J. Chem. Thermodynamics **1971**, 3, 675–687

Low-temperature thermal properties of 2-methylheptane and 2-methyldecane: the thermodynamic properties of the 2-methylalkanes † ‡

J. F. MESSERLY and H. L. FINKE

Bartlesville Petroleum Research Center, Bureau of Mines,
U.S. Department of the Interior, Bartlesville, Oklahoma 74003, U.S.A.

(*Received 27 March 1971*)

Experimental measurements were made of the low-temperature thermal properties of 2-methylheptane and 2-methyldecane from 12 to 360 K and 12 to 390 K, respectively. From these measured values and data from the literature the following chemical thermodynamic properties were calculated at selected temperatures for the condensed phases of 2-methylbutane, 2-methylpentane, 2-methylhexane, 2-methylheptane, and 2-methyldecane: Gibbs energy function, enthalpy function, enthalpy, entropy, and heat capacity. The entropies of 2-methylheptane and 2-methyldecane in the ideal gas state at 298.15 K were calculated and methylene entropy increments obtained for the 2-methylalkanes, C_5 to C_{11}.

1. Introduction

The low-temperature thermal studies reported in this paper are part of a long-range continuing program to determine the thermodynamic properties of hydrocarbons. For several series of hydrocarbons at 298.15 K the incremental increase in molar entropy associated with the addition of a methylene group has been found to be nearly constant: the *n*-paraffins,(1) the *n*-alkylcyclopentanes,(2) the *n*-alkylcyclohexanes,(3) the *n*-alkylbenzenes,(4) and the 1-olefins.(5) For several years values of the entropy have been available for 2-methylpropane,(6) 2-methylbutane,(7) 2-methylpentane,(8) and 2-methylhexane.(9) The limited number of experimental data and the irregular increments found in the API 44 tables(10) for the first four members of the series of 2-methylalkanes indicated a need for more measurements. Third-law studies were made on 2-methylheptane and 2-methyldecane to extend the series and provide a solid basis for extrapolation.

---

† This investigation was part of American Petroleum Institute Research Project 62, "Thermodynamics of Hydrocarbons from Petroleum," which the Bureau of Mines conducts at Bartlesville, Oklahoma.

‡ Contribution No. 185 from the thermodynamics laboratory of the Bartlesville Petroleum Research Center.

2. Experimental

METHODS AND APPARATUS

Measurements of the low-temperature thermal properties of 2-methylheptane and 2-methyldecane were made in an adiabatic calorimeter similar to one previously described by Huffman and co-workers.(11–13) Heat capacities and enthalpies of transition were determined by measuring the equilibrium temperature, adding a measured quantity of energy, and again measuring the equilibrium temperature. Adiabatic conditions were maintained during this process by automatically controlling the temperature of the heated shield within 0.005 K of the sample container. The experimental quantities are recorded in terms of the 1962 International Atomic Weights(14) and 1963 fundamental physical constants.(15) Temperature was measured by means of platinum resistance thermometers calibrated in terms of the International Practical Temperature Scale of 1948(16) from 90 to 400 K, and the provisional scale of the National Bureau of Standards(17) from 11 to 90 K, and later converted to terms of the International Practical Scale of 1968.(18) Celsius temperatures were converted to thermodynamic temperatures by the relation $0\ ^\circ\mathrm{C} \triangleq 273.15\ \mathrm{K}$. Measurements of mass, time, electrical resistance, and potential were made with standards traceable to the U.S. National Bureau of Standards. Energies were calculated in joules and converted to calories by the relation $1\ \mathrm{cal} = 4.184\ \mathrm{J}$.

MATERIALS

The samples of 2-methylheptane and 2-methyldecane used in this study were API research hydrocarbons, purified and made available by American Petroleum Institute Research Project 58B at the Carnegie-Mellon University, A. J. Streiff, Director. The sample of 2-methylheptane was dried with a molecular sieve, and 28.906 g was forced into the calorimeter by helium gas at a pressure of 14 Torr. As the sample of 2-methyldecane did not show ice "floaters" when frozen and allowed partially to melt, it was used as received: 39.266 g was forced into the calorimeter with helium gas at a pressure of 31 Torr. The purities of 2-methylheptane and 2-methyldecane samples were later found to be 99.969 moles per cent and 99.979 moles per cent, respectively, as discussed in the section on melting-temperature studies and purity.

3. Results

HEAT CAPACITIES

The heat capacities of the condensed phases of 2-methylheptane and 2-methyldecane were measured under saturation pressure from 11 to 370 K and from 12 to 385 K, respectively. In either compound only one crystalline phase was found, and the heat capacity curves of the crystals showed the normal sigmoid shape from the lowest temperatures to the melting temperatures with no regions of anomalous behavior. The molar heat capacities (table 1) were corrected for partial vaporization into the gas space in the sample containers but were *not* corrected for the effects of premelting. The measurements were made with temperature increments small enough to eliminate the need for a correction for curvature; the temperature rise was approximately 10 per cent

TABLE 1. Experimental molar heat capacity

T_m[a] / K	C_s[b] / cal K^{-1} mol^{-1}	T_m[a] / K	C_s[b] / cal K^{-1} mol^{-1}	T_m[c] / K	C_s[b] / cal K^{-1} mol^{-1}
2-Methylheptane (crystals)					
11.448	0.970	46.558	12.095	115.723	26.747
11.867	1.062	51.738	13.540	116.379	26.993
12.906	1.315	51.871	13.532	120.187	27.510
13.239	1.411	57.558	15.043	120.991	27.721
14.429	1.741	63.688	16.595	121.341	27.636
14.693	1.812	69.721	17.983	124.863	28.309[c]
15.961	2.197	75.602	19.279	126.043	28.522[c]
16.313	2.296	79.723	20.248	126.859	28.641[c]
17.476	2.666	81.851	20.615	127.224	28.588[c]
18.240	2.905	83.817	21.080	130.921	29.044[c]
19.163	3.209	86.691	21.608	133.334	29.571[c]
20.365	3.605	88.107	21.898	133.798	29.878[c]
21.109	3.867	89.923	22.246	134.069	29.625[c]
22.739	4.420	93.740	22.980	137.739	30.325[c]
23.214	4.576	98.425	23.863	139.229	30.343[c]
25.421	5.354	101.661	24.421	141.042	30.691[c]
25.675	5.451	103.598	24.831	142.922	31.155[c]
27.927	6.216	106.715	25.341	144.680	31.344[c]
28.124	6.286	108.811	25.683	145.363	31.470[c]
30.912	7.233	109.939	25.751	146.770	31.750[c]
34.239	8.334	111.649	26.147	147.872	31.613[c]
38.040	9.543	114.170	26.570	151.753	32.317[c]
42.005	10.753	115.423	26.814		
2-Methylheptane (liquid)					
177.622	50.877	226.062	53.419	301.474	60.587
177.734	50.891	234.923	54.111	312.974	61.892
183.390	51.165	244.616	54.942	321.830	62.907
187.203	51.244	254.999	55.905	334.111	64.372
188.983	51.347	258.198	56.164	345.776	65.818
196.657	51.661	268.299	57.135	357.604	67.327
205.991	52.113	278.688	58.168	369.590	68.868
217.029	52.900	289.763	59.339		
2-Methyldecane (crystals)					
12.165	1.244	36.592	11.307	120.046	34.896
13.335	1.549	40.664	13.068	124.364	35.767
13.889	1.725	45.444	15.056	124.556	35.759
14.645	1.968	50.800	16.903	130.803	36.915
15.473	2.257	54.470	18.132	138.330	38.304
16.056	2.457	56.198	18.718	146.461	39.765
17.186	2.877	60.441	20.115	154.763	41.248
17.568	3.023	66.158	21.946	162.684	42.641
19.199	3.666	72.116	23.655	170.854	44.104[d]
19.418	3.764	78.267	25.341	179.224	45.654[d]
21.458	4.612	78.311	25.349	187.365	47.211[d]
21.623	4.691	81.220	26.149	194.570	48.657[d]
23.978	5.714	86.742	27.601	195.245	48.711[d]
24.180	5.805	94.453	29.423	200.163	49.669[d]
26.753	6.950	98.952	30.473	202.930	50.353[d]
27.053	7.107	102.494	31.266	209.459	51.719[d]
29.688	8.245	107.485	32.333	216.110	53.541[d]
32.928	9.691	116.259	34.151		

TABLE 1—*continued*

T_m[a] / K	C_s / cal K^{-1} mol^{-1} [b]	T_m[a] / K	C_s / cal K^{-1} mol^{-1} [b]	T_m[a] / K	C_s / cal K^{-1} mol^{-} [b]
		2-Methyldecane (liquid)			
235.442	74.766	276.589	78.786	335.446	86.880
237.710	74.979	286.251	79.967	342.460	88.058
240.659	75.149	295.783	81.216	345.155	88.357
246.507	75.659	302.598	82.195	356.085	90.053
248.285	75.744	311.950	83.525	366.848	91.779
256.182	76.511	321.850	84.954	375.231	93.178
257.243	76.599	332.247	86.479	384.795	94.739
266.800	77.627				

[a] T_m is the mean temperature 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] The temperature increments of these measurements are, in order of increasing T: [c] $\Delta T/\mathrm{K} = 9.166$, 5.544, 6.605, 6.224, 4.220, 6.008, 8.719, 2.089, 5.261, 5.905, 5.836, 5.112, 6.841, 6.401, 5.645, 4.833, 7.313; [d] $\Delta T/\mathrm{K} = 8.451$, 8.302, 7.995, 5.851, 7.793, 5.361, 7.608, 6.756, 6.576.

of the absolute temperature below 50 K, from 5 to 7 K in the solid, and approximately 10 K in the liquid state.

The precision uncertainty of the heat capacity was quite high, about 1 per cent, at the lowest temperature, decreasing rapidly above 20 K to 0.2 per cent for the measurements made in the solid state and to 0.1 per cent for the liquid. Accuracy uncertainties are estimated to be slightly greater than precision uncertainties for temperatures below 300 K, but are believed to increase gradually to 0.3 per cent at 380 K.

