whereas all the other three tetrachlorides show at least a small tendency toward compound formation with both of these ethers. This would tend to lead one to the conclusion that the availability of a stable orbital on the central atom of the tetrachloride plays a major role in compound formation in these systems. The carbon atom in carbon tetrachloride has no such stable orbital available.

The fact that anisole has a much stronger tendency than diphenyl ether to react with the tetrachlorides is interesting in light of the fact that a phenyl group has a greater electron withdrawing effect than a methyl group. The electron density about the oxygen atom in diphenyl ether is, therefore, less than about the oxygen atom in anisole; hence, anisole would be expected to have a greater tendency to share a pair of electrons than diphenyl.

The effects of the differences in the electronegativities of carbon, silicon, germanium, and tin, as well as various steric effects are undoubtedly of some significance in interpreting the results obtained in this study. It is hoped that further studies will, to some extent at least, aid in the evaluation and delineation of these effects.

Summary

1. The systems of carbon tetrachloride, silicon tetrachloride, germanium tetrachloride and tin tetrachloride with diphenyl ether and anisole, respectively, have been studied throughout the entire concentration range. Carbon tetrachloride showed no tendency toward compound formation with either of these ethers.

2. The existence of the compounds $C_6H_5OCH_3 \cdot SiCl_4$, $C_6H_5OCH_3 \cdot GeCl_4$, $C_6H_5OCH_3 \cdot SnCl_4$, $C_6H_5OCH_3 \cdot 2SiCl_4$, $C_6H_5OCH_3 \cdot 2GeCl_4$ and $C_6H_5OCH_3 \cdot 2SnCl_4$ has been demonstrated.

3. The probable existence of addition compounds of diphenyl ether with silicon tetrachloride, germanium tetrachloride, and tin tetrachloride, presumably of the general formula $2(C_6H_5)_2O \cdot MCl_4$, has been indicated.

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[CONTRIBUTION NO. 6 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Heat Capacities, Heats of Fusion and Entropies of the Six Pentenes[1]

BY SAMUEL S. TODD, GEORGE D. OLIVER AND HUGH M. HUFFMAN

In continuation of the program[2] of the Bureau of Mines to obtain systematically thermodynamic data on hydrocarbons and related compounds, low-temperature calorimetric studies have been made on the six pentenes over the temperature range 12 to 300 K.

Parks and Huffman[3] have studied 2-methyl-2-butene over the temperature range 93 to 294° K. and also have made measurements on the liquid form of a substance they called pentene-2, which was apparently a mixture of *cis-* and *trans-*2-pentene. Because of incomplete crystallization of this mixture they were unable to calculate a value for its entropy.

The Materials

The hydrocarbons used in this investigation were A.P.I.-N.B.S. samples purified by A.P.I. Research Project 6 at the National Bureau of Standards.[4] The methods of purification and estimates of the purity are given in a report[5] by A.P.I. Research Project 6 (at the National Bureau of Standards).

The Apparatus.—The measurements were made in the apparatus described by Ruehrwein and Huffman,[6] which was loaned to the Bureau of Mines by the California Institute of Technology. Very briefly, the method is as follows: About 0.5 mole of 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 meas-

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(1) Published by permission of the Director, Bureau of Mines, U. S. Dept. of the Interior.

(2) Douslin and Huffman, THIS JOURNAL, **68**, 173 (1946).

(3) Parks and Huffman, *ibid.*, **52**, 4381 (1930).

(4) These samples of API-NBS 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:

1-Pentene, by the Phillips Petroleum Company, Bartlesville, Okla., through the courtesy of F. E. Frey.

***cis*-2-Pentene** and ***trans*-2-pentene,** by the A. P. I. Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under supervision of Cecil E. Boord.

2-Methyl-1-butene and **2-methyl-2-butene,** by the General Motors Corporation, through the courtesy of T. A. Boyd and Wheeler G. Lovell.

3-Methyl-1-butene, by the Houdry Process Corporation through the courtesy of E. A. Smith.

(5) Streiff, Murphy, Sedlak, Willingham and Rossini, *J. Research Natl. Bur. Standards*, **37**, 331 (1946).

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

ured 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 that the accuracy uncertainty should not be greater than 0.2%. The energy measurements were made in terms of the international joule and were converted to calories by dividing by 4.1833.

Experimental

Equilibrium melting temperatures, as summarized in Table I, were determined in the usual way by supplying measured amounts of electrical energy to the calorimeter and contents and then waiting until the temperature was apparently constant. During all of this time the adiabatic shield surrounding the calorimeter was maintained at essentially the same temperature as the calorimeter so there could be no significant energy interchange with the environment. From the measured heats of fusion and heat-capacity measurements it was possible to calculate the fraction of the contents which had been fused. Measurements of the above type were made for several different ratios of liquid to solid for each compound. If Raoult's law is obeyed over the entire concentration range studied and no solid solutions are formed, the relation between N_x, the mole fraction of solute, and the depression of the triple point is given by the simplified expression $N_x = K\Delta T$ (when N_x and ΔT are both small). If it is recalled that N_x is proportional to $1/F$, where F is the fraction of the compound in the liquid form, and that ΔT is equal to $T_{(\text{T.P.})}$[7] $- T^{(\text{obs.})}$ it is readily seen that a plot of $1/F$ against $T_{(\text{obs.})}$ should give a straight line passing through $T_{\text{T.P.}}$ for $1/F = 0$ when Raoult's law is obeyed.

In the melting-temperature studies on five of the pentenes the experimental data fitted an equation of this type quite well over a wide range of liquid–crystal ratios. Consequently, for these compounds the triple point of the pure material and the amount of impurity in the actual sample could be estimated with considerable certainty.

However, in the case of 1-pentene the first set of measurements of the melting temperatures indicated that there was a break in the curve at approximately 50% melted. A second set of measurements at 73.0 and 89.6% melted were in essential agreement with the first data. If the curve through the points 52% liquid and less were extrapolated to zero impurity they gave a triple point in fair agreement with the melting point determined at the N.B.S.[5] by the time-temperature freezing-point method.[8] The curve through the lower values of $1/F$ extrapolated to a triple point several tenths of a degree higher.

TABLE I

MELTING TEMPERATURES OF THE PENTENES

0°C. = 273.16° K.

% Melted	T, °K. Obs.	T, °K. Calcd.	% Melted	T, °K. Obs.	T, °K. Calcd.
1-Pentene,[a] $N_x = 0.0600\ \Delta T$			1-Pentene,[c] $N_x = 0.0600\ \Delta T$		
11.5	107.124		13.7	107.209	
27.3	.562		40.7	.656	
51.9	.713		62.6	.772	
90.2	.936		92.6	.929	
73.0	.894[b]		55.5	.563[d]	
89.6	.938[b]		57.8	.601[c]	
Pure[f]			Pure[f]		
cis-2-Pentene, $N_x = 0.0577\ \Delta T$			*trans*-2-Pentene, $N_x = 0.0568\ \Delta T$		
10.5	121.692	121.680	9.0	132.908	132.908
27.0	.752	.752	24.1	.934	.935
51.8	.773	.774	48.7	.944	.943
78.6	.782	.782	88.3	.947	.947
95.1	.784	.784	100	..	.947
100	..	.785	Pure	..	.951
Pure	..	.797			
Triple point, 121.80 ± 0.05° K.			Triple point, 132.95 ± 0.05° K.		
Impurity, 0.071 ± 0.005 mole %			Impurity, 0.022 ± 0.005 mole %		
2-Methyl-1-butene, $N_x = 0.0517\ \Delta T$			3-Methyl-1-butene, $N_x = 0.0588\ \Delta T$		
12.3	134.715	134.706	8.9	104.626	104.609
25.0	135.170	135.170	24.1	.6771	.6771
49.5	.384	.391	48.5	.6972	.6972
93.3	.498	.498	73.4	.7043	.7040
100	..	.506	91.7	.7065	.7065
Pure	..	.618	100	..	.7074
Triple point, 135.62 ± 0.05° K.			Pure	..	.7170
Impurity, 0.58 ± 0.05 mole %			Triple point, 104.72 ± 0.05° K.		
			Impurity, 0.056 ± 0.005 mole %		
2-Methyl-2-butene, $N_x = 0.0470\ \Delta T$					
8.5	139.142	139.142			
25.8	.327	.329			
51.2	.375	.375			
98.2	.397	.397			
100	..	.397			
Pure	..	.421			
Triple point, 139.42 ± 0.05° K.					
Impurity, 0.11 ± 0.05 mole %					

[a] Series I, temperature measurements with thermometer H-8. [b] Check measurements. [c] Series II, measurements made on same sample using a different calorimeter and thermometer H-9. [d] Equilibrium approached by cooling into melting point. [e] Measurement made after melting small amount of crystals from preceding experiment. [f] The anomalous results obtained preclude a reliable estimate of the triple point and the amount of impurity. See text for discussion.

It was suspected that perhaps the 1-pentene

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[7] $T_{\text{T.P.}}$ is the triple-point temperature for the pure compound and corresponds to the temperature at which the crystals are in equilibrium with the liquid under its own vapor pressure.

[8] A. R. Glasgow, Jr., A. R. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

sample had partly polymerized or had been contaminated in some way. For this reason it was removed from the calorimeter and returned to the Bureau of Standards for a recheck of the melting point. Their check measurement agreed with the original. The material was returned to this Laboratory and another series of measurements was made, using another calorimeter and thermometer. Again the check measurements were in fair agreement and showed the same break in the curve as originally noted.

In order to further check the validity of our measurements an experiment was carried out in which the equilibrium temperature was approached from the cooling side rather than the heating side. This was done by contacting the calorimeter and allowing the cooling process to initiate crystallization, breaking the contact, bringing the shield into balance and allowing the system to come to temperature equilibrium. This point at a composition of only 55.5% liquid due to the large amount of undercooling before freezing was definitely lower than observed in the melting experiments. At the conclusion of this experiment the amount of liquid was increased to 57.8% by melting, and there was a sharp increase in the observed equilibrium temperature, but it was still below the original melting curve.

A possible explanation of the apparent behavior of 1-pentene in the melting-temperature studies is that the observed temperature equilibria are not characteristic of the calculated composition of the system. For example, in making the calculations it is assumed that all of the impurity remains in the liquid phase and that the liquid phase is uniform in concentration. If part of the impurity were removed from the liquid phase by adsorption or occlusion, the effective concentration would be less than that calculated and the observed temperature would be too high for the assumed composition. If this phenomenon does occur it seems probable that the effect would be more pronounced when the ratio of liquid to crystals is small.

In this research the equilibrium temperatures corresponding to 90% or more melted were actually higher, by significant amounts, than those reported by the N.B.S. for the melting point of this sample of 1-pentene. The hypothesis given above will not explain this result since it is obvious that the removal of all of the impurity would only bring the melting temperature up to that of the pure material. The only immediately apparent explanation for an observed melting temperature above that of the melting point of a pure compound is the formation of a solid solution. However, the assumption of the formation of a solid solution does not explain the discrepancy, since there is no obvious reason why a solid solution would be formed under the conditions of this investigation and not in the N.B.S. freezing point apparatus.

The present state of this problem is that the observed discrepancy in the measurements from the two laboratories cannot be satisfactorily explained.

The above results suggest that caution should be used in interpreting studies of this sort made in the usual type of specific heat calorimeter, especially when the amount of impurity is large, with consequent large changes in equilibrium temperatures with the fraction melted. When the amount of impurity is small, the observed temperature differences are also small so that large percentage errors in the composition would have only small absolute effects on the observed temperatures. This only means that the melting point can be measured with more certainty, not that the amount of impurity can be determined with high percentage accuracy.

It is the opinion of the authors that the observed melting temperatures, in this type of a calorimetric system, may well be a function of the conditions under which the sample has been crystallized and melted.

Results

In general, the specific-heat measurements on these compounds were quite straightforward. During the early measurements on *cis*-2-pentene between 85° K. and the triple point it was noted that the heat capacity appeared to be a function of the voltage applied to the heater. This was confirmed by measurements at about 280° K. The calorimeter was dismounted and the thermometer heater assembly given a new coat of grease in order to improve the thermal conductivity After this treatment the measurements were satisfactorily reproducible. All of the experimental points have been listed for *cis*-2-pentene, but those at 89.32, 97.62, 106.26 and 281.80° were definitely low and were given no weight in plotting the smooth curve.

The heat-capacity data on 1-pentene are not as reliable as those on the other compounds. Because of the anomalous results obtained in studying the melting temperatures and because of the large apparent amount of impurity the mass was not determined with the usual accuracy and may be uncertain to as much as 0.1%. The heat-capacity measurement at 75+ °K. is above the smooth curve by nearly 0.5%; no reason is known for this discrepancy and this point was not checked.

These measurements indicate that the sample of 1-pentene has a minimum of about 0.5% impurity, and 2-methyl-1-butene has about 0.6% impurity. Where the amount of impurity is small the usual practice in the past has been to assume that it has no significant effect on the heat capacity of the solid or the liquid. However in a recent study on butadiene[9] by the National Bureau of Standards, evidence has been presented

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[9] Scott, Meyers, Rands, Brickwedde and Bekkedahl, *J. Research Natl. Bur. Standards*, **35**, 39 (1946).

to show that this is not necessarily true. Furthermore, as far as we are aware, there is no way to determine what effect the unknown impurity will have on the heat of fusion.

The actual fusion measurements will be made on a system whose composition and phase relations are unknown, with the consequent inability to state definitely what processes are involved. For this reason the heat of fusion is uncertain by an unknown amount. Hence, it is obvious that it is desirable to make measurements on compounds of high purity and it is planned to repeat the measurements on 1-pentene when a better sample is made available. It is unlikely, however, that the uncertainty in the fusion will affect the entropy by more than 0.1 entropy unit.

The experimental results of the heat-capacity measurements on these six compounds are listed in Table II. In Table III are listed the values of the specific heats at integral temperatures. The experimental data were plotted on a large chart and a curve, the smoothness of which was determined by eye, was drawn through the points; the data in Table III were then read off this curve.

It will be of interest to see how the heat capacities of a series of isomers of this type differ among themselves. As the heat capacities are not very greatly different, the differences would not show on a small scale plot of C_p–T. For this reason we have constructed a plot of C_p (1-pentene) $-C_p$ (x-pentene) using the smoothed data in Table III. It is interesting to note that there is no regularity in these difference plots. These curves may be taken as an indication of the pre-

TABLE II

THE MOLAL HEAT CAPACITIES, $C_{\text{sat.}}$, OF THE PENTENES

Molecular weight = 70.130; 0°C. = 273.16° K.

T, °K.	ΔT	Cal./ degree	T, °K.	ΔT	Cal./ degree
		1-Pentene			
	Crystals		94.05	10.490	31.34[a]
12.72	1.478	0.83	104.50	10.404	31.02[a]
14.53	2.049	1.19	125.73	10.224	30.75
15.30	3.482	1.36	135.12	10.139	30.76
16.67	2.166	1.67	145.20	10.026	30.83
19.12	4.077	2.29	155.17	9.915	30.92
19.28	3.011	2.33	165.04	9.814	31.04
22.87	4.39	3.32	174.80	9.719	31.23
23.99	5.647	3.65	184.47	9.617	31.44
26.95	4.005	4.48	194.98	11.402	31.76
29.68	5.711	5.21	201.97	9.400	31.96
31.15	4.391	5.63	206.29	11.236	32.10
35.66	6.251	6.81	211.32	9.288	32.30
41.78	5.981	8.27	217.45	11.070	32.54
48.10	6.654	9.62	220.47	9.019	32.69
54.65	6.447	10.88	228.44	10.910	33.00
61.06	6.346	11.96	229.51	9.055	33.09
61.86	5.916	12.08	238.51	8.946	33.48
67.84	7.210	13.01	239.26	10.732	33.54
68.39	7.151	13.09	244.40	10.515	33.78
75.47	7.016	14.23	249.90	10.566	34.08
83.28	8.599	15.26	254.82	10.345	34.35
91.56	7.957	16.34	265.09	10.176	34.94
99.07	7.059	18.68[b]	275.18	10.016	35.55
	Liquid		285.11	9.843	36.23
86.35	4.025	31.71[a]	295.28	10.490	36.90
91.57	6.423	31.44[a]			
		cis-2-Pentene			
	Crystals		107.20	11.206	18.784[b]
13.51	1.441	0.817	109.96	6.382	19.194[b]
15.26	1.968	1.111	110.93	6.426	19.323[b]
17.36	2.133	1.529	116.25	6.197	20.693[b]
19.96	3.014	2.125	117.20	6.120	20.305[b]
23.56	4.137	3.029		Liquid	
27.65	3.988	4.118	128.69	5.492	31.87
31.81	4.307	5.214	129.73	5.556	31.87
36.36	6.081	6.388	135.09	7.308	31.73
42.30	5.804	7.824	136.18	7.362	31.70
48.43	6.441	9.194	143.30	9.113	31.56
54.70	6.252	10.468	144.45	9.183	31.55
54.76	6.224	10.487	153.30	10.893	31.44
55.09	6.494	10.567	153.62	9.146	31.46
56.84	6.277	10.898	163.66	10.932	31.38
60.89	6.138	11.655	164.17	10.840	31.38
62.12	7.560	11.887	165.87	10.935	31.34
63.67	7.371	12.173	174.55	10.865	31.40
67.40	6.885	12.812	174.98	10.771	31.40
70.07	8.341	13.254	176.76	10.845	31.42
71.46	8.200	13.468	185.38	10.783	31.50
74.23	6.768	13.904	187.56	10.764	31.51
77.51	6.542	14.444	196.12	10.694	31.65
78.78	6.455	14.634	198.28	10.667	31.69
81.21	7.189	15.001	208.90	10.564	31.91
85.75	9.915	15.742	219.40	10.440	32.23
86.92	9.815	15.912	229.75	10.313	32.56
87.54	7.745	15.944	240.00	10.180	32.98
88.22	7.830	16.069	250.11	10.028	33.47
88.62	7.642	16.162	254.94	9.892	33.69
89.32	7.682	16.156	260.06	9.881	33.98
91.80	3.925	16.546	264.76	9.728	34.27
95.03	7.221	17.021	269.86	9.704	34.51
95.61	9.839	17.136	272.01	4.783	34.64
95.79	7.311	17.134	278.71	7.998	35.02
96.17	7.443	17.182	279.15	9.504	35.06
96.71	9.775	17.283	281.71	7.107	35.22
97.35	7.182	17.329	281.78	7.123	35.21
97.62	8.932	17.285	281.79	7.138	35.09
102.04	6.815	17.983	281.93	7.112	35.21
102.90	6.907	18.088	286.65	7.894	35.51
103.33	6.886	18.162	288.59	9.364	35.66
104.33	6.776	18.324[b]	295.27	9.336	36.08
104.53	8.000	18.389[b]			
106.26	8.338	18.456[b]			
		trans-2-Pentene			
	Crystals		113.70	8.336	18.757
12.77	1.975	0.613	113.82	8.388	18.779
14.79	1.935	0.937	121.82	7.895	19.835[b]
16.71	1.849	1.300		Liquid	
18.45	5.587	1.681	134.98	5.123	30.502
18.70	2.078	1.720	140.59	6.098	30.610
21.68	3.837	2.429	143.46	7.878	30.671
24.52	6.528	3.136	144.88	10.132	30.701

TABLE II (*Continued*)

T, °K.	ΔT	Cal./ degree	T, °K.	ΔT	Cal./ degree
25.64	4.011	3.405	152.27	9.742	30.831
30.34	5.367	4.583	154.95	10.005	30.913
30.46	5.335	4.608	158.09	11.962	30.956
35.57	4.877	5.888	164.90	9.881	31.114
40.90	5.782	7.131	169.95	11.755	31.257
46.66	5.737	8.390	174.72	9.764	31.359
52.40	5.742	9.566	181.62	11.594	31.582
54.70	4.500	10.008	185.38	11.554	31.690
58.15	5.769	10.662	193.13	11.419	31.943
60.08	6.259	11.004	196.84	11.378	32.110
64.25	6.428	11.789	204.47	11.264	32.381
66.02	5.634	12.102	208.14	11.209	32.540
71.85	6.027	13.058	219.25	11.051	32.975
78.04	6.346	14.021	230.23	10.878	33.481
81.67	6.619	14.539	240.81	10.707	34.005
81.81	6.531	14.590	251.65	10.530	34.599
84.16	5.905	14.963	262.08	10.362	35.192
89.05	8.144	15.664	272.31	10.183	35.848
89.11	8.077	15.666	280.52	8.280	36.344
90.58	6.920	15.864	282.47	10.027	36.411
96.92	7.597	16.694	288.74	8.172	36.874
96.92	7.542	16.675	296.06	6.457	37.372
105.11	8.839	17.709	301.68	4.798	37.764
105.17	8.909	17.715			
		2-Methyl-1-butene			
	Crystals		88.24	5.964	14.813
12.69	1.391	0.826	91.06	7.291	15.169
12.84	1.344	.855	94.74	7.053	15.582
14.43	1.960	1.167	98.63	7.840	16.024
14.46	1.942	1.179	102.11	7.677	16.430
15.79	3.022	1.498	106.71	8.321	16.923
16.45	2.075	1.646	110.03	8.169	17.313
16.50	2.092	1.655	117.53	6.822	18.477^b
18.95	2.939	2.285		Liquid	
19.04	2.906	2.305	133.58	5.854	31.807^a
19.20	3.787	2.353	140.14	7.277	31.813
19.26	7.455	2.390	143.92	5.717	31.802
22.46	4.093	3.233	144.95	9.470	31.798
22.53	4.036	3.256	148.12	8.678	31.823
23.77	5.365	3.573	151.52	9.477	31.809
26.73	4.446	4.360	154.39	9.403	31.834
26.77	4.395	4.385	155.84	9.394	31.841
29.23	5.580	5.004	160.95	9.397	31.900
31.06	4.215	5.442	164.22	10.260	31.916
31.10	4.204	5.468	165.66	10.246	31.930
31.98	6.457	5.668	174.44	10.171	32.053
35.15	6.264	6.434	175.85	10.143	32.083
41.31	6.048	7.748	186.40	10.954	32.297
43.52	4.225	8.176	197.29	10.826	32.584
47.72	6.766	8.965	208.05	10.691	32.912
54.39	6.592	10.105	218.67	10.554	33.280
55.82	4.367	10.338	229.15	10.410	33.708
58.44	6.343	10.752	239.49	10.264	34.162
61.31	6.610	11.197	249.68	10.114	34.671
65.39	7.566	11.802	259.72	9.964	35.204
68.33	7.433	12.209	270.41	11.429	35.833
73.42	8.503	12.898	281.74	11.219	36.506
75.85	7.607	13.213	292.86	11.027	37.221
83.54	7.762	14.236			
		3-Methyl-1-butene			
	Crystals		92.95	7.231	15.265
13.27	1.294	0.949	99.42	6.817	16.079
14.92	1.907	1.282	99.89	6.653	16.681^b
16.96	2.096	1.733		Liquid	
19.04	4.236	2.236	103.08	6.711	29.089^a
19.54	3.012	2.357	110.58	8.297	29.077
23.16	4.208	3.306	113.08	6.645	29.079
23.82	5.296	3.486	117.95	6.447	29.077
27.15	4.156	4.347	119.63	6.451	29.117
29.50	6.052	4.934	125.42	8.486	29.180
31.50	4.510	5.425	126.92	8.126	29.226
35.82	6.572	6.443	133.66	8.006	29.327
42.24	6.275	7.791	142.83	10.327	29.520
48.86	6.968	9.029	153.07	10.167	29.771
54.18	6.191	9.927	163.16	10.016	30.046
54.79	6.131	10.018	173.10	9.861	30.395
55.72	6.737	10.167	183.38	10.692	30.739
60.50	6.448	10.901	193.98	10.513	31.201
61.25	6.794	11.019	204.42	10.361	31.585
68.45	7.603	12.051	214.70	10.196	32.074
68.47	9.484	12.056	225.27	10.936	32.624
69.31	7.532	12.175	236.10	10.746	33.203
76.62	8.740	13.153	246.75	10.551	33.841
77.32	8.499	13.241	257.22	10.375	34.446
77.43	8.452	13.256	266.66	8.515	35.010
84.88	7.773	14.272	273.48	5.131	35.472
85.45	7.761	14.329	281.03	9.965	35.994
86.09	8.860	14.410	289.77	7.504	36.660
92.39	7.246	15.183	298.35	9.660	37.315
		2-Methyl-2-butene			
	Crystals		117.28	8.005	20.085
12.52	1.623	0.708	125.08	7.603	21.146^b
14.49	2.216	1.032	127.22	7.796	21.513^b
15.57	3.562	1.258		Liquid	
16.77	2.263	1.504	140.90	4.300	31.602
19.45	4.116	2.142	146.62	7.138	31.574
19.48	3.119	2.144	148.52	5.713	31.575
23.18	4.256	3.088	149.79	9.319	31.595
24.32	5.604	3.397	156.11	9.471	31.579
27.36	4.099	4.186	160.01	11.115	31.565
29.97	5.683	4.877	165.52	9.417	31.608
31.16	3.499	5.173	171.08	11.016	31.669
35.95	6.273	6.399	174.93	9.344	31.710
42.08	5.982	7.839	182.04	10.916	31.824
48.38	6.623	9.218	184.00	9.270	31.853
52.31	7.042	10.032	192.91	10.819	32.009
54.55	5.711	10.476	193.47	9.188	32.031
59.85	8.023	11.496	203.67	10.706	32.261
60.57	6.330	11.636	214.32	10.585	32.530
67.29	7.079	12.869	224.84	10.463	32.852
74.15	6.442	13.975	235.24	10.329	33.260
80.36	5.966	14.979	245.50	10.194	33.684
82.81	6.386	15.341	255.62	10.045	34.180
86.35	6.022	15.953	265.60	9.907	34.650
90.89	9.768	16.580	275.43	9.770	35.164
93.13	7.532	16.918	285.13	9.629	35.695
100.29	9.032	17.849	293.90	7.910	36.247
100.45	7.104	17.878	300.98	6.255	36.708
109.04	8.474	18.992			

[a] Supercooled liquid. [b] These points include premelting.

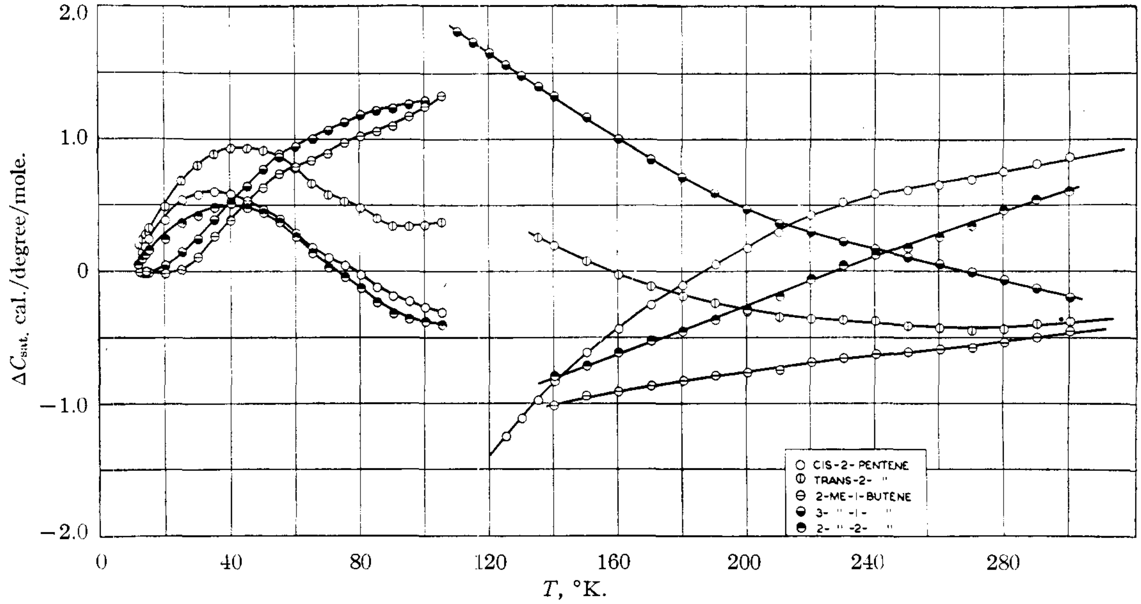

Fig. 1.—Plot of $\Delta C_{sat.}$ against T, showing the difference in specific heat of each of the pentenes from that of 1-pentene.

cision of the measurements since they are all reasonably smