	43.43	9554	82.52	78.38
230	41.06	45.02	10354	86.08	81.76
240	43.00	46.63	11190	89.63	85.39
250	44.94	48.26	12064	93.20	89.55
260	46.87	49.93	12983	96.80	94.38
270	48.78	51.69	13955	100.47	100.47
280	50.70	53.58	15002	104.28	109.31
284.22	51.51	54.44	15472	105.95	113.79
Crystals I					
284.22	51.51	63.64	18088	115.15	155.61
290	52.81	65.77	19074	118.58	185.54
295.14	53.98	68.09	20096	122.07	212.17
Liquid					
295.14	53.98	100.61	29695	154.59	127.50
298.15	55.00	100.89	30080	155.89	127.71
300	55.61	101.07	30320	156.68	127.87
310	58.95	101.94	31600	160.89	129.09
320	62.21	102.81	32900	165.02	130.67
330	65.39	103.67	34210	169.06	132.38
340	68.48	104.56	35550	173.04	134.17
350	71.53	105.43	36900	176.96	136.04
360	74.51	106.31	38270	180.82	137.93
370	77.43	107.19	39660	184.62	139.85
380	80.33	108.05	41060	188.38	141.76
390	83.13	108.95	42490	192.08	143.69
n-Octadecane					
Crystals					
10	0.057	0.171	1.71	0.228	0.681
12	0.098	0.294	3.53	0.392	1.164

(*Continued on page 345*)

Table V. Gram-Molal Thermodynamic Functions for Condensed Phases[a] (*Continued*)

T, °K.	$-(G_s - H^\circ_0)/T$, Cal./° K.	$(H_s - H^\circ_0)/T$, Cal./° K.	$H_s - H^\circ_0$, Cal.	S_s, Cal./° K.	C_s, Cal./° K.
			n-Octadecane Crystals		
14	0.156	0.462	6.47	0.618	1.809
16	0.232	0.676	10.82	0.908	2.558
18	0.326	0.933	16.80	1.259	3.442
20	0.439	1.233	24.66	1.672	4.428
25	0.808	2.146	53.64	2.954	7.227
30	1.294	3.246	97.37	4.540	10.309
35	1.886	4.488	157.08	6.374	13.582
40	2.572	5.830	233.2	8.402	16.846
45	3.339	7.224	325.1	10.563	19.885
50	4.173	8.644	432.2	12.817	23.007
60	6.007	11.565	693.9	17.572	29.141
70	8.008	14.463	1012.4	22.471	34.40
80	10.123	17.250	1380.0	27.373	39.09
90	12.309	19.918	1792.6	32.23	43.29
100	14.540	22.435	2243.5	36.98	46.86
110	16.790	24.811	2729.2	41.60	50.21
120	19.044	27.058	3247	46.10	53.27
130	21.297	29.185	3794	50.48	56.18
140	23.539	31.21	4370	54.75	58.97
150	25.758	33.15	4973	58.91	61.63
160	27.95	35.02	5603	62.97	64.27
170	30.14	36.81	6258	66.95	66.89
180	32.28	38.56	6940	70.84	69.52
190	34.41	40.26	7649	74.67	72.23
200	36.52	41.93	8385	78.45	74.98
210	38.61	43.57	9149	82.18	77.88
220	40.67	45.20	9943	85.87	80.95
230	42.72	46.82	10768	89.54	84.09
240	44.75	48.44	11626	93.19	87.53
250	46.75	50.08	12520	96.83	91.20
260	48.76	51.73	13451	100.49	95.14
270	50.74	53.42	14424	104.16	99.58
273.15	51.36	53.96	14740	105.32	101.07
280	52.71	55.16	15444	107.87	104.47
290	54.67	56.96	16517	111.63	110.42
298.15	56.28	58.49	17440	114.77	116.07
300	56.64	58.85	17656	115.49	117.48
301.33	56.90	59.11	17813	116.01	118.53
			Liquid		
301.33	56.90	108.05	32561	164.96	135.59
310	59.98	108.84	33740	168.82	136.77
320	63.44	109.75	35120	173.19	138.30
330	66.83	110.64	36510	177.47	140.02
340	70.15	111.53	37920	181.68	141.87
350	73.39	112.43	39350	185.82	143.85
360	76.59	113.31	40790	189.90	145.77
370	79.70	114.22	42260	193.92	147.77
380	82.76	115.13	43750	197.89	149.93
385	84.28	115.58	44500	199.86	151.04

[a] The values tabulated are the Gibbs energy function, enthalpy function, enthalpy, entropy, and the heat capacity of the condensed phase at saturation pressure.

If the impurities form ideal solutions in the liquid phase and are insoluble in the solid phase, the relation between mole fraction of total impurity, N_2^*, and melting-point depression, ΔT, is (*3*)

$$-\ln(1 - N_2) = A\Delta T(1 + B\Delta T + C\Delta T^2 \ldots) \qquad (1)$$

where $N_2 = N_2^*/F$. The cryoscopic constants, $A = \Delta Hm/RT_{tp}^2$ and $B = 1/T_{tp} - \Delta Cm/2\Delta Hm$, were calculated from the values of ΔHm and T_{tp} in Table IV and from values of ΔCm, the difference between the heat capacities of the compound in the solid and liquid states at the triple point, obtained from data in Table V (discussed below). Values of A and B are included in Table III. Impurity values given in Table IV were calculated using Equation 1 in its simplified form (for $N_2^* << 1$), $N_2^* = AF\Delta T$.

The value of the transition temperature for *n*-heptadecane was calculated by plotting equilibrium temperature, T_F, as a function of $1/F$, the reciprocal of the fraction transposed, and taking as the temperature of transition, T_T, the value of T_F from a linear extrapolation to $1/F = 1$.

Chemical Thermodynamic Properties in the Solid and Liquid States. The low-temperature thermal data for *n*-pentane, *n*-heptadecane, and *n*-octadecane, together with data previously obtained in this laboratory for the *n*-alkanes from C_6 to C_{16} (*1, 2, 8*), were used to calculate values of the Gibbs energy function, enthalpy function, enthalpy, entropy, and heat capacity for the 14 *n*-alkanes from C_5 to C_{18} in the condensed phases at selected temperatures from 10° to 300° or 390° K. The values at 10° K. were calculated from a Debye function whose parameters (Values of degrees of freedom, F°, and Debye characteristic temperature, θ_D, are respectively: for *n*-pentane, 4° and 123.6°; *n*-heptadecane, 9.5° and 128.7°; and *n*-octadecane, 10° and 131.34°. Values of F° and θ_D for the other *n*-alkanes may be found in references *1, 2,* and *8*.) were evaluated from the heat capacity data between 11° and 20° K. Thermodynamic properties above 10° K. were calculated from values of the heat and temperature of phase changes and from appropriate integration of smoothed values of C_s at regular intervals. The results are listed in Table V. Corrections for the effects of premelting were applied as necessary, using the impurities measured in the melting point studies, in computing the smoothed data in Table V.

DISCUSSION AND CONCLUSIONS

On the basis of the data available in 1954, the values of the entropy at 298.16° K. for the liquid *n*-alkanes from C_8 through C_{16} fit a linear equation in N, the number of carbon atoms (*2*). Only insignificant improvement could be attained by the use of a quadratic in N. The recalculation of the values of the 298.15° entropy for the C_8 to C_{16} alkanes lowered the values for *n*-octane and *n*-nonane slightly while raising all others a small amount. The maximum change amounted to 0.05% for *n*-dodecane.

By the use of a program written for a CDC G-15 computer, polynomials in N could be fitted to the entropy data by a least-squares technique based on orthogonal polynomials. The recalculated values of the entropy at 298.15° K. for all 14 *n*-alkanes from C_5 to C_{18} were fitted by this means to first- and second-degree polynomials giving equal weight to all data. The constants of the equations obtained are given below:

$$S_{298.15^\circ\,\mathrm{K.}} = 24.363 + 7.735N;\ sy = 0.07085$$

$$S_{298.15^\circ\,\mathrm{K.}} = 23.972 + 7.821N - 0.0037315N^2;\ sy = 0.02414$$

In these equations, *sy*, the standard error of estimate (*17*), is defined by

$$sy = \left[\frac{\Sigma(S_{\mathrm{obsd}} - S_{\mathrm{calcd}})^2}{k}\right]^{1/2}$$

k is the number of observations, in this case 14. The smaller standard error of estimate indicates a better fit to the data for the quadratic, as would be expected. To determine if the improvement was significant, the null hypothesis for the quadratic term was tested by statistical procedures and was significant with about 95% confidence. [Student's *t* (*7*) was 2.38 for 11 degrees of freedom.]

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LITERATURE CITED

(1) Douslin, D.R., Huffman, H.M., *J. Am. Chem. Soc.* **68**, 1704 (1946).
(2) Finke, H.L., Gross, M.E., Waddington, G., Huffman, H.M., *Ibid.*, **76**, 333 (1954).
(3) Glasgow, A.R., Jr., Streiff, A.J., Rossini, F.D., *J. Res. Natl. Bur. Std.* **35**, 355 (1945).
(4) Hoge, H.J., Brickwedde, F.G., *Ibid.*, **22**, 351 (1939).
(5) Huffman, H.M., *Chem. Rev.* **40**, 1 (1947).
(6) Huffman, H.M., Todd, S.S., Oliver, G.D., *J. Am. Chem. Soc.* **71**, 584 (1949).
(7) Mandel, John, "The Statistical Analysis of Experimental Data," Interscience, New York, 1964.
(8) McCullough, J.P., Messerly, J.F., *U.S. Bur. Mines Bull.* **596** (1961).
(9) McCullough, J.P., Waddington, G., *Anal. Chim. Acta* **17**, 80 (1957).
(10) Messerly, G.H., Kennedy, R.M., *J. Am. Chem. Soc.* **62**, 2988 (1940).
(11) Parks, G.S., Huffman, H.M., "The Free Energies of Some Organic Compounds," Chemical Catalog Co., New York, 1932.
(12) Rossini, F.D., Gucker, F.T., Jr., Johnston, H.L., Pauling, L., Vinal, G. W., *J. Am. Chem. Soc.* **74**, 2699 (1952).
(13) Scott, D.W., Douslin, D.R., Gross, M.E., Oliver, G.D., Huffman, H.M., *Ibid.*, **74**, 883 (1952).
(14) Stimson, H.F., *Am. J. Phys.* **23**, 614 (1955).
(15) Stimson, H.F., *J. Res. Natl. Bur. Std.* **42**, 209 (1949).
(16) Wichers, E., *J. Am. Chem. Soc.* **74**, 2447 (1952).
(17) Worthing, A.G., Geffner, J., "Treatment of Experimental Data," p. 273, Wiley, New York, 1943.

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Thermodynamic Excess Properties for Ethanol–*n*-Heptane

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Thermodynamic property changes of mixing, both total and partial, are presented as functions of temperature and composition for the binary liquid system ethanol–*n*-heptane. Results are applied to the calculation of vapor-liquid equilibria at atmospheric pressure.

IN A RECENT paper (*14*) correlations were presented for the property changes of mixing ΔC_p, ΔH, ΔS^E, and ΔG^E as functions of temperature at a series of compositions for the ethanol-toluene, 1-propanol-*n*-heptane, and 2-propanol-*n*-heptane systems. This paper is devoted to a similar correlation of an extensive set of data for the binary liquid system ethanol-*n*-heptane. No attempt is made here to relate these data to any theory of molecular interactions. However, in another publication (*15*) the heat-of-mixing data reported are used in conjunction with infrared spectral data to determine the nature of ethanol association in hydrocarbon solutions.

It is assumed that the heat capacity change of mixing for a solution of given composition is given as a function of temperature by:

$$\frac{\Delta C_p}{x_1x_2R} = A + BT + DT^2 \qquad \text{(constant composition)} \tag{1}$$

The following equations then result from basic thermodynamic relations (*12*):

$$\frac{\Delta H}{x_1x_2R} = AT + \frac{BT^2}{2} + \frac{DT^3}{3} + C \tag{2}$$

$$\frac{\Delta G^E}{x_1x_2R} = -AT\ln T - \frac{BT^2}{2} - \frac{DT^3}{6} + C + IT \tag{3}$$

$$\frac{\Delta S^E}{x_1x_2R} = A\ln T + BT + \frac{DT^2}{2} + (A - I) \tag{4}$$

where T is the absolute temperature, and A, B, C, D, and I are constants. B has the dimensions of T^{-1}; D, the dimensions of T^{-2}; and C, the dimensions of T. A and I are dimensionless.

If the property changes of mixing ΔC_p, ΔH, ΔG^E, and ΔS^E of Equations 1 through 4 are each represented by ΔM, then the corresponding partial molar property changes of mixing are designated $\overline{\Delta M}_i$, where by definition

$$\overline{\Delta M}_i = \frac{\partial(n\Delta M)}{\partial n_i}$$

The temperature dependence of these partial molar property changes of mixing is given by equations analogous to Equations 1 through 4, namely:

$$\frac{\overline{\Delta C}_{p_i}}{R} = A_i + B_iT + D_iT^2 \tag{5}$$

$$\frac{\overline{\Delta H}_i}{R} = A_iT + \frac{B_iT^2}{2} + \frac{D_iT^3}{3} + C_i \tag{6}$$

$$\frac{\overline{\Delta G}_i^E}{R} = -A_iT\ln T - \frac{B_iT^2}{2} - \frac{D_iT^3}{6} + C_i + I_iT \tag{7}$$

and

$$\frac{\overline{\Delta S}_i^E}{R} = A_i\ln T + B_iT + \frac{D_iT^2}{2} + (A_i - I_i) \tag{8}$$

Since the total property changes of mixing for a binary system are obtained from partial molar values according to the relation:

$$\Delta M = x_1\overline{\Delta M}_1 + x_2\overline{\Delta M}_2$$

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