The measured heat capacities for liquid 2-methylheptane and 2-methyldecane were expressed by cubic equations in T, fitted by least-squares adjustments. The parameters are given in table 2, together with parameters for 2-methylbutane, 2-methylpentane, and 2-methylhexane obtained from literature data corrected to IPTS-68.(18)

TABLE 2. Equations for the molar heat capacity of the liquid:

$$C_s(\mathrm{l})/\mathrm{cal\,K^{-1}\,mol^{-1}} = A + B(T/\mathrm{K}) + C(T/\mathrm{K})^2 + D(T/\mathrm{K})^3;$$

where T_1 and T_2 are the lower and upper bounds of the temperature range; $\langle\delta\rangle$ is the average deviation and $\delta_{\max}$ the maximum deviation of the measured values of $C_s(\mathrm{l})/\mathrm{cal\,K^{-1}\,mol^{-1}}$ from the equation

Compound	A	$B \times 10^2$	$C \times 10^4$	$D \times 10^7$	T_1/K	T_2/K	$\delta_{\max}$	$\langle\delta\rangle$
2-Methylbutane	26.172	2.79891	−0.210397	2.55883	115	294	0.04	0.02
2-Methylpentane	34.591	−2.05280	+2.19155	−0.615477	103	303	0.04	0.02
2-Methylhexane	41.839	−3.00163	2.42310	−0.429397	160	300	0.03	0.01
2-Methylheptane	63.335	−19.6637	8.42352	−7.30726	178	370	0.07	0.03
2-Methyldecane	111.065	−46.9445	16.9980	−15.3468	235	385	0.09	0.04

ENTHALPIES OF FUSION, TRIPLE-POINT TEMPERATURES, AND SAMPLE PURITIES

The enthalpies of fusion for 2-methylheptane and 2-methyldecane were determined by replicate enthalpy measurements over temperature intervals that included the triple points. By use of the integrals of the heat capacity curves, corrected for premelting, below and above the triple points, the isothermal enthalpies of fusion for the pure materials at the triple point were calculated.(20) The values obtained for the enthalpies of fusion, together with values of the triple-point temperatures and derived cryoscopic constants, are given in table 3.

TABLE 3. Enthalpies of fusion ΔH_m, triple point temperatures T_{tp}, and cryoscopic constants

Compound	ΔH_m/cal mol^{-1}	T_{tp}/K	A/K^{-1} [a]	B/K^{-1} [b]
2-Methylheptane	2852.3	164.193	0.05318	0.003 347
	2846.8			
	2848.4			
Average:	2849			
2-Methyldecane	5989.0	224.311	0.05997	0.002 891
	6002.3			
	5998.1			
Average:	5996			

[a] The value of A is calculated from the equation, $A = \Delta H_m/RT_{tp}^2$.

[b] The value of B is calculated from the equation, $B = 1/T_{tp} - \Delta C_m/2\Delta H_m$, where ΔC_m is the difference in molar heat capacity of liquid and solid at the triple point.

MELTING-TEMPERATURE STUDIES AND PURITY

The melting temperatures of 2-methylheptane and 2-methyldecane were studied calorimetically by melting successive fractions of each crystal and observing the equilibrium temperature T corresponding to the fraction melted F. Under the assumptions that the solute–solvent system obeys Raoult's law and that the solute is liquid-soluble, solid-insoluble, the relation between the mole fraction x_2 of solute and the depression ΔT of the melting temperature is expressed by the equation:(21)

$$-\ln(1-x_2/F) = A\Delta T(1+B\Delta T+C\Delta T^2+\ldots). \tag{1}$$

The cryoscopic constants, $A = \Delta H_m/RT_{tp}^2$ and $B = (1/T_{tp}-\Delta C_m/2\Delta H_m)$, were calculated from the observed values of ΔH_m and T_{tp} as shown in table 4, and from values of ΔC_m, the difference between the heat capacities of the compound in the liquid and solid states at the triple point, obtained from the data listed in table 5 (discussed below). In table 4 are listed the melting-temperature summaries of 2-methylheptane and 2-methyldecane. If equation (1) is truncated after the first term and the approximation, $-\ln(1-x_2/F) = x_2/F$, is made, the resultant equation is a linear equation between $1/F$ and T.

$$x_2/F = A\Delta T = AT_{tp}-AT. \tag{2}$$

Equation (2) was fitted to the data in table 4. Extrapolation of equation (2) to $1/F = 0$ gives the triple-point temperature T_{tp} of the pure material. The mole fraction x_2 of impurity in each sample, evaluated from the slope of equation (2), is listed in table 4.

TABLE 4. Melting-temperature summaries

F	$1/F$	$T(\text{obs.})/\text{K}$	$T(\text{calc.})/\text{K}$
2-Methylheptane ($x_2 = 0.00031$)			
0.10666	9.376	164.1438	164.1383
0.25590	3.908	164.1701	164.1701
0.50597	1.976	164.1817	164.1813
0.70715	1.414	164.1848	164.1846
0.90622	1.103	164.1864	164.1864
1.00000	1.000		164.1870
Pure	0		164.1928
2-Methyldecane ($x_2 = 0.00021$)			
0.09603	10.413	224.2795	224.2736
0.22415	4.461	224.2947	224.2947
0.38553	2.594	224.3013	224.3013
0.61228	1.633	224.3046	224.3043
0.78389	1.276	224.3060	224.3060
0.95603	1.046	224.3066	224.3069
1.00000	1.000		224.3070
Pure	0		224.3106

THERMODYNAMIC PROPERTIES IN THE SOLID AND LIQUID STATES

Chemical thermodynamic properties at selected temperatures for the condensed phases of the 2-methylalkanes are given in table 5. The values for 2-methylbutane, 2-methylpentane, and 2-methylhexane have been calculated from the data of Guthrie and Huffman,(7) Douslin and Huffman,(8) and Huffman *et al.*,(9) respectively. The values for 2-methylheptane and 2-methyldecane are based on the results of this investigation. All values are reported in terms of IPTS-68; the older data were converted to IPTS-68 by the method of Douglas.(19) Properties calculated are Gibbs energy function, enthalpy function, enthalpy, entropy, and heat capacity. In each case the thermodynamic functions were calculated by combining the properties at 10 K, evaluated from a Debye function, the enthalpies of fusion, and numerical integration of the heat capacities. The parameters of the Debye functions, the characteristic temperature Θ, and the degrees of freedom assigned, were evaluated from the measured heat capacities from 14 to 20 K; $\Theta = 108.6$ and 115.8 K, and the degrees of freedom are 5.5 and 7.0, for 2-methylheptane and 2-methyldecane, respectively. The values listed in table 5 were corrected for the effects of premelting.(20)

IDEAL GAS ENTROPIES AT 298.15 K

The standard entropies $S^\circ(\text{g}, 298.15\ \text{K})$ of gaseous 2-methylheptane and 2-methyldecane at 298.15 K were calculated by adding to the entropy $S(\text{l})$ in the liquid state the entropy ΔS_v of vaporization at 298.15 K, plus the entropy ΔS_{comp} of compression,

TABLE 5. Molar thermodynamic functions for condensed phases

T/K	$\{G_s(T)-H(0)\}/T$ / cal K^{-1} mol^{-1}	$\{H_s(T)-H(0)\}/T$ / cal K^{-1} mol^{-1}	$H_s(T)-H(0)$ / cal mol^{-1}	S_s / cal K^{-1} mol^{-1}	C_s / cal K^{-1} mol^{-1}
		2-Methylbutane (crystals)			
10	0.043	0.127	1.27	0.170	0.504
15	0.142	0.414	6.21	0.556	1.579
20	0.322	0.882	17.63	1.203	3.004
25	0.578	1.454	36.33	2.031	4.471
30	0.897	2.074	62.21	2.971	5.863
35	1.265	2.709	94.82	3.973	7.164
40	1.667	3.340	133.61	5.008	8.334
45	2.097	3.955	177.98	6.052	9.398
50	2.545	4.549	227.47	7.094	10.387
60	3.475	5.691	341.47	9.167	12.412
70	4.436	6.808	476.6	11.244	14.663
80	5.417	7.846	627.6	13.262	15.340
90	6.395	8.768	789.2	15.163	16.940
100	7.365	9.678	967.8	17.043	18.839
110	8.331	10.608	1167.0	18.939	21.017
113.364	8.656	10.928	1238.8	19.584	21.755
		2-Methylbutane (liquid)			
113.364	8.656	21.797	2471.0	30.454	29.419
120	9.907	22.227	2667.2	32.134	29.677
130	11.710	22.814	2965.8	34.524	30.037
140	13.421	23.343	3268.0	36.763	30.398
150	15.048	23.825	3574	38.875	30.773
160	16.600	24.272	3883	40.872	31.167
170	18.084	24.689	4197	42.773	31.583
180	19.507	25.084	4515	44.591	32.017
190	20.872	25.462	4838	46.334	32.470
200	22.187	25.824	5165	48.012	32.955
210	23.457	26.176	5497	49.632	33.466
220	24.683	26.519	5834	51.201	34.012
230	25.869	26.857	6177	52.726	34.594
240	27.019	27.192	6526	54.211	35.200
250	28.135	27.525	6881	55.660	35.844
260	29.221	27.859	7243	57.080	36.540
270	30.280	28.193	7612	58.473	37.260
273.15	30.607	28.299	7730	58.906	37.492
280	31.311	28.530	7989	59.841	37.998
290	32.317	28.870	8372	61.187	38.764
298.15	33.121	29.149	8691	62.270	39.410
300	33.302	29.213	8764	62.515	39.558
		2-Methylpentane (crystals)			
10	0.043	0.127	1.27	0.170	0.501
12	0.074	0.230	2.78	0.304	0.957
14	0.119	0.360	5.04	0.479	1.321
16	0.177	0.512	8.19	0.689	1.859
18	0.248	0.694	12.49	0.942	2.443
20	0.332	0.898	17.95	1.228	3.011
25	0.591	1.469	36.71	2.060	4.499
30	0.914	2.095	62.86	3.009	5.943
35	1.286	2.743	95.98	4.027	7.295
40	1.694	3.391	135.64	5.085	8.540
45	2.130	4.029	181.29	6.159	9.713

TABLE 5—*continued*

$\frac{T}{\mathrm{K}}$	$\frac{\{G_s(T)-H(0)\}/T}{\mathrm{cal\ K^{-1}\ mol^{-1}}}$	$\frac{\{H_s(T)-H(0)\}/T}{\mathrm{cal\ K^{-1}\ mol^{-1}}}$	$\frac{H_s(T)-H(0)}{\mathrm{cal\ mol^{-1}}}$	$\frac{S_s}{\mathrm{cal\ K^{-1}\ mol^{-1}}}$	$\frac{C_s}{\mathrm{cal\ K^{-1}\ mol^{-1}}}$
		2-Methylpentane (crystals)—*continued*			
50	2.588	4.653	232.67	7.241	10.823
60	3.543	5.857	351.43	9.401	12.862
70	4.532	6.992	489.5	11.524	14.728
80	5.536	8.068	645.4	13.604	16.432
90	6.546	9.086	817.8	15.633	18.040
100	7.554	10.059	1005.9	17.613	19.577
110	8.557	10.988	1208.6	19.545	20.964
119.53	9.507	11.843	1415.6	21.350	22.366
		2-Methylpentane (liquid)			
119.53	9.507	24.372	2913	33.879	35.147
120	9.600	24.411	2929	34.013	35.164
130	11.589	25.253	3282	36.841	35.491
140	13.488	25.998	3639	39.486	35.868
150	15.305	26.669	4000	41.974	36.236
160	17.046	27.282	4365	44.327	36.688
170	18.717	27.848	4734	46.564	37.149
180	20.323	28.379	5108	48.703	37.658
190	21.872	28.880	5487	50.752	38.162
200	23.366	29.359	5871	52.723	38.741
210	24.808	29.820	6262	54.628	39.360
220	26.206	30.268	6659	56.474	40.000
230	27.562	30.706	7062	58.267	40.701
240	28.878	31.137	7473	60.014	41.406
250	30.158	31.564	7891	61.721	42.208
260	31.404	31.989	8317	63.392	43.022
270	32.619	32.412	8751	65.031	43.825
273.15	32.996	32.545	8890	65.541	44.084
280	33.806	32.834	9193	66.640	44.667
290	34.965	33.258	9645	68.223	45.592
298.15	35.892	33.606	10020	69.497	46.345
300	36.100	33.685	10105	69.784	46.499
310	37.211	34.110	10574	71.321	47.197
		2-Methylhexane (crystals)			
10	0.062	0.184	1.843	0.246	0.726
15	0.203	0.575	8.622	0.778	2.021
20	0.442	1.135	22.713	1.578	3.648
25	0.765	1.808	45.19	2.573	5.336
30	1.159	2.536	76.07	3.695	6.997
35	1.606	3.287	115.07	4.894	8.575
40	2.094	4.043	161.70	6.137	10.079
45	2.615	4.790	215.57	7.405	11.440
50	3.157	5.520	275.99	8.677	12.731
60	4.290	6.937	416.2	11.227	15.241
70	5.462	8.311	581.7	13.773	18.310
80	6.671	9.681	774.4	16.352	18.769
90	7.876	10.785	970.6	18.661	20.462
100	9.067	11.840	1184.0	20.906	22.159
110	10.244	12.851	1413.6	23.095	23.785
120	11.403	13.830	1659.6	25.233	25.396
130	12.548	14.782	1921.6	27.330	27.037
140	13.678	15.722	2201.0	29.400	28.865
150	14.795	16.665	2499.8	31.460	30.911
154.91	15.339	17.133	2654.1	32.473	31.973

TABLE 5—*continued*

T/K	$\{G_s(T)-H(0)\}/T$ / cal K^{-1} mol^{-1}	$\{H_s(T)-H(0)\}/T$ / cal K^{-1} mol^{-1}	$H_s(T)-H(0)$ / cal mol^{-1}	S_s / cal K^{-1} mol^{-1}	C_s / cal K^{-1} mol^{-1}
		2-Methylhexane (liquid)			
154.91	15.339	31.303	4849.1	46.642	42.847
160	16.36	31.67	5068	48.02	43.056
170	18.30	32.35	5500	50.65	43.531
180	20.16	32.98	5938	53.15	44.042
190	21.96	33.58	6382	55.55	44.584
200	23.70	34.15	6830	57.85	45.186
210	25.37	34.69	7285	60.07	45.827
220	27.00	35.21	7747	62.22	46.506
230	28.58	35.71	8216	64.30	47.222
240	30.11	36.22	8692	66.33	47.997
250	31.60	36.70	9175	68.30	48.809
260	33.04	37.18	9668	70.23	49.670
270	34.46	37.66	10169	72.12	50.547
273.15	34.90	37.81	10329	72.71	50.837
280	35.83	38.14	10679	73.98	51.491
290	37.18	38.61	11199	75.80	52.466
298.15	38.26	39.00	11630	77.28	53.285
300	38.50	39.09	11728	77.61	53.481
		2-Methylheptane (crystals)			
10	0.056	0.165	1.654	0.221	0.655
12	0.095	0.282	3.384	0.377	1.091
14	0.150	0.433	6.063	0.583	1.611
16	0.219	0.617	9.873	0.836	2.209
18	0.304	0.829	14.909	1.133	2.829
20	0.403	1.062	21.219	1.469	3.481
25	0.709	1.723	43.078	2.433	5.197
30	1.087	2.447	73.423	3.534	6.925
35	1.520	3.206	112.22	4.727	8.580
40	1.999	3.976	159.06	5.975	10.146
45	2.512	4.746	213.57	7.258	11.643
50	3.051	5.508	275.38	8.559	13.061
60	4.188	6.989	419.3	11.177	15.672
70	5.372	8.402	588.1	13.774	18.057
80	6.582	9.752	780.2	16.335	20.304
90	7.806	11.035	993.1	18.841	22.252
100	9.032	12.252	1225.2	21.285	24.139
110	10.255	13.413	1475.4	23.668	25.876
120	11.470	14.524	1742.8	25.993	27.584
130	12.675	15.586	2026.2	28.261	29.064
140	13.867	16.605	2324.6	30.472	30.664
150	15.046	17.594	2639.1	32.640	32.292
160	16.213	18.570	2971.2	34.783	34.121
164.193	16.697	18.976	3115.7	35.673	34.909
		2-Methylheptane (liquid)			
164.193	16.697	36.328	5964.7	53.025	50.537
170	17.971	36.817	6259	54.788	50.685
180	20.097	37.595	6767	57.692	51.000
190	22.149	38.311	7279	60.461	51.388
200	24.132	38.976	7795	63.108	51.813
210	26.048	39.599	8316	65.648	52.335
220	27.905	40.192	8842	68.096	52.974

TABLE 5—*continued*

T / K	$\{G_s(T)-H(0)\}/T$ / cal K^{-1} mol^{-1}	$\{H_s(T)-H(0)\}/T$ / cal K^{-1} mol^{-1}	$H_s(T)-H(0)$ / cal mol^{-1}	S_s / cal K^{-1} mol^{-1}	C_s / cal K^{-1} mol^{-1}
		2-Methylheptane (liquid)—*continued*			
230	29.703	40.764	9376	70.467	53.719
240	31.450	41.321	9917	72.771	54.538
250	33.148	41.867	10467	75.015	55.453
260	34.801	42.406	11026	77.207	56.325
270	36.411	42.940	11594	79.351	57.297
273.15	36.910	43.107	11775	80.018	57.610
280	37.983	43.471	12172	81.452	58.306
290	39.517	44.000	12760	83.517	59.361
298.15	40.743	44.432	13247	85.175	60.228
300	41.018	44.530	13359	85.548	60.430
310	42.486	45.061	13969	87.547	61.550
320	43.925	45.594	14590	89.519	62.696
330	45.337	46.130	15223	91.467	63.874
340	46.722	46.670	15868	93.392	65.096
350	48.082	47.214	16525	95.296	66.354
360	49.420	47.764	17195	97.184	67.636
370	50.736	48.318	17878	99.054	68.919
		2-Methyldecane (crystals)			
10	0.058	0.174	1.741	0.232	0.692
12	0.100	0.298	3.572	0.398	1.165
14	0.158	0.463	6.482	0.621	1.762
16	0.233	0.666	10.662	0.899	2.437
18	0.325	0.904	16.279	1.229	3.191
20	0.433	1.173	23.457	1.606	3.994
25	0.776	1.952	48.81	2.729	6.177
30	1.210	2.843	85.28	4.053	8.385
35	1.718	3.794	132.76	5.512	10.609
40	2.290	4.781	191.26	7.071	12.785
45	2.910	5.789	260.49	8.699	14.869
50	3.573	6.788	339.38	10.360	16.640
60	4.981	8.710	522.6	13.691	19.973
70	6.463	10.544	738.1	17.007	23.064
80	7.985	12.284	982.7	20.269	25.815
90	9.528	13.932	1253.9	23.460	28.372
100	11.078	15.496	1549.6	26.574	30.713
110	12.625	16.978	1867.6	29.603	32.865
120	14.163	18.387	2206.5	32.550	34.887
130	15.688	19.730	2564.9	35.418	36.771
140	17.198	21.012	2941.8	38.210	38.605
150	18.690	22.245	3336.8	40.935	40.400
160	20.164	23.435	3750	43.599	42.170
170	21.619	24.590	4180	46.208	43.943
180	23.057	25.715	4629	48.772	45.786
190	24.477	26.822	5096	51.299	47.692
200	25.880	27.915	5583	53.795	49.691
210	27.269	29.000	6090	56.269	51.750
220	28.642	30.087	6619	58.729	54.054
224.311	29.226	30.551	6853	59.777	55.073

TABLE 5—*continued*

$\frac{T}{\mathrm{K}}$	$\frac{\{G_s(T)-H(0)\}/T}{\mathrm{cal\,K^{-1}\,mol^{-1}}}$	$\frac{\{H_s(T)-H(0)\}/T}{\mathrm{cal\,K^{-1}\,mol^{-1}}}$	$\frac{H_s(T)-H(0)}{\mathrm{cal\,mol^{-1}}}$	$\frac{S_s}{\mathrm{cal\,K^{-1}\,mol^{-1}}}$	$\frac{C_s}{\mathrm{cal\,K^{-1}\,mol^{-1}}}$
		2-Methyldecane (liquid)			
224.311	29.226	57.282	12849	86.508	73.867
230	30.671	57.706	13272	88.377	74.325
240	33.143	58.415	14020	91.557	75.131
250	35.541	59.100	14775	94.640	75.955
260	37.872	59.766	15539	97.637	76.894
270	40.140	60.420	16313	100.560	77.997
273.15	40.842	60.625	16560	101.466	78.369
280	42.349	61.069	17099	103.418	79.196
290	44.503	61.716	17897	106.218	80.447
298.15	46.221	62.242	18557	108.462	81.554
300	46.606	62.362	18709	108.969	81.818
310	48.661	63.013	19534	111.674	83.248
320	50.673	63.668	20374	114.340	84.686
330	52.642	64.327	21228	116.968	86.142
340	54.572	64.989	22096	119.562	87.596
350	56.466	65.657	22980	122.122	89.100
360	58.325	66.330	23879	124.654	90.673
370	60.151	67.009	24793	127.161	92.305
380	61.947	67.697	25725	129.644	93.960
390	63.715	68.391	26672	132.106	95.577

and a correction ΔS_{corr} to the entropy for the effects of gas imperfection. From Cox equations fitted to the vapor pressures of 2-methylheptane and 2-methyldecane measured in this laboratory,(22) and the Clapeyron equation, the entropies of vaporization and compression were calculated. The standard entropies of 2-methylheptane and 2-methyldecane at 298.15 K are listed in table 6, together with values for 2-methylbutane, 2-methylpentane, and 2-methylhexane from the literature, converted to IPTS-68.

4. Discussion

COMPARISON WITH LITERATURE VALUES

Osborne and Ginnings(23) had measured the heat capacity of liquid 2-methylheptane over a limited range from 283 to 308 K; no third law studies on this compound have been published. As of this date, no heat capacity measurements on 2-methyldecane have been published.

A comparison of the values of heat capacity of liquid 2-methylheptane obtained in this work with the published values of Osborne and Ginnings(23) over the range 283 to 308 K has been made. The values reported here are 0.06 per cent higher at 283 K, increasing to 0.23 per cent higher at 308 K. These comparisons were made with the present data converted to the IPTS-48, which is nearly identical in this range to the 1927 scale used by Osborne and Ginnings.(23) The differences in heat capacity lie just within the estimated accuracy intervals for both sets of data. The value of the enthalpy of vaporization calculated for 2-methylheptane at 298.15 K, 9481 cal mol^{-1}, agrees closely with that reported by Osborne and Ginnings,(23) 9484 cal mol^{-1}.

TABLE 6. Standard entropies of gaseous substances at 298.15 K

Compound	S(l, 298.15 K) / cal K^{-1} mol^{-1}	$\Delta S(-CH_2-, l)$ / cal K^{-1} mol^{-1}	ΔS_v / cal K^{-1} mol^{-1}
2-Methylbutane	62.27[a] ±0.12[f]		19.91[b] ±0.03[f]
2-Methylpentane	69.50[c] ±0.14[f]	7.227	23.95[d] ±0.03[f]
2-Methylhexane	77.28[e] ±0.15[f]	7.783	27.92[e] ±0.04[f]
2-Methylheptane	85.17 ±0.17[f]	7.895	31.80 ±0.04[f]
2-Methyldecane	108.46 ±0.22[f]	7.762	43.83 ±0.20[f]

Compound	ΔS_{comp} / cal K^{-1} mol^{-1}	ΔS_{corr} / cal K^{-1} mol^{-1}	$S°$(g, 298.15 K) / cal K^{-1} mol^{-1}	$\Delta S°(-CH_2-, g)$ / cal K^{-1} mol^{-1}
2-Methylbutane	− 0.20[b] ±0.00[f]	0.016[b]	82.14±0.15[f]	
2-Methylpentane	− 2.54[d] ±0.00[f]	0.11[d]	91.02±0.17[f]	8.88
2-Methylhexane	− 4.86[e] ±0.00[f]	0.042[e]	100.38±0.19[f]	9.36
2-Methylheptane	− 7.17 ±0.01[f]	0.020	109.82±0.21[f]	9.44
2-Methyldecane	− 14.07 ±0.05[f]	—	138.22±0.47[f]	9.46

[a] Reference 7 recomputed to IPTS-68.
[b] Reference 24.
[c] Reference 8 recomputed to IPTS-68.
[d] Reference 25.
[e] Reference 9 entropy of liquid at 298.15 K recomputed to IPTS-68.
[f] Authors estimate of accuracy uncertainty for each quantity.

The results of this investigation have been compared with estimates of standard gas entropy at 298.15 K made by use of the group contribution correlation of Benson *et al.*(27, 28) and by use of the correlation of Mulyava and Shevchuk(29) based on additivity of atomic and bond entropies. As shown in table 7, the experimental results in each case lie between the two estimates and are within the expected uncertainties for each method of estimation.

TABLE 7. Comparison of standard gas entropies $S°$(g, 298.15 K)/cal K^{-1} mol^{-1}

Compound	Experimental	Benson & Buss Predicted	Mulyava & Shevchuk Predicted
2-Methylheptane	109.82	110.29	109.63
2-Methyldecane	138.22	138.55	137.67

THE METHYLENE ENTROPY INCREMENT

The values of the molar entropy increment per CH_2 group $\Delta S(-CH_2-)$ determined from the results of this investigation (table 6) are nearly constant for both liquid and ideal gas state. The apparent trend for the ideal gas from C_6 to C_{11} is probably coincidental. The larger, irregular increments which had been found for C_4 to C_5 and C_5 to C_6(7, 8, 10) are not found for data beyond C_6. In each case the increment beyond 2-methylpentane is nearly that obtained previously for the *n*-alkanes,(1) the 1-olefins,(5) the *n*-alkylcyclopentanes,(2) and the *n*-alkylcyclohexanes(3) as shown in table 8.

TABLE 8. Methylene entropy increment at 298.15 K for the liquid state $\Delta S(-\mathrm{CH_2}-, \mathrm{l})$ and ideal gas state $\Delta S^\circ(-\mathrm{CH_2}-, \mathrm{g})$

	$\Delta S(-\mathrm{CH_2}-, \mathrm{l})$ / cal $\mathrm{K^{-1}\,mol^{-1}}$	$\Delta S^\circ(-\mathrm{CH_2}-, \mathrm{g})$ / cal $\mathrm{K^{-1}\,mol^{-1}}$
n-Alkanes	7.735 [a]	9.31 [b]
1-Olefins	7.725 [c]	—
n-Alkylcyclopentanes	7.76 [d]	9.33 [d]
n-Alkylcyclohexanes	7.78 [e]	9.35 [e]
2-Methylalkanes	7.762	9.46

[a] Reference 1. [b] Reference 26. [c] Reference 5. [d] Reference 2. [e] Reference 3.

REFERENCES

1. Messerly, J. F.; Guthrie, G. B.; Todd, S. S.; Finke, H. L. *J. Chem. Eng. Data* **1967,** 12, 338.
2. Messerly, J. F.; Todd, S. S.; Finke, H. L. *J. Phys. Chem.* **1965,** 69, 353.
3. Finke, H. L.; Messerly, J. F.; Todd, S. S. *J. Phys. Chem.* **1965,** 69, 2094.
4. Messerly, J. F.; Todd, S. S.; Finke, H. L. *J. Phys. Chem.* **1965,** 69, 4304.
5. McCullough, J. P.; Finke, H. L.; Gross, M. E.; Messerly, J. F.; Waddington, G. *J. Phys. Chem.* **1957,** 61, 289.
6. Pitzer, K. S.; Kilpatrick, J. E. *Chem. Rev.* **1946,** 39, 435.
7. Guthrie, G. B., Jr.; Huffman, H. M. *J. Amer. Chem. Soc.* **1943,** 65, 1139.
8. Douslin, D. R.; Huffman, H. M. *J. Amer. Chem. Soc.* **1946,** 68, 1704.
9. Huffman, H. M.; Gross, M. E.; Scott, D. W.; McCullough, J. P. *J. Phys. Chem.* **1961,** 65, 495.
10. American Petroleum Institute Research Project 44, Chemical Thermodynamics Properties Center, Texas A & M University, College Station, Texas, *Selected Values of Properties of Hydrocarbons and Related Compounds* (Loose leaf sheets, extant **1970**).
11. Huffman, H. M. *Chem. Rev.* **1947,** 40, 1.
12. Scott, D. W.; Douslin, D. R.; Gross, M. E.; Oliver, G. D.; Huffman, H. M. *J. Amer. Chem. Soc.* **1952,** 74, 883.
13. Ruehrwein, R. A.; Huffman, H. M. *J. Amer. Chem. Soc.* **1943,** 65, 1620.
14. Cameron, A. E.; Wichers, E. *J. Amer. Chem. Soc.* **1962,** 84, 4175.
15. Rossini, F. D. *J. Pure Appl. Chem.* **1964,** 9, 453.
16. Stimson, H. F. *J. Res. Nat. Bur. Stand.* **1949,** 42, 209.
17. Hoge, H. J.; Brickwedde, F. G. *J. Res. Nat. Bur. Stand.* **1939,** 22, 351.
18. International Practical Temperature Scale of 1968: *Metrologia* **1969,** 5, 35.
19. Douglas, T. B. *J. Res. Nat. Bur. Stand.* **1969,** 73A, 451.
20. Westrum, E. F., Jr.; Furukawa, G. T.; McCullough, J. P. In *Experimental Thermodynamics Vol. I,* Chap. 5. J. P. McCullough and D. W. Scott; editors. Plenum: New York. **1968,** p. 135.
21. Glasgow, A. R., Jr.; Streiff, A. J.; Rossini, F. D. *J. Res. Nat. Bur. Stand.* **1945,** 35, 355.
22. Osborn, A.; Douslin, D. R. Thermodynamics Research Group, Bartlesville Petroleum Research Center, U.S. Bureau of Mines, Bartlesville, Okla., to be published.
23. Osborne, N. S.; Ginnings, D. C. *J. Res. Nat. Bur. Stand.* **1947,** 39, 453.
24. Scott, D. W.; McCullough, J. P.; Williamson, K. D.; Waddington, G. *J. Amer. Chem. Soc.* **1951,** 73, 1707.
25. Waddington, G.; Smith, J. C.; Scott, D. W.; Huffman, H. M. *J. Amer. Chem. Soc.* **1949,** 71, 3902
26. Person, W. B.; Pimentel, G. C. *J. Amer. Chem. Soc.* **1953,** 75, 532.
27. Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958,** 29, 546.
28. Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969,** 69, 279.
29. Mulyava, M. P.; Shevchuk, V. U. *Russ. J. Phys. Chem.* **1970,** 44, 795.