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## Low-temperature Thermal Data for the Nine Normal Paraffin Hydrocarbons from Octane to Hexadecane

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Low-temperature thermal studies have been made on nine *n*-paraffin hydrocarbons ( $C_8$  to  $C_{16}$ ) over the temperature range 12 to 300°K. For each compound values are given for the heat capacities in the solid and the liquid state, triple point and heat of fusion. The *n*-paraffins containing an odd number of carbon atoms exhibited solid-phase transitions; transition temperatures and heats of transition are given. From the calorimetric data a value of the entropy of each compound in the liquid state at 298.16°K. has been computed. These entropy values are represented by the equation,  $S_{298.16}(\text{liq.}) = 24.539 + 7.725N \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ , where  $N$  is the number of carbon atoms in the molecule.

Because of the importance of the *n*-paraffins in petroleum technology, a redetermination of the entropies of the compounds from *n*-octane to *n*-hexadecane inclusive has been made. Previously reported values of the entropy of some of these hydrocarbons<sup>2</sup> were based on heat capacity measurements over a somewhat limited temperature range on compounds of uncertain purity. The new measurements provide a more reliable value of the entropy of each compound in the liquid state at 298.16°K., which, when appropriately combined with heat of vaporization and vapor pressure data, yields a value of the entropy of each compound in the ideal gaseous state.<sup>3</sup>

The compounds studied, except *n*-tridecane and *n*-pentadecane, have been investigated by Parks<sup>2</sup> and his collaborators over the temperature range 80 to 300°K. The accuracy uncertainties of these earlier data were reported to be about 1%. Heat capacities of *n*-octane, *n*-nonane and *n*-decane in the liquid state from 5 to 45° have been measured by Osborne and Ginnings.<sup>4</sup>

**The Materials.**—The materials used in this investigation were A.P.I. Research samples.<sup>5</sup> Their purities will be discussed in a separate section of this paper.

**The Apparatus.**—All measurements were made in the apparatus described by Ruehrwein and Huffman.<sup>6</sup> In each study about 55 ml. of the material was sealed in a copper calorimeter that contained horizontal copper discs to facilitate attainment of thermal equilibrium and prevent settling of the solid phase during fusion experiments. To minimize heat interchange between the calorimeter and its environ-

ment, the temperature of the electrically heated adiabatic shield system was maintained as close as possible to that of the calorimeter surface. The temperature difference between the calorimeter and its environment was determined by a system of interconnected thermocouples in conjunction with a high-sensitivity galvanometer. The combination heater-thermometer unit used in the calorimeter was one of the set of five previously described.<sup>6</sup> Measurements of the electrical energy supplied to the calorimeter and the resistance of the platinum resistance thermometer were made on a "White" double potentiometer. Measurements of potential were in terms of a bank of six saturated cadmium cells. The electrical stopclock used for time measurements was driven by a constant-frequency ( $\pm 0.002\%$ ) a.c. power source.

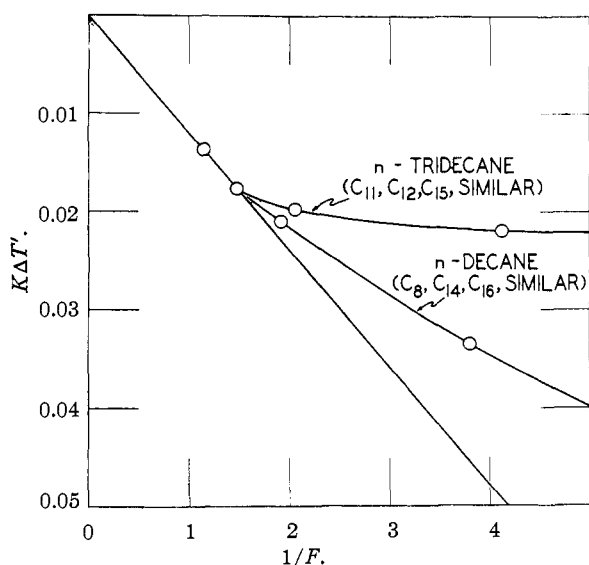
**Numerical Constants.**—The energy measurements were made in terms of the international joule and converted to calories by dividing by 4.1833. The ice point (0°C.) was taken to be 273.16°K. The 1951 International Atomic Weights<sup>7</sup> were used.

**Triple Point and Purity Determinations.**—The results of melting point studies made for each of the *n*-paraffins investigated are summarized in Table I. The observed equilibrium melting temperatures for these compounds were plotted as a function of the reciprocal of the fraction melted. If Raoult's law were obeyed and no solid solutions were formed, the experimental points would lie on straight lines.<sup>8</sup> However, in each case, with the possible exception of *n*-nonane, the plots exhibited curvature that was concave upward, and in no specific instance was "ideal" behavior evidenced. For the sake of consistency, the concentration of the impurity, the melting point of the sample, and the triple point were calculated from a straight line through the points at which the sample was 70 and 90% liquid. The selection of these two points yields maximum values of the concentration of the impurity and the triple point.

To permit a comparison of the melting behavior of the several substances, the observed data for each hydrocarbon were plotted with the reciprocal of the fraction of sample melted ( $1/F$ ) as abscissa and  $K\Delta T'$  as ordinate.  $K$  is an arbitrary constant for each compound, so chosen that the slope of the straight lines through the 70 and 90% liquid points for the different compounds is the same;  $\Delta T'$  is the difference between the temperatures corresponding to 90% liquid and the various fractions melted. Figure 1 illustrates the curves obtained by this treatment. "Ideal" behavior (characteristic of solutions containing no solid-soluble material and obeying Raoult's law) is represented by the straight

(1) Deceased.

(2) (a) G. S. Parks, H. M. Huffman and S. B. Thomas, *THIS JOURNAL*, **52**, 1032 (1930); (b) H. M. Huffman, G. S. Parks and M. Barmore, *ibid.*, **53**, 3876 (1931); (c) G. S. Parks and D. W. Light, *ibid.*, **56**, 1511 (1934); and (d) G. S. Parks, G. E. Moore, M. L. Renquist, B. F. Naylor, L. A. McClaine, P. S. Fujii and J. A. Hatton, *ibid.*, **71**, 3387 (1949).(3) The extension of the data of this report to the ideal gaseous state and to the evaluation of the entropy increment per  $CH_2$  group for the ideal gaseous state has been carried out by others. See W. B. Person and G. C. Pimentel, *ibid.*, **75**, 532 (1953).(4) N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947).(5) These samples of A. P. I. Research hydrocarbons have been made available through the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on Properties of Hydrocarbons." These samples were purified by the American Petroleum Institute Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons," from materials supplied by the following laboratories: *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tetradecane, *n*-hexadecane by the American Petroleum Institute Research Project 6 now located at the Carnegie Institute of Technology, Pittsburgh, Pa., *n*-tridecane and *n*-pentadecane by the American Petroleum Institute Research Project 42 at the Pennsylvania State College, State College, Pa.(6) R. A. Ruehrwein and H. M. Huffman, *THIS JOURNAL*, **65**, 1620 (1943).(7) E. Wichers, *ibid.*, **74**, 2447 (1952).(8) S. S. Todd, G. D. Oliver and H. M. Huffman, *ibid.*, **69**, 1519 (1947).

Fig. 1.—Melting point curves for the *n*-paraffins.

line. With the possible exception of *n*-nonane, none of the materials studied shows this "ideal" behavior. The curves fall into two groups, one containing *n*-octane, *n*-decane, *n*-tetradecane and *n*-hexadecane and the other containing *n*-undecane, *n*-dodecane, *n*-tridecane and *n*-pentadecane. Similar curves may be reproduced by applying van't Hoff's law for freezing point lowering to systems in which solid-soluble material is present. For a par-

TABLE I

NORMAL PARAFFIN HYDROCARBONS FROM OCTANE THROUGH HEXADECANE: MELTING POINT SUMMARY<sup>a</sup>

Liq., %	1/F	<i>T</i> <sub>obsd.</sub> , °K.	<i>T</i> <sub>calcd.</sub> , °K.
<i>n</i> -Octane			
7.88	12.69	216.2664	216.2224
25.00	4.000	216.3414	216.3267
50.00	2.000	216.3528	216.3507
70.63 <sup>b</sup>	1.416	216.3576	216.3576
91.16 <sup>b</sup>	1.097	216.3615	216.3615
100.0	1.000		216.3627
Pure	0		216.375
<i>N</i> <sub>2</sub> <sup>*</sup> / <i>F</i> = 0.0533 Δ <i>T</i> ; impurity = 0.06 ± 0.03 mole%			
<i>n</i> -Nonane			
13.3	7.52	219.4661	219.4225
23.8	4.20	219.5406	219.5271
46.8	2.14	219.5987	219.5920
64.5 <sup>b</sup>	1.55	219.6105	219.6105
82.2 <sup>b</sup>	1.22	219.6210	219.6210
100.0	1.00		219.6279
Pure	0		219.659
<i>N</i> <sub>2</sub> <sup>*</sup> / <i>F</i> = 0.0386 Δ <i>T</i> ; impurity = 0.12 ± 0.05 mole%			
<i>n</i> -Decane			
10.74	9.31	243.4128	243.3701
26.30	3.802	243.4691	243.4538
52.32	1.911	243.4851	243.4826
73.14 <sup>b</sup>	1.367	243.4909	243.4909
93.96 <sup>b</sup>	1.064	243.4955	243.4955
100.0	1.000		243.4964
Pure	0		243.512
<i>N</i> <sub>2</sub> <sup>*</sup> / <i>F</i> = 0.0582 Δ <i>T</i> ; impurity = 0.09 ± 0.04 mole%			

<i>n</i> -Undecane			
3.4	29.4	247.5749	247.4892
23.9	4.18	247.5852	247.5775
48.2	2.07	247.5864	247.5849
68.7 <sup>b</sup>	1.45	247.5870	247.5870
89.1 <sup>b</sup>	1.12	247.5882	247.5882
100.0	1.00		247.5886
Pure	0		247.592

*N*<sub>2</sub><sup>\*</sup>/*F* = 0.0435 Δ*T*; impurity = 0.02 ± 0.01 mole%

<i>n</i> -Dodecane			
10.86	9.21	263.5656	263.4846
25.69	3.893	263.5691	263.5447
50.70	1.972	263.5717	263.5664
70.15 <sup>b</sup>	1.426	263.5725	263.5725
89.59 <sup>b</sup>	1.116	263.5760	263.5760
100.0	1.000		263.5774
Pure	0		263.589

*N*<sub>2</sub><sup>\*</sup>/*F* = 0.0638 Δ*T*; impurity = 0.07 ± 0.05 mole%

<i>n</i> -Tridecane			
12.0	8.34	267.7735	267.7160
24.3	4.12	267.7750	267.7529
48.7	2.05	267.7766	267.7725
68.4 <sup>b</sup>	1.47	267.7783	267.7783
88.0 <sup>b</sup>	1.14	267.7814	267.7814
100.0	1.00		267.7827
Pure	0		267.792

*N*<sub>2</sub><sup>\*</sup>/*F* = 0.0478 Δ*T*; impurity = 0.05 ± 0.04 mole%

<i>n</i> -Tetradecane			
8.90	11.24	278.9497	278.915
23.54	4.248	278.9962	278.9848
49.37	2.026	279.0085	279.0070
69.16 <sup>b</sup>	1.445	279.0129	279.0129
89.81 <sup>b</sup>	1.113	279.0162	279.0162
96.69	1.034	279.0173	279.0170
100.0	1.000		279.0173
Pure	0		279.027

*N*<sub>2</sub><sup>\*</sup>/*F* = 0.0696 Δ*T*; impurity = 0.07 ± 0.04 mole%

<i>n</i> -Pentadecane			
12.3	8.12	283.0902	283.0267
27.4	3.66	283.0915	283.0713
52.1	1.92	283.0919	283.0887
72.5 <sup>b</sup>	1.38	283.0941	283.0941
92.8 <sup>b</sup>	1.08	283.0971	283.0971
100.0	1.00		283.0979
Pure	0		283.108

*N*<sub>2</sub><sup>\*</sup>/*F* = 0.0519 Δ*T*; impurity = 0.05 ± 0.04 mole%

<i>n</i> -Hexadecane			
10.72	9.328	291.2500	291.1944
25.80	3.876	291.2982	291.2794
50.44	1.983	291.3097	291.3090
70.23 <sup>b</sup>	1.424	291.3178	291.3178
90.01 <sup>b</sup>	1.111	291.3226	291.3226
100.0	1.000		291.3242
Pure	0		291.340

*N*<sub>2</sub><sup>\*</sup>/*F* = 0.0756 Δ*T*; impurity = 0.12 ± 0.06 mole%

<sup>a</sup> The impurity concentration was obtained from the equation  $N_2^*/F = A\Delta T$ , where  $N_2^*$  is the mole fraction of impurity in the whole sample,  $F$  is the fraction of the sample in the liquid state,  $A$  is the cryoscopic constant ( $\Delta H/RT^2_{T.P.}$ ), and  $\Delta T$  is  $T_{T.P.} - T_{obsd.}$  <sup>b</sup> Calculation based on these experimental points.

TABLE II

MOLAL HEAT CAPACITIES OF THE NORMAL PARAFFIN HYDROCARBONS FROM OCTANE THROUGH HEXADECANE

T, °K.	$\Delta T$	$C_{\text{satd.}}$ cal. deg. <sup>-1</sup>	T, °K.	$\Delta T$	$C_{\text{satd.}}$ cal. deg. <sup>-1</sup>
<i>n</i> -Octane					
Crystals					
12.60	1.985	0.885	110.06	7.302	25.743
14.57	1.959	1.335	116.92	7.881	26.837
16.50	1.889	1.839	117.63	7.838	26.937
16.74	3.626	1.915	125.04	8.367	28.090
18.81	2.732	2.543	125.71	8.327	28.151
20.27	3.417	2.998	133.63	8.816	29.295
21.65	2.951	3.464	133.67	7.606	29.307
23.60	3.255	4.118	142.18	9.397	30.495
24.63	2.986	4.469	151.39	9.035	31.786
27.26	4.056	5.394	160.75	9.677	33.036
28.04	3.846	5.666	170.25	9.331	34.380
31.37	4.156	6.839	179.43	9.016	35.754
35.91	4.928	8.410	188.72	9.571	37.254
40.78	4.808	10.014	197.88	8.748	38.920
45.72	5.079	11.564	206.95	9.385	41.237
50.89	5.257	13.121	Liquid		
56.50	5.970	14.748	222.61	7.336	55.590
62.65	6.336	16.369	226.74	7.371	55.696
67.30	4.902	17.472	230.21	8.145	55.790
68.69	5.741	17.805	231.95	11.329	55.837
72.92	6.321	18.748	234.90	8.948	55.967
74.64	6.160	19.149	239.13	9.695	56.161
79.39	6.638	20.192	242.81	10.404	56.338
84.22	5.624	21.236	249.17	10.395	56.689
86.17	6.916	21.628	252.76	9.493	56.907
90.21	6.355	22.403	259.50	10.259	57.420
93.25	7.248	22.952	262.19	9.367	57.650
96.40	6.034	23.473	269.68	10.113	58.195
96.68	6.035	23.476	271.88	10.002	58.378
100.78	7.805	24.240	279.35	9.223	59.012
102.30	5.759	24.508	281.43	9.116	59.189
103.05	6.702	24.593	289.27	10.609	59.917
107.95	5.541	25.413	290.49	8.992	60.047
108.83	8.295	25.548	297.58	5.192	60.680
<i>n</i> -Nonane					
Crystals I					
11.93	1.792	0.837	67.85	6.004	19.322
13.80	1.962	1.278	73.61	5.518	20.798
15.75	1.947	1.790	79.44	6.134	22.240
15.94	2.666	1.863	85.37	5.721	23.665
17.76	2.075	2.378	91.46	6.474	24.963
19.30	4.056	2.893	97.77	6.143	26.202
20.31	3.028	3.226	103.78	5.867	27.339
22.74	2.821	4.082	109.99	6.560	28.466
23.57	3.487	4.380	116.42	6.296	29.617
25.94	3.575	5.250	118.30	4.976	29.911
26.97	3.313	5.637	122.52	5.902	30.678
29.57	3.680	6.613	124.25	6.921	30.887
29.98	2.701	6.774	128.88	6.840	31.716
33.38	3.927	8.096	131.86	8.307	32.175
37.37	4.046	9.541	135.61	6.614	32.801
41.76	4.743	11.141	140.35	8.674	33.531
46.56	4.852	12.802	142.65	7.471	33.915
51.11	4.247	14.360	149.38	9.377	34.939
55.75	5.041	15.843	150.01	7.238	35.062
56.21	6.240	15.990	158.58	9.022	36.377
61.09	5.626	17.466	167.44	8.710	37.805
62.09	5.524	17.750	176.01	8.421	39.274
			184.29	8.143	40.833

TABLE II (Continued)

T, °K.	$\Delta T$	$C_{\text{satd.}}$ cal. deg. <sup>-1</sup>	T, °K.	$\Delta T$	$C_{\text{satd.}}$ cal. deg. <sup>-1</sup>
192.30	7.872	42.504	258.08	9.639	64.354
200.44	8.409	44.569	262.13	9.619	64.621
208.24	7.191	47.487	267.72	9.643	65.062
<i>n</i> -Decane					
Crystals II					
218.65	0.210	167	272.08	10.274	65.480
218.86	0.206	233	274.23	9.422	65.607
			277.25	9.407	65.889
Liquid					
225.03	5.769	63.264	282.29	10.159	66.319
230.09	6.623	63.193	283.59	9.301	66.453
232.85	9.869	63.227	286.59	9.284	66.778
237.93	9.070	63.309	292.38	10.014	67.360
242.69	9.811	63.467	292.82	9.171	67.439
247.38	9.829	63.641	295.81	9.158	67.739
252.46	9.723	63.960	301.94	9.058	68.364
			304.91	9.036	68.693
			313.88	8.906	69.699
<i>n</i> -Decane					
Crystals					
12.28	1.890	0.873	171.53	9.745	40.875
14.07	1.681	1.303	175.36	9.589	41.577
14.45	1.558	1.399	175.71	3.529	41.529
15.82	1.830	1.784	179.22	3.480	42.172
16.23	1.990	1.912	179.33	8.668	42.250
17.65	1.841	2.353	181.11	9.414	42.566
18.79	3.134	2.749	182.67	3.429	42.893
19.93	2.716	3.156	183.62	6.529	42.871
21.97	3.233	3.920	186.08	3.389	43.572
22.78	2.985	4.225	187.85	8.390	43.874
25.57	3.882	5.306	189.45	3.337	44.234
25.79	3.044	5.408	190.36	9.096	44.326
29.29	3.962	6.845	190.51	7.246	44.403
29.99	5.041	7.146	192.76	3.295	44.884
34.46	3.894	8.987	196.04	3.269	45.277
38.43	4.038	10.578	196.14	8.171	45.207
42.86	4.822	12.308	197.24	6.212	45.420
47.34	4.151	13.995	199.29	3.233	45.847
51.71	4.581	15.597	199.77	9.712	45.869
54.55	4.277	16.571	203.81	6.936	46.670
59.38	5.373	18.180	204.19	7.940	46.750
64.76	5.387	19.863	209.32	9.393	47.732
70.40	5.902	21.472	218.14	8.253	49.741
76.51	6.322	23.140	226.26	7.977	51.858
82.60	5.863	24.764	233.70	6.903	54.448
86.44	4.852	25.650	239.27	4.238	60.440
Liquid					
88.68	6.285	26.230	247.02	4.830	70.978
92.16	6.594	26.958	251.70	4.840	71.173
95.03	6.411	27.578	252.30	7.981	71.202
98.58	6.249	28.306	252.63	6.405	71.261
101.28	6.101	28.864	256.53	4.818	71.441
105.18	6.940	29.632	260.61	9.535	71.709
111.97	6.637	30.915	261.03	9.493	71.739
118.96	7.390	32.230	270.08	9.418	72.411
126.21	7.101	33.520	270.48	9.389	72.426
133.19	6.856	34.721	279.46	9.304	73.179
140.48	7.735	35.930	279.82	9.298	73.242
148.09	7.485	37.168	289.09	9.944	74.171
155.47	7.264	38.348	289.44	9.944	74.219
158.07	7.157	38.752	298.59	9.053	75.222
163.13	8.062	39.545	299.31	9.800	75.299
166.11	8.924	40.045	309.04	9.656	76.416
171.08	7.829	40.839	318.62	9.511	77.588

(TABLE II Continued)

T, °K.	$\Delta T$	$C_{\text{satd. cal.}}^{\text{cal.}}$ deg. <sup>-1</sup>	T, °K.	$\Delta T$	$C_{\text{satd. cal.}}^{\text{cal.}}$ deg. <sup>-1</sup>
<i>n</i> -Undecane					
Crystals I					
12.15	1.663	0.967	110.35	8.562	33.414
13.74	1.552	1.380	111.01	8.561	33.553
14.56	1.981	1.616	117.38	8.301	34.729
15.38	1.981	1.616	119.51	9.785	35.286
16.51	1.730	1.844	120.15	9.713	35.375
16.51	1.923	2.204	126.81	10.561	36.620
17.31	2.149	2.455	129.51	10.258	37.246
18.87	2.779	3.008	129.64	9.278	37.223
19.65	2.533	3.290	137.10	10.023	38.588
21.76	3.001	4.114	139.20	9.838	39.009
22.33	2.841	4.327	147.84	11.460	40.536
24.77	2.027	5.320	159.53	11.905	42.597
25.37	3.244	5.568	171.17	11.377	44.766
28.24	3.905	6.774	182.31	10.907	46.904
28.87	3.743	7.049	193.00	10.474	49.116
31.98	3.591	8.398	203.27	10.063	51.424
35.86	4.168	10.095	214.07	11.545	54.216
39.83	3.765	11.777			
43.86	4.302	13.479			
Crystals II					
48.12	4.208	15.226	240.82	3.384	83.068
53.07	5.704	17.175	242.25	2.680	83.992
56.78	5.210	18.559	243.82	2.615	86.517
58.44	5.027	19.174			
Liquid					
62.36	5.951	20.593			
67.89	5.564	22.406	251.74	6.299	78.838
68.96	7.250	22.778	255.08	7.001	78.892
74.05	6.762	24.289	259.76	9.748	79.085
76.64	8.116	25.117	262.76	8.349	79.275
80.91	6.949	26.350	269.46	9.654	79.661
84.92	8.449	27.526	271.07	8.278	79.758
87.60	6.445	28.202	279.07	9.568	80.439
93.52	8.747	29.683	280.00	9.575	80.524
94.69	7.735	29.915	288.58	9.458	81.394
101.98	8.172	31.612	289.52	9.461	81.521
102.65	8.169	31.701	297.98	9.340	82.461
109.75	6.968	33.109	298.92	9.350	82.515
<i>n</i> -Dodecane					
Crystals					
11.82	1.520	0.850	57.81	4.796	20.241
13.34	1.564	1.235	60.63	5.273	21.344
14.89	1.536	1.667	61.80	6.897	21.742
15.04	2.234	1.716	62.39	4.366	21.998
16.40	1.488	2.158	65.67	4.806	23.170
17.21	2.097	2.417	68.32	6.142	24.085
17.97	2.097	2.417	71.03	5.912	24.983
17.97	1.648	2.692	74.65	6.529	26.142
19.64	1.695	3.327	76.72	5.459	26.805
19.72	2.932	3.377	81.34	6.844	28.263
21.67	2.354	4.170	82.41	5.937	28.588
22.77	3.146	4.631	88.45	6.345	30.350
24.23	2.746	5.256	88.74	7.955	30.393
25.92	3.157	6.026	94.73	6.007	31.911
27.05	2.894	6.534	96.43	7.434	32.300
29.23	3.454	7.544	100.95	6.432	33.408
29.97	2.938	7.894	104.16	8.010	34.131
32.92	3.928	9.280	107.24	6.149	34.845
36.68	3.604	11.050	111.96	7.597	35.893
40.40	3.822	12.761	113.59	6.555	36.243
44.62	4.625	14.664	119.40	7.265	37.492
48.94	4.017	16.584	120.49	7.243	37.702
53.18	4.460	18.393	126.95	7.846	39.044
55.00	5.980	19.099	127.60	6.966	39.156

TABLE II (Continued)

T, °K.	$\Delta T$	$C_{\text{satd. cal.}}^{\text{cal.}}$ deg. <sup>-1</sup>	T, °K.	$\Delta T$	$C_{\text{satd. cal.}}^{\text{cal.}}$ deg. <sup>-1</sup>
134.64	7.548	40.580	225.15	9.556	58.729
138.41	6.615	41.084	234.53	9.221	61.282
142.48	8.127	42.076	243.59	8.901	63.994
143.56	9.849	42.260	251.86	7.623	66.932
146.04	8.638	42.761	258.41	5.493	70.340
153.21	9.456	44.052			Liquid
155.04	9.357	44.326	266.69	4.605	86.984
162.50	9.120	45.741	272.39	10.719	87.249
164.72	10.020	46.135	272.82	7.656	87.377
171.48	8.827	47.418	281.20	9.118	88.040
174.83	10.187	48.034	283.06	10.616	88.198
180.64	9.495	49.175	290.28	9.027	88.960
184.79	9.748	49.958	293.61	10.485	89.340
194.96	10.585	51.968	299.25	8.930	89.999
205.37	10.228	54.149	304.03	10.347	90.585
215.42	9.885	56.394	308.13	8.827	91.085
			317.41	8.721	92.282
<i>n</i> -Tridecane					
Crystals I					
11.78	1.424	0.950	128.48	8.484	42.574
12.93	1.605	1.263	135.09	9.022	43.993
13.23	1.503	1.356	137.15	8.846	44.452
14.67	1.884	1.780	144.40	9.591	45.953
14.73	1.501	1.790	153.81	9.244	47.887
16.35	1.725	2.319	162.90	8.930	49.692
16.46	1.693	2.357	167.95	7.800	50.675
18.21	1.983	2.999	172.09	8.715	51.439
18.39	2.152	3.062	172.63	10.523	51.744
20.23	2.058	3.854	176.10	8.510	52.412
20.76	2.594	4.003	181.13	9.365	53.445
22.60	2.682	4.790	182.51	9.235	53.840
23.52	2.921	5.240	184.94	9.161	54.341
25.39	2.895	6.090	190.79	9.948	55.605
26.49	3.029	6.600	191.58	8.918	55.842
28.18	2.675	7.396	200.89	10.254	57.975
29.80	3.582	8.192	210.95	9.876	60.572
30.91	2.782	8.733	223.99	9.384	64.438
33.71	4.230	10.130	233.18	8.998	67.741
37.96	4.267	12.224	241.51	7.655	71.580
42.58	4.982	14.519	248.97	7.264	76.324
47.68	5.213	16.952			
Crystals II					
52.97	5.362	19.418	258.31	2.795	104.0
55.88	4.997	20.700	260.69	3.421	107.9
58.39	5.484	21.810	261.39	3.349	109.3
60.98	5.202	22.884	264.02	3.251	114.6
63.93	5.599	24.084			
Liquid					
66.26	5.372	25.026			
72.74	7.582	27.368	271.66	4.502	94.950
79.97	6.879	29.906	276.53	5.239	95.132
86.97	7.135	32.181	278.11	6.044	95.223
94.21	7.406	34.236	283.24	8.185	95.646
101.92	8.013	36.274	285.26	8.255	95.828
110.64	9.417	38.458	291.39	8.114	96.487
119.79	8.898	40.632	299.11	7.313	97.320
126.28	8.594	42.060	306.38	7.243	98.298
<i>n</i> -Tetradecane					
Crystals					
12.09	2.120	1.004	15.93	1.949	2.167
12.19	1.380	1.026	17.39	1.808	2.707
13.83	1.897	1.492	17.87	1.932	2.890
14.05	1.819	1.557	19.29	1.991	3.474
15.63	1.706	2.062	19.94	2.200	3.759
			21.51	2.445	4.461



TABLE II (Continued)

$T$ , °K.	$\Delta T$	$C_{\text{satd}}$ , cal. deg. <sup>-1</sup>	$T$ , °K.	$\Delta T$	$C_{\text{satd}}$ , cal. deg. <sup>-1</sup>
178.53	7.369	62.148	256.92	10.268	85.252
180.76	10.789	62.808	267.41	10.725	89.709
182.69	10.118	63.298	277.89	10.222	95.164
186.39	8.357	64.252		Liquid	
191.92	11.540	65.562	295.41	5.633	119.622
192.64	9.785	65.739	298.93	6.973	119.945
195.19	9.243	66.427	301.73	7.002	120.282
202.69	10.323	68.319	302.50	5.649	120.389
204.84	10.046	68.929	305.88	6.923	120.832
215.25	10.790	71.749	308.13	5.611	121.204
225.85	10.407	74.811	308.70	6.938	121.176
236.08	10.055	77.959	312.77	6.864	121.859
246.45	10.672	81.361	320.28	8.163	123.091

ticular case, a family of such curves may be generated by assuming various distribution coefficients of the solute between the solid and liquid phases. Thus the deviation from linearity of the curves in Fig. 1 probably is caused primarily by the presence of solid-soluble material.

**Heat Capacities of Solid and Liquid.**—The experimentally determined heat capacity values are given in Table II. The property measured was  $C_{\text{satd}}$ , the heat capacity of the condensed phase under its own vapor pressure. Under the experimental conditions involved in this investigation  $C_{\text{satd}}$  is equivalent to  $C_p$ . The precision uncertainty of the measurements was, in general, less than  $\pm 0.1\%$  and above  $30^\circ\text{K}$ ., it is believed that the accuracy uncertainty should not exceed  $\pm 0.2\%$ . The heat capacity data for *n*-nonane, *n*-undecane, *n*-tridecane and *n*-pentadecane between the temperatures of transition and fusion may be less accurate than at other temperatures because of the very small temperature range and uncertainty in determining the exact amount of solution formation caused by liquid-soluble impurities.

In Table III are listed heat capacity data at integral temperatures as read from a smooth curve through all the data for each hydrocarbon.

A comparison of the heat capacity data for *n*-octane, *n*-nonane and *n*-decane in the liquid state, between  $5^\circ$  and  $45^\circ$ , with those of Osborne and Ginnings<sup>4</sup> shows for *n*-octane and *n*-nonane an average deviation of  $-0.07\%$  and a maximum deviation of  $-0.14\%$ ; for *n*-decane the average and maximum deviations are  $-0.08$  and  $-0.17\%$ , respectively. Osborne and Ginnings estimate accuracy uncertainties of  $\pm 0.1\%$  for *n*-octane and *n*-nonane and  $\pm 0.3\%$  for *n*-decane. The results of the two investigations agree within the estimated accuracy uncertainty of each.

**Heats of Fusion.**—Duplicate determinations were made of the heats of fusion of each compound. Mean values are listed in Table IV, together with the cryoscopic constants ( $\Delta H_{\text{fusion}}/RT^2_{\text{T.P.}}$ ). In the calculation of the isothermal heats of fusion from enthalpies measured over finite temperature intervals, the heat capacity data of Table II, approximately corrected for heterophase premelting effects, were used. Because of lack of knowledge of the nature of the impurities and the exact amount of heterophase premelting, the accuracy uncertainty

in the heats of fusion may be considerably greater than the precision uncertainty listed in Table IV. For each of the hydrocarbons that contains an odd number of carbon atoms, all of which underwent transitions only a few degrees below their melting points, the total enthalpy change between a temperature below that of the transition and one above the melting point may be determined precisely, but division of this total enthalpy change into heat of transition, heat of fusion and  $\int C_{\text{satd}} dT$  is somewhat arbitrary. Fortunately, this arbitrariness introduces little error into the value of the entropy computed from the calorimetric data.

**Transition Temperatures and Heats of Transition.**—The transition temperatures were studied by observing the equilibrium temperatures corresponding to various fractions transposed. From plots of the equilibrium temperatures *vs.* fraction of sample transposed the temperatures corresponding to 100% transposed were determined. The transition temperatures and corresponding heats of transition are listed in Table V.

**Entropies.**—The molal entropies of the *n*-paraffins in the liquid state at  $298.16^\circ\text{K}$ . were computed from the thermal data over the temperature range 12 to  $298.16^\circ\text{K}$ . The results of these calculations are summarized in Table VI. By means of a least-squares adjustment the following equation for the molal entropies of the *n*-paraffin hydrocarbons ( $C_8$  to  $C_{16}$ , inclusive) in the liquid state at  $298.16^\circ\text{K}$ . was fitted to the experimental data:

$$S_{298.16}(\text{liq.}) = 24.539 + 7.725 N \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

where  $N$  is the number of carbon atoms in the *n*-paraffin hydrocarbon chain. For the sake of internal consistency more significant figures were retained in this equation than the accuracy of the data warrants. The maximum and average deviations from this equation for the compounds *n*-octane through *n*-hexadecane are 0.04 and 0.02%, respectively. Extrapolation of this equation to give the entropies of *n*-heptane and *n*-hexane in the liquid state at  $298.16^\circ\text{K}$ . yields values that are 0.16 and 0.19% higher, respectively, than experimental entropy values determined in this Laboratory.<sup>9</sup> These larger deviations indicate that the entropy increment per  $\text{CH}_2$  group for the liquid is not precisely a constant below  $C_8$ .

**Discussion.**—The measurements of the heat capacities of the normal paraffins studied were straightforward, with one exception. Crystalline *n*-decane exhibited anomalous behavior in the temperature region between  $170$  and  $200^\circ\text{K}$ . In this region heat capacity data were not reproducible within the normal precision of the measurements. Various slow rates of cooling and heating were used during four separate series of measurements through the region of anomalous behavior, and in no case was any discontinuity detected in the  $C_{\text{satd}}$  *vs.*  $T$  curve that might have been caused by a lambda-type transition or eutectic melting (caused by an impurity).

Parks and Light,<sup>20</sup> in measurements of the heat

(9) *n*-Hexane, D. R. Douslin and H. M. Huffman, *THIS JOURNAL*, **68**, 1708 (1940); *n*-Heptane, 78.51 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, unpublished data, this Laboratory.

TABLE III  
SMOOTHED HEAT CAPACITIES OF THE NORMAL PARAFFIN HYDROCARBONS FROM OCTANE THROUGH HEXADECANE, CAL. DEG.<sup>-1</sup> MOLE<sup>-1</sup>

<i>T</i> , °K.	Octane	Nonane	Decane	Undecane	Dodecane	Tridecane	Tetradecane	Pentadecane	Hexadecane
12	0.75	0.85	0.81	0.93	0.90	1.02	0.98	1.08	1.08
13	.98	1.08	1.04	1.18	1.15	1.29	1.25	1.37	1.38
14	1.20	1.33	1.29	1.45	1.41	1.58	1.54	1.68	1.69
15	1.45	1.60	1.55	1.74	1.70	1.89	1.86	2.02	2.03
20	2.91	3.12	3.18	3.43	3.48	3.72	3.79	4.03	4.11
25	4.60	4.92	5.09	5.41	5.60	5.89	6.14	6.44	6.65
30	6.36	6.80	7.15	7.53	7.90	8.29	8.70	9.07	9.49
35	8.10	8.69	9.21	9.72	10.25	10.79	11.37	11.92	12.42
40	9.76	10.53	11.18	11.84	12.58	13.27	13.98	14.72	15.41
45	11.35	12.29	13.11	13.96	14.82	15.71	16.58	17.46	18.32
50	12.85	13.99	14.98	15.97	17.01	18.05	19.09	20.14	21.13
55	14.34	15.63	16.72	17.89	19.07	20.32	21.45	22.70	23.89
60	15.69	17.14	18.38	19.74	21.08	22.48	23.74	25.14	26.47
65	16.94	18.55	19.94	21.46	22.92	24.53	25.89	27.48	28.85
70	18.10	19.86	21.37	23.09	24.64	26.41	27.90	29.58	31.07
75	19.23	21.12	22.77	24.62	26.25	28.18	29.79	31.62	33.23
80	20.34	22.38	24.08	26.09	27.85	29.93	31.61	33.62	35.30
85	21.40	23.59	25.33	27.52	29.37	31.59	33.33	35.48	37.28
90	22.35	24.66	26.49	28.82	30.73	33.05	34.87	37.18	39.09
95	23.23	25.65	27.58	30.02	31.97	34.45	36.33	38.76	40.72
100	24.08	26.63	28.60	31.17	33.16	35.79	37.72	40.28	42.26
110	25.74	28.47	30.55	33.33	35.46	38.29	40.36	43.14	45.23
120	27.31	30.22	32.42	35.36	37.61	40.68	42.82	45.81	48.00
130	28.78	31.88	34.18	37.28	39.64	42.90	45.13	48.36	50.62
140	30.19	33.48	35.85	39.11	41.60	45.05	47.34	50.78	53.09
150	31.58	35.03	37.47	40.90	43.45	47.10	49.51	53.10	55.48
160	32.94	36.58	39.06	42.68	45.28	49.12	51.60	55.40	57.84
170	34.30	38.19	40.65	44.54	47.13	51.13	53.73	57.69	60.20
180	35.81	39.95	42.31	46.44	49.05	53.23	55.87	60.02	62.62
190	37.41	41.90	44.05	48.47	50.97	55.45	58.04	62.42	65.12
200	39.19	44.18	45.86	50.66	53.01	57.78	60.29	64.95	67.63
210	41.21	47.16	47.81	53.10	55.15	60.30	62.68	67.56	70.28
220	55.54	63.43	50.06	55.81	57.46	63.18	65.23	70.47	73.11
230	55.78	63.19	52.58	58.55	60.03	66.50	67.96	73.80	76.05
240	56.19	63.37	55.32	82.69	62.88	70.79	70.95	77.49	79.18
250	56.74	63.82	71.10	78.75	66.20	77.12	74.29	81.92	82.57
260	57.45	64.47	71.67	79.14	69.99	106.6	78.03	87.68	86.42
270	58.22	65.27	72.39	79.72	87.18	94.93	82.78	98.73	90.71
280	59.07	66.14	73.24	80.52	87.93	95.37	102.82	148.8	95.61
290	59.99	67.11	74.27	81.55	88.91	96.32	103.91	111.51	100.83
298.16	60.74	67.97	75.16	82.47	89.86	97.25	104.79	112.32	119.85
300	60.90	68.16	75.37	82.68	90.08	97.47	105.01	112.53	120.08
310		69.25	76.53		91.32	98.72		113.82	121.43
320		70.40	77.76		92.61				123.05

capacity of *n*-tetradecane, observed a "hump" in the  $C_{\text{satd}}$  vs.  $T$  curve in the neighborhood of 194°K. corresponding to an excess enthalpy of 43.6 cal. mole<sup>-1</sup>. This anomaly was not observed in the present study.

The increase of heat capacity with temperature is abnormal in the melting region for the hydrocarbons containing an even number of carbon atoms and in the region immediately below the transition temperature for the "odd" *n*-paraffins. In Fig. 2 the specific heat vs. reduced temperature ( $\tau = T/T_{\text{T.P.}}$ ) curves for *n*-nonane (representative of the "odd" *n*-paraffins), *n*-dodecane and *n*-hexadecane (representative of the "even" *n*-paraffins) are given to permit comparison of the shapes of the

various curves in these temperature regions. The reduced temperature was chosen as abscissa to permit a comparison in spite of widely different transition or melting points. The dashed lines are visual extrapolations of the "normal" specific heat curves. In each case the onset of the marked increase of slope of these curves occurs at a value of the specific heat of about 0.3 cal. deg.<sup>-1</sup> g.<sup>-1</sup>. It is difficult to estimate quantitatively the amount of excess heat capacity above the "normal" value. However, it is considerably larger than heterophase premelting effects that may be calculated from impurity values determined in the melting point studies by a factor ranging from 2 for *n*-octane to 8 for *n*-hexadecane. Similar phenomena have been reported by other in-

TABLE IV

HEATS OF FUSION AND CRYOSCOPIC CONSTANTS OF THE NORMAL PARAFFIN HYDROCARBONS OCTANE TO HEXADECANE

Compound	Heat of fusion, cal. mole <sup>-1</sup>	Cryoscopic constant, <sup>a</sup> deg. <sup>-1</sup>
<i>n</i> -Octane	4957 ± 1 <sup>b</sup>	0.05328
<i>n</i> -Nonane	3697 <sup>c</sup>	.03856
<i>n</i> -Decane	6863 ± 2	.05824
<i>n</i> -Undecane	5301 <sup>c</sup>	.04352
<i>n</i> -Dodecane	8804 ± 5	.06376
<i>n</i> -Tridecane	6812 ± 1	.04780
<i>n</i> -Tetradecane	10772 ± 1	.06962
<i>n</i> -Pentadecane	8268 ± 4	.05191
<i>n</i> -Hexadecane	12753 ± 3	.07561

<sup>a</sup>  $\Delta H_{\text{fusion}}/RT_{\text{T.P.}}$ . <sup>b</sup> Precision uncertainty. <sup>c</sup> Obtained from enthalpy measurements of transition and fusion heats combined.

TABLE V

MOLAL HEATS OF TRANSITION AND TRANSITION TEMPERATURES

Compound	Transition temp., °K.	Heats of transition, cal./mole <sup>-1</sup>		
		I	II	Mean
<i>n</i> -Nonane	217.2			1501 <sup>a</sup>
<i>n</i> -Undecane	236.6			1639 <sup>a</sup>
<i>n</i> -Tridecane	255.0	1832	1829	1831 ± 2 <sup>b</sup>
<i>n</i> -Pentadecane	270.9	2186	2195	2191 ± 5 <sup>b</sup>

<sup>a</sup> Obtained from enthalpy measurements of transition and fusion heats combined. <sup>b</sup> Precision uncertainty.

TABLE VI

ENTROPY SUMMARY: *n*-PARAFFIN HYDROCARBONS OCTANE THROUGH HEXADECANE, CAL. DEG.<sup>-1</sup> MOLE<sup>-1</sup>

<i>n</i> -Octane		
0-12°K.	Debye extrapolation, 7 degrees of freedom, $\theta = 134.0^\circ\text{K}$ .	0.258
12-216.38	Solid, graphical, $\int C_{\text{satd}} d \ln T$	44.708
216.38	Fusion, 4957/216.38	22.909
216.38-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	18.451
Entropy (±0.17)	of liquid at 298.16°K.	86.326
<i>n</i> -Nonane		
0-12°K.	Debye extrapolation, 7 degrees of freedom, $\theta = 129.5^\circ\text{K}$ .	0.286
12-217.19	Solid, graphical, $\int C_{\text{satd}} d \ln T$	49.579
217.19	Transition, 1501/217.19	6.911
217.19-219.66	Solid, graphical, $\int C_{\text{satd}} d \ln T$	0.712
219.66	Fusion, 3697/219.66	16.831
219.66-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	19.772
Entropy (±0.19)	of liquid at 298.16°K.	94.091
<i>n</i> -Decane		
0-12°K.	Debye extrapolation, 8 degrees of freedom, $\theta = 137.1^\circ\text{K}$ .	0.276
12-243.51	Solid, graphical, $\int C_{\text{satd}} d \ln T$	58.643
243.51	Fusion, 6863/243.51	28.184
243.51-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	14.690
Entropy (±0.20)	of liquid at 298.16°K.	101.793

<i>n</i> -Undecane		
0-12°K.	Debye extrapolation, 7 degrees of freedom, $\theta = 124.9^\circ\text{K}$ .	0.318
12-236.6	Solid, graphical, $\int C_{\text{satd}} d \ln T$	62.104
236.6	Transition, 1639/236.6	6.927
236.6-247.59	Solid, graphical, $\int C_{\text{satd}} d \ln T$	3.850
247.59	Fusion, 5301/247.59	21.410
247.59-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	14.886
Entropy (±0.22)	of liquid at 298.16°K.	109.495

<i>n</i> -Dodecane		
0-12°K.	Debye extrapolation, 8 degrees of freedom, $\theta = 132.3^\circ\text{K}$ .	0.304
12-263.59	Solid, graphical, $\int C_{\text{satd}} d \ln T$	72.728
263.59	Fusion, 8804/263.59	33.400
263.59-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	10.835
Entropy (±0.23)	of liquid at 298.16°K.	117.267

<i>n</i> -Tridecane		
0-12°K.	Debye extrapolation, 8 degrees of freedom, $\theta = 127.6^\circ\text{K}$ .	0.341
12-255.0	Solid, graphical, $\int C_{\text{satd}} d \ln T$	76.382
255.0	Transition, 1831/255.0	7.180
255.0-267.79	Solid, graphical, $\int C_{\text{satd}} d \ln T$	5.339
267.79	Fusion, 6812/267.79	25.438
267.79-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	10.286
Entropy (±0.25)	of liquid at 298.16°K.	124.966

<i>n</i> -Tetradecane		
0-12°K.	Debye extrapolation, 8.5 degrees of freedom, $\theta = 131.1^\circ\text{K}$ .	0.335
12-279.03	Solid, graphical, $\int C_{\text{satd}} d \ln T$	86.925
279.03	Fusion, 10,772/279.03	38.605
279.03-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	6.881
Entropy (±0.26)	of liquid at 298.16°K.	132.746

<i>n</i> -Pentadecane		
0-12°K.	Debye extrapolation, 9 degrees of freedom, $\theta = 130.2^\circ\text{K}$ .	0.362
12-270.9	Solid, graphical, $\int C_{\text{satd}} d \ln T$	90.782
270.9	Transition, 2191/270.9	8.088
270.9-283.11	Solid, graphical, $\int C_{\text{satd}} d \ln T$	6.195
283.11	Fusion, 8268/283.11	29.204
283.11-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	5.784
Entropy (±0.28)	of liquid at 298.16°K.	140.416

<i>n</i> -Hexadecane		
0-12°K.	Debye extrapolation, 9 degrees of freedom, $\theta = 129.6^\circ\text{K}$ .	0.367
12-291.34	Solid, graphical, $\int C_{\text{satd}} d \ln T$	101.189
291.34	Fusion, 12,753/291.34	43.774
291.34-298.16	Liquid, graphical, $\int C_{\text{satd}} d \ln T$	2.765
Entropy (±0.29)	of liquid at 298.16°K.	148.095



investigators. Ubbelohde<sup>10</sup> also observed a marked increase of the heat capacities below the melting point of *n*-tetradecane, *n*-pentadecane, *n*-hexadecane and *n*-octadecane. Pitzer,<sup>11</sup> in studies of the heat capacities of ethylene dichloride and dibromide, found a gradual increase in the heat capacity of the crystals which he attributed to the beginning of rotation of the whole molecules about their long axes. From a study of the change of dielectric constant with temperature of some long-chain alkyl alcohols, amines and bromides, Hoffman and Smyth<sup>12</sup> observed that a marked increase in dielectric constant takes place below the melting point and attributed this to the gradual onset of molecular rotational freedom. This phenomenon has been termed "prerotation."<sup>13</sup> From X-ray studies, Müller<sup>14</sup> concluded that *n*-paraffin molecules tend to rotate about their longitudinal axes at temperatures below their melting points. The specific heat measurements on the normal paraffins, below their melting and transition temperatures, accord with the concepts of Pitzer, Hoffman and Smyth, and Müller. However, from the heat capacity data alone it can only be said that an abnormal energy-

- (10) A. R. Ubbelohde, *Trans. Faraday Soc.*, **34**, 282 (1938).  
 (11) K. S. Pitzer, *THIS JOURNAL*, **62**, 331 (1940).  
 (12) J. P. Hoffman and C. P. Smyth, *ibid.*, **71**, 431 (1949); *ibid.*, **71**, 3591 (1949); *ibid.*, **72**, 171 (1950).  
 (13) C. P. Smyth, *Trans. Faraday Soc.*, **42A**, 175 (1946).  
 (14) A. Müller, *Proc. Roy. Soc. (London)*, **A127**, 417 (1930); *ibid.*, **A138**, 514 (1932).

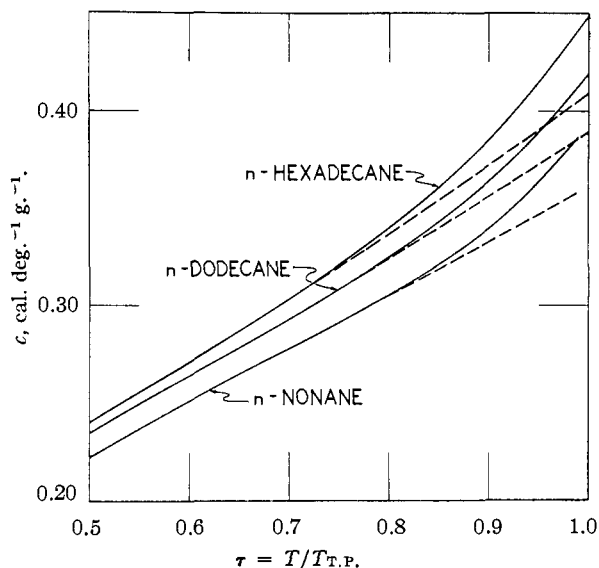


Fig. 2.—Specific heat vs. reduced-temperature curves for several *n*-paraffins.

absorbing process occurs below the melting or transition temperatures and that the effect of this phenomenon is too large to attribute to heterophase pre-melting.

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## Thermodynamics of the In-In<sub>2</sub>S<sub>3</sub> System

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The phase diagram for In-In<sub>2</sub>S<sub>3</sub> (previously published) indicated the probable existence of four sulfides of indium, In<sub>2</sub>S<sub>3</sub>, In<sub>3</sub>S<sub>4</sub>, In<sub>5</sub>S<sub>8</sub> and InS. In the present work each of these compounds was prepared by melting together the calculated amounts of indium metal and In<sub>2</sub>S<sub>3</sub> under a helium atmosphere. Each compound was then reduced at various temperatures with hydrogen gas in a dynamic system so that the exit gases could be analyzed for hydrogen and hydrogen sulfide. From the equilibrium data obtained, free energies of reaction for each reduction were obtained. From these values, free energies of formation for each of the four sulfides of indium were calculated. Free energies of each reaction as a function of temperature are shown graphically.

Published literature gives no values for the thermodynamic properties of the sulfides of indium. The phase diagram for the In-In<sub>2</sub>S<sub>3</sub> system previously published<sup>1</sup> showed that the In-In<sub>2</sub>S<sub>3</sub> system was quite complex, and indicated the probable existence of four sulfides of indium: In<sub>2</sub>S<sub>3</sub>, (In<sub>3</sub>S<sub>4</sub>), (In<sub>5</sub>S<sub>8</sub>) and InS. An attempt has been made to calculate the thermodynamic values of these compounds from the equilibrium constants obtained by reduction of these sulfides with hydrogen. The results help to give a more coherent picture of the In-In<sub>2</sub>S<sub>3</sub> system, and agree well with the results of the thermal analysis.<sup>4</sup>

### Experimental Part

The equilibrium values for the reduction of the sulfides of indium were determined in a dynamic system similar to

(1) M. F. Stubbs, J. A. Schufle, A. J. Thompson and J. M. Duncan, *THIS JOURNAL*, **74**, 1441 (1952).

the one previously described<sup>2</sup> which was modified to permit analysis of the exit gases for hydrogen and hydrogen sulfide. The charge of 10–12 g. of the various sulfides was suspended on washed and ignited asbestos in the Vycor reaction tube. The incoming gas passed into the reaction tube at a rate of 5–10 cc. per minute. The total volume of the exit gases was measured in a gas buret, and the mixture was then analyzed for H<sub>2</sub>S and H<sub>2</sub>. When the per cent. of H<sub>2</sub>S in the exit mixture was high, the H<sub>2</sub>S was removed by bubbling the mixture through 44% aqueous KOH solution. The volume of H<sub>2</sub> collected over the KOH solution was then determined, and the volume of H<sub>2</sub>S was determined by difference. When the amount of H<sub>2</sub>S in the exit mixture was small, titration with standard iodine solution, by means of a Tutwiler apparatus, provided the determination. In the case of the reduction of In<sub>2</sub>S<sub>3</sub>, where the value of the equilibrium constant ( $K_e = P_{H_2S}/P_{H_2}$ ) was large, the equilibrium was approached from both sides, and separate determinations were made with pure H<sub>2</sub>, pure H<sub>2</sub>S, and mixtures of the two as incoming gases. In the case of all the other sulfides, where the value of the equilibrium constant was small, pure H<sub>2</sub> was

(2) M. F. Stubbs, J. A. Schufle and A. J. Thompson, *ibid.*, **74**, 6201 (1952).