7. The reaction rate was retarded by increased viscosity.

8. The reaction is composed of two separate zero order reactions, the initial reaction being partially chemically and diffusion controlled, and the later reaction being definitely diffusion controlled.

9. Thermodynamic considerations and influence of ionic strength, varied by chloride ion addition, indicate that the rate controlling step for the initial part of the reaction is $OH^- + OH^- + Cu^0 = X^=$.

Low-Temperature Thermal Data on the Five Isomeric Hexanes[1]

BY DONALD R. DOUSLIN[2] AND HUGH M. HUFFMAN[3]

The Bureau of Mines is carrying on a research program to obtain precise and accurate values of the thermodynamic constants of petroleum hydrocarbons and related compounds. In this paper are presented the results of low-temperature thermal studies on the five isomeric hexanes. All of these compounds have been studied by other workers. Parks, Huffman and Thomas[4] and Parks, Huffman and Barmore[5] studied n-hexane over the temperature range 90 to 300° K. Stull[6] has also made a superficial investigation of all of the hexanes over the temperature range 90 to 320° K. More recently Pitzer and Kilpatrick[7] have made a careful study of 2,2-dimethylbutane over the temperature range 15 to 280° K. This duplication again affords an opportunity to compare results from (different) laboratories which claim high accuracy for their measurements.

Experimental

The Materials.—The hydrocarbons used in this investigation were A. P. I.–N. B. S. "Best" samples purified by the A. P. I. Research Project 6 at the National Bureau of Standards[8] and certified by them in regard to their purity.

In the course of the measurements the melting points of these compounds have been studied under equilibrium conditions in the usual manner.[9]

(1) Published by permission of the Director of the Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Associate Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

(3) Principal Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

(4) Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032 (1930).

(5) Parks, Huffman and Barmore, ibid., **53**, 3876 (1931).

(6) Stull, ibid., **59**, 2726 (1937).

(7) Kilpatrick and Pitzer, ibid., **68**, 1066 (1946).

(8) These samples of A.P.I.–N.B.S. hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the A. P. I. Research Project 44 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by the A. P. I. Research Project 6 on the "Analysis, purification and properties of hydrocarbons," under the supervision of Frederick D. Rossini, from material supplied by the following laboratories: n-hexane, 2-methylpentane, 3-methylpentane, and 2,2-dimethylbutane, by the A. P. I. Research Project 6 on the "Analysis, purification and properties of hydrocarbons," at the National Bureau of Standards; 2,3-dimethylbutane, by the Standard Oil Company (Indiana), Whiting, Indiana, and M. W. Kellogg Company, New York, N. Y.

(9) Douslin and Huffman, ibid., **68**, 173 (1946).

Unfortunately it was impossible to crystallize 3-methylpentane, so its purity could not be checked by the freezing-point method. The experimental and certain derived data for four of these compounds are summarized in Table I.

TABLE I

MELTING POINT SUMMARY

$0°C. = 273.16° K.$

% Melted	T, °K. Obs.	T, °K. Calcd.	Melted	T, °K. Obs.	T, °K. Calcd.
	n-Hexane, $N_x = 0.0498 \Delta T$			2-Methylpentane $N_x = 0.0527 \Delta T$	
9.3	177.8202	177.8202	11.4	119.5075	119.504
26.1	.8307	.8307	24.2	.5300	.529
54.2	.8336	.8336	48.2	.5405	.541
77.4	.8346	.8345	72.2	.5445	.544
88.6	.8346	.8347	89.6	.5465	.546
100.0	...	.8349	100.0	...	.546
Pure	...	.8364	Pure	...	.552

Triple pt. 177.84 ± 0.05°K.   Triple pt. 119.55 ± 0.05°K.
Impurity 0.0075 mole%   Impurity 0.029 mole%

	2,3-Dimethylbutane N_x 0.00458 ΔT			2,2-Dimethylbutane N_x 0.00229 ΔT	
22	145.058	145.038	27.3	174.095	174.035
47	.118	.117	51.8	.159	.150
58	.129	.130	77.4	.193	.193
90	.150	.150	91.1	.206	.206
100	...	.154	100.0	...	.212
Pure	...	.186	Pure	...	.279

Triple pt. 145.19 ± 0.05°K.   Triple pt. 174.28 ± 0.05°K.
Impurity 0.015 mole%   Impurity 0.015 mole%

A study of these data indicates that 2,3-dimethylbutane and 2,2-dimethylbutane do not obey Raoult's law over the entire range of composition (liquid–solid) studied. The differences between T(obs) and T(calcd) are much greater than the probable uncertainty in the temperature measurements. Both compounds have extremely low heats of fusion and consequently suffer large depressions in the melting point for small amounts of impurity, thus making the measurements more sensitive to deviations from ideal behavior. It is also possible that these measurements may indicate that solid solutions are formed. The calculated triple point temperatures and impurity are

therefore more or less arbitrary. It is quite unlikely that this uncertainty will have a very large effect on the thermal data.

The materials were placed in a glass container connected to a high vacuum system and were alternately frozen and melted *in vacuo* to remove any dissolved gases. They were then distilled into the copper calorimeter, which was joined to the glass system by means of a Housekeeper seal. When the calorimeter was full, the small (1.0 mm. o.d.) filling tube was pinched off and immediately closed with a drop of soft solder.

The Apparatus.—The measurements were made in the apparatus described by Ruehrwein and Huffman,[10] which was loaned to the Bureau of Mines by the California Institute of Technology. Very briefly, the method is as follows: The material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for the determination of the resistance of the thermometer and for the electrical energy were made on a "White" double potentiometer in conjunction with a high-sensitivity galvanometer and accurately calibrated resistances. The potential was in terms of a bank of six saturated cadmium cells which had been certified by the National Bureau of Standards. Time measurements were made with an electric stop clock, which was frequently compared against a stop watch. The precision of the measurements was, in general, better than 0.1%, and above 30° K. it is believed the accuracy uncertainty should not be greater than 0.2% in this temperature range. The energy measurements were made in terms of the international joule and were converted to calories by dividing by 4.1833.

Experimental Results

One of these compounds, 2-methylpentane, could be obtained either in the crystalline or glassy state. Measurements were made on both forms from hydrogen temperatures to slightly below the melting point.

It was not possible to crystallize 3-methylpentane by any of the methods used. Measurements were made on the glass and liquid from approximately 48° K. to room temperature.

The results of the specific-heat measurements on these five compounds are listed in Table II. In Table III are listed the values of the specific heats at integral temperatures as selected from smooth curves drawn through all of the data. Due to the relatively large uncertainties in the

(10) Ruehrwein and Huffman, THIS JOURNAL, **65**, 1620 (1943).

TABLE II

THE MOLAL HEAT CAPACITY OF THE HEXANES

0°C. = 273.16° K., mol. wt. = 84.176

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
		n-Hexane			
13.08	1.517	0.942	151.66	9.968	26.283
14.92	2.175	1.305	153.43	10.167	26.465
17.18	2.301	1.839	161.32	5.593	27.574
18.24	5.204	2.135	161.40	9.527	27.582
19.96	3.220	2.574	167.50	6.779	28.488
23.20	4.642	3.495	173.50	5.219	29.808
23.48	3.793	3.570		Liquid	
27.82	4.880	4.833	180.42	5.375	40.647
28.90	6.727	5.148	190.44	8.932	40.764
32.53	4.543	6.207	191.03	7.120	40.796
34.72	4.912	6.830	193.87	8.869	40.840
39.57	4.784	8.161	199.34	8.876	40.900·
44.95	5.984	9.557	200.77	12.361	41.015
51.30	6.708	11.102	202.70	8.797	41.073
55.89	7.106	12.114	208.18	8.802	41.164
58.26	7.206	12.667	212.33	10.462	41.330
62.56	6.249	13.551	213.05	12.207	41.419
69.43	7.475	14.861	222.73	10.331	41.739
76.57	6.805	16.158	225.19	12.052	41.862
83.13	6.313	17.271	233.00	10.209	42.240
84.15	11.901	17.446	237.98	13.531	42.584
90.51	8.452	18.470	243.13	10.059	42.862
95.47	10.746	19.155	251.40	13.291	43.332
98.69	7.904	19.603	253.12	9.920	43.489
106.38	7.482	20.634	262.97	9.783	44.051
112.00	22.331	21.340	264.95	13.832	44.256
114.56	8.873	21.686	272.68	9.628	44.775
123.21	8.437	22.771	278.24	12.758	45.182
131.81	8.773	23.834	282.23	9.475	45.512
133.77	21.187	24.044	290.87	12.506	46.141
141.44	10.470	24.963	300.98	7.691	46.941
143.02	10.663	25.196			
		2-Methylpentane			
13.00	1.364	1.128	110.54	6.725	21.058
14.50	1.560	1.428	111.67	5.342	21.224
16.13	1.600	1.903		Liquid	
17.90	1.891	2.417	103.56	3.483	34.601[a]
20.30	2.872	3.095	117.41	5.646	35.057[a]
23.21	2.938	3.965	121.16	4.481	35.182
23.70	6.290	4.133	123.58	6.697	35.256
26.43	3.485	4.920	125.62	4.436	35.408
29.06	4.419	5.681	126.25	5.550	35.350
30.06	3.746	5.957	130.24	6.614	35.498
33.88	3.894	6.998	132.24	8.798	35.611
33.89	5.224	7.002	136.81	6.535	35.752
38.42	5.152	8.174	142.04	10.807	35.985
40.16	7.304	8.580	145.44	10.721	36.118
44.22	6.431	9.537	152.76	10.624	36.379
46.80	5.994	10.114	156.07	10.537	36.556
50.19	5.500	10.868	163.79	10.427	36.870
52.42	5.229	11.334	173.63	10.255	37.373
55.37	4.905	11.956	181.68	9.509	37.749
57.39	4.721	12.342	183.80	10.096	37.867
62.62	5.728	13.363	193.82	9.948	38.376
68.11	5.254	14.385	203.69	9.786	38.974
74.50	7.522	15.492	213.40	9.633	39.562
81.70	6.895	16.721	222.96	9.481	40.184

Table II (Concluded)

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
86.21	6.566	17.462	232.36	9.328	40.853
88.36	6.425	17.831	241.62	9.187	41.495
92.58	6.184	18.451	251.62	10.820	42.323
94.62	6.079	18.756	262.34	10.619	43.183
98.61	5.877	19.360	272.86	10.421	44.036
100.55	5.791	19.637	283.19	10.232	44.929
104.36	5.624	20.176	293.33	10.032	45.891
106.22	5.553	20.442	303.27	9.864	46.751

2-Methylpentane Glass

T, °K.	C_p	T, °K.	C_p
11.93	1.441	72.86	16.98
13.26	1.805	73.94	17.24
16.04	2.575	76.45	18.85
20.16	3.848	77.33	19.23
22.37	4.493	78.80	23.54
25.95	5.586	79.10	32.30
26.33	5.715	79.98	33.44
31.78	7.184	80.36	40.07
32.72	7.472	80.41	32.74
37.95	8.830	81.29	34.46
43.54	10.112	81.39	35.27
48.52	11.43	82.48	38.48
48.92	11.37	82.74	34.32
52.84	12.48	84.18	34.45
53.67	12.54	85.01	34.23
54.22	12.76	85.78	34.53
57.83	13.53	86.95	34.88
58.11	13.45	87.36	34.57
62.96	14.58	91.76	34.57
63.62	14.96	92.63	34.58
63.83	15.24	97.83	34.56
68.06	15.70	103.6	34.59
69.69	16.33	117.4	35.04

3-Methylpentane Glass and Liquid

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
50.89	7.709	11.899	136.12	10.658	35.493
58.08	6.660	13.400	146.67	10.451	35.944
65.30	7.790	14.976	157.04	10.281	36.342
70.78	3.517	16.500	167.23	10.115	36.777
74.37	3.221	18.117	177.27	9.956	37.242
77.15	2.34	26.684	187.14	9.797	37.758
79.81	2.845	34.004	196.88	9.662	38.236
84.59	6.717	34.154	206.46	9.516	38.767
86.00	6.654	34.222	215.91	9.380	39.317
91.46	7.021	34.234	217.67	14.971	39.404
92.61	6.570	34.229	225.22	9.243	39.913
99.13	6.481	34.313	230.66	10.994	40.239
99.57	9.209	34.332	242.44	12.576	41.074
105.57	6.399	34.400	254.89	12.313	41.983
108.70	9.039	34.509	267.07	12.058	42.934
114.34	11.130	34.699	279.00	11.800	43.959
117.65	8.869	34.810	290.68	11.569	44.929
125.34	10.883	35.071	302.14	11.338	45.947

2,3-Dimethylbutane

Cryst. 1

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
13.74	1.227	1.077	139.14	1.529	32.809
15.32	1.793	1.466	140.96	2.520	33.083
15.46	1.752	1.500		Liquid	
17.20	1.652	1.958	149.37	4.852	34.746
17.24	1.972	1.960	150.86	9.695	34.910
19.67	2.834	2.726	151.01	7.769	34.871
19.90	3.670	2.801	154.19	4.796	35.045
			158.97	4.754	35.292
22.81	3.409	3.721	159.66	9.535	35.388
23.65	3.796	3.981	160.47	9.531	35.338
26.10	3.149	4.736	163.70	4.736	35.578
27.69	4.228	5.196	168.40	4.642	35.828
29.39	3.407	5.680	169.12	9.368	35.900
32.27	4.921	6.513	169.90	9.327	36.019
32.88	3.562	6.680	173.03	4.629	36.113
36.72	4.064	7.670	177.65	4.591	36.351
37.66	5.843	7.828	178.41	9.227	36.351
41.09	4.664	8.685	179.16	9.199	36.397
45.96	5.071	9.719	187.56	9.075	36.900
51.17	5.360	10.759	188.95	18.008	36.987
52.52	7.678	11.038	196.57	8.934	37.449
61.42	10.116	12.646	205.44	8.802	37.977
70.86	8.764	14.238	206.69	17.487	38.009
79.18	7.870	15.632	214.18	8.683	38.468
87.04	6.206	16.922	222.80	8.555	39.058
87.22	8.202	16.986	223.93	16.989	39.129
93.04	5.854	17.878	231.29	8.429	39.655
96.03	9.439	18.368	239.66	8.308	40.257
99.65	7.364	18.896	240.68	16.514	40.300
105.12	8.739	19.778	247.91	8.196	40.828
106.80	6.941	20.028	252.98	8.082	41.220
113.57	6.589	21.109	256.05	8.072	41.492
115.11	11.237	21.249	261.01	7.967	41.839
120.01	6.286	22.175	264.84	9.524	42.246
124.03	7.637	22.854	268.91	7.849	42.525
125.92	10.386	23.195	274.30	9.378	42.955
126.15	6.008	23.259	276.70	7.732	43.248
131.45	7.207	24.338	284.39	7.632	43.856
	Crystals II		291.97	7.528	44.533
137.61	1.527	32.905	299.44	7.427	45.205
138.30	2.795	32.857	306.46	6.599	45.864

2,2-Dimethylbutane

Crystals I

T, °K.	ΔT	C_p	T, °K.	ΔT	C_p
12.86	1.593	0.951	134.56	5.622	30.935
14.75	2.116	1.437	136.98	4.045	30.968
17.22	2.774	2.163		Crystals III	
20.49	3.728	3.169	144.58	6.475	32.288
24.30	3.905	4.400	147.84	11.436	32.382
28.42	4.324	5.706	151.31	6.978	32.494
33.14	5.109	7.014	159.12	8.631	32.652
38.76	6.133	8.387	161.40	15.686	32.756
45.83	8.006	9.844	167.68	8.504	33.019
52.62	8.101	11.053		Liquid	
52.87	11.563	11.100	177.25	6.208	35.975
53.22	6.776	11.177	180.06	10.296	36.089
61.26	9.199	12.520	181.00	8.199	36.188
64.88	12.458	13.115	185.46	10.203	36.436
70.84	9.953	14.056	190.26	10.102	36.721
76.43	10.631	14.954	195.57	10.017	37.090
80.24	8.837	15.551	205.49	9.834	37.769
87.59	11.693	16.765	215.24	9.670	38.408
89.26	9.215	17.027	224.83	9.506	39.085
99.13	10.517	18.544	234.26	9.359	39.719
101.66	16.456	18.920	243.54	9.200	40.450
109.23	9.686	20.144	252.67	9.044	41.201
118.58	9.024	21.663	261.64	8.895	41.947
	Crystals II		270.46	8.744	42.752
129.83	3.837	30.217	279.13	8.612	43.456
132.32	4.098	30.650	287.68	8.485	44.201
			296.10	8.361	44.940

a Supercooled liquid.

TABLE III
HEXANES
TABLE OF SMOOTHED VALUES

T, °K.	n-Hexane	2-Methyl-pentane	3-Methyl-pentane	2,3-Di-methyl-butane	2.2-Di-methyl-butane	P. & K. % diff.[b]
13	0.92	1.13		0.92	0.98	
14	1.12				1.24	
15	1.32	1.59		1.38	1.50	3.65
20	2.59	3.00		2.83	3.00	2.56
25	4.00	4.49		4.40	4.62	2.94
30	5.48	5.94		5.86	6.16	2.03
35	6.91	7.30		7.24	7.48	
40	8.28	8.54		8.44	8.68	0.12
45	9.57	9.70		9.52	9.69	
50	10.79	10.82		10.54	10.60	.66
55	11.94	11.86		11.48	11.46	
60	13.03	12.86		12.40	12.32	.77
65	14.02	13.80		13.26	13.13	
70	14.97	14.72		14.11	13.92	.18
75	15.88	15.58		14.94	14.72	
80	16.75	16.44		15.78	15.53	−.26
85	17.58	17.26		16.60	16.34	
90	18.38	18.06		17.40	17.14	−.29
95	19.09	18.81		18.18	17.90	
100	19.78	19.55	34.33	18.96	18.68	− .05
110	21.10	20.98[a]	34.56	20.54	20.27	− .15
120	22.36	35.14	34.88	22.18	21.89	− .27
130	23.61	35.50	35.25	24.04	30.30	.20
140	24.82	35.89	35.65	32.74[a]	31.42	− .76
150	26.05[a]	36.29	36.06	34.83	32.44	− .28
160	27.27[a]	36.72	36.47	35.36	32.72	− .15
170	28.48[a]	37.18	36.90	35.90	32.99[a]	.06
180	40.64	37.66	37.38	36.46	36.11	− .08
190	40.77	38.18	37.88	37.05	36.72	.00
200	40.98	38.74	38.40	37.64	37.38	− .08
210	41.26	39.34	38.96	38.24	38.05	− .16
220	41.64	39.98	39.56	38.88	38.74	− .08
230	42.10	40.68	40.20	39.56	39.43	.15
240	42.66	41.40	40.90	40.28	40.17	.20
250	43.27	42.16	41.62	41.02	40.98	.17
260	43.91	42.97	42.37	41.80	41.81	.24
270	44.59	43.80	43.17	42.64	42.67	.33
280	45.32	44.66	44.00	43.50	43.53	.46
290	46.07	45.56	44.88	44.37	44.41	.58
300	46.72	46.47	45.77	45.28	45.27	

[a] Corrected for premelting.   [b] This column gives the % difference between smoothed data of Pitzer and Kilpatrick and this research for neohexane.

measurements on the glassy material no smoothed data are given.

2,3-Dimethylbutane was found to have two crystalline forms and 2,2-dimethylbutane to have three crystalline forms, as observed by Pitzer and Kilpatrick.[7] Observations were made of the equilibrium temperatures with various amounts transposed. The results of this study are summarized in Table IV. Studies were also made of the heats of transition. The data are summarized in Table V, and the values for the heats of fusion are tabulated in Table VI. These values are probably less accurate than the precision would indicate because of the large uncertainty in the measure-

ment of the specific heat in the short temperature intervals between the transition temperatures and fusion temperatures. As is usual, this should have an insignificant effect on the entropy calculated from the data.

TABLE IV
TRANSITION TEMPERATURE SUMMARY

% in high Temp. form	T, °K.
2,3-Dimethylbutane	
25	136.064
61	136.060
90	136.068
Trans. temp.	136.07 ± 0.05° K.
2.2-Dimethylbutane (lower)	
16	126.798
37	126.807
72	126.812
76	126.814
Trans. temp.	126.81 ± 0.05° K.
2.2-Dimethylbutane (upper)	
28	140.749
75	140.777
86	140.791
Trans. temp.	140.79 ± 0.05° K.

TABLE V
HEATS OF TRANSITION

Substance	Expt. 1	Expt. 2	Expt. 3	Mean
		ΔH, cal./mole		
2,3-Dimethylbutane	1551.9	1552.2		1552.0 ± 1.0
2,2-Dimethylbutane (lower)	1292.0	1293.7	1292.6	1292.7 ± 1.0
2,2-Dimethylbutane (upper)	68.32	68.14	68.14	68.20 ± 0.12

TABLE VI
HEATS OF FUSION

Substance	Expt. 1	Expt. 2	Expt. 3	Mean
		ΔH, cal./mole		
n-Hexane	3127.0	3127.4	3123.9	3126.1 ± 2.2
2-Methylpentane	1496.4	1499.2	1497.2	1497.6 ± 1.6
2,3-Dimethylbutane	191.45	191.38		191.42 ± 0.2
2,2-Dimethylbutane	138.24	138.57		138.40 ± 0.2

The above data have been utilized to calculate the molal entropies of four of these compounds in the liquid form and at 298.16° K. The results of these calculations have been summarized in Table VII.

Discussion

In addition to the above, a calculation was made of the entropy increment between 0° K. and the melting point for 2-methylpentane. From this datum and the entropy of the liquid at the melting point the residual entropy at 0° K. of supercooled 2-methylpentane was found to be 6.7 cal. degrees⁻¹ mole⁻¹.

The first measurements of the heat capacity of supercooled 2-methylpentane were made after it had been cooled rapidly from 163 to 51° K. After the fourth measurement in this series, which ended at 72.7° K., it was observed that the cal-

TABLE VII

SUMMARY OF THE MOLAL ENTROPY DATA

n-Hexane	Cal. deg.$^{-1}$ mole^{-1}
S_{13} (Debye, 6° freedom, = 131.12)	0.299
$\Delta S_{13-177.84}$ (graphical)	30.838
$\Delta S_{177.84}$ (3126.1/177.84)	17.579
$\Delta S_{177.84-298.16°}$ (graphical)	22.045
$S_{298.16°}$ liq.	70.76 ± 0.14

n-Hexane
2-Methylpentane

S_{13} (Debye, 6° freedom, = 122.12)	0.369
$\Delta S_{13-119.55°}$ (graphical)	20.942
$\Delta S_{119.55°}$ (1497.6/119.55)	12.527
$\Delta S_{119.55-298.16}$ (graphical)	35.613
$S_{298.16}$ liq.	69.45 ± 0.14

2,3-Dimethylbutane

S_{13} (Debye, 6° freedom, = 128.5)	0.318
$\Delta S_{13-136.07°}$ (graphical)	23.326
$\Delta S_{136.07°}$ (1552.0/136.07)	11.406
$\Delta S_{136.07-145.19°}$ (graphical)	2.127
$\Delta S_{145.19°}$ (191.42/145.19)	1.318
$\Delta S_{145.19-298.16}$ (graphical)	27.833
$S_{298.16}$ liq.	66.33 ± 0.14

2,2-Dimethylbutane

S_{13} (Debye 7° freedom, = 132.37)	0.340
$\Delta S_{13-126.81°}$ (graphical)	21.713
$\Delta S_{126.81°}$ (1292.7/126.81)	10.194
$\Delta S_{126.81-140.79°}$ (graphical)	3.209
$\Delta S_{140.79}$ (68.20/140.79)	0.484
$\Delta S_{140.79-174.28°}$ (graphical)	6.966
$\Delta S_{174.28°}$ (138.40/174.28)	0.794
$\Delta S_{174.28-298.16}$ (graphical)	21.313
$S_{298.16}$ liq.	65.01 ± 0.13

orimeter was definitely warming, thus indicating an evolution of heat. The same phenomenon was observed after the fifth run which ended at 80.2° K. After the sixth run, which ended at 84.8° K., the calorimeter no longer showed any tendency to warm and measurements were continued up to 101.3° K., where crystallization definitely set in. Since these data indicated that some energy-liberating process other than crystallization was taking place in the temperature region 73–80° K., the calorimeter was again cooled to 56° K. and then rapidly heated to 75° K. Heat was again evolved. The calorimeter was allowed to stand for fifteen hours with the environing temperature at approximately 77° K. A series of eight measurements was made, covering the range 76.5 to 88.2 without any evidence of evolution of heat.

A calculation was made of the energy required to heat the system from 76.54 to 88.16° K. in the two series of measurements. It was found that 6.6 calories additional was required to heat over this range after the system had been allowed to equilibrate. The data obtained in this region are not very accurate because of slow attainment of equilibrium but there can be little question of the qualitative evidence. Furthermore, the slope of the heat-capacity curve in the rapid part of the rise became steeper. The second curve showed no maximum, within the experimental error, thus indicating that the change from the high heat capacity to the low is a continuous process but probably more abrupt than has been hitherto suspected.

It is interesting to note that the same phenomenon of heat evolution was noted with 3-methylpentane in the temperature region 69 to 76°. In this case the heat capacity was not studied after allowing to equilibrate.

The data obtained in this paper can be compared with those obtained by Stull. His data differ from those reported here by such large amounts as to make precise comparison unprofitable. In the case of 2-methylpentane Stull's sample was obviously never completely crystallized, since he obtained a value for the heat of fusion only 6% as large as that reported here and obtained specific heat values for the crystals 38% greater than in this research. Apparently equilibrium was never attained in his apparatus. Strangely the entropies calculated from his data are in good agreement with those of this research.

In the last column of Table V we have listed the percentage of difference between the smoothed data of Pitzer and Kilpatrick[7] and this research for neohexane. Above 30° K. the agreement is fairly good over most of the range. At 130 and 140° K. the difference is probably due to poor attainment of equilibrium on crystals II. The cause of the large discrepancy at 50 and 60° K. is not explained. This comparison again illustrates that the source of these discrepancies should be investigated.

In the case of n-hexane the measurements of Parks, Huffman and Barmore agree with those of this research within the limits of error of the former workers.

Summary

Thermal studies on the five hexanes have been made over the temperature range 13 to 300° K.

Experimental values of the specific heat, heats of transition, heats of fusion, transition temperatures and triple points are given.

The entropies at 298.16° K. of four of the liquid hexanes have been calculated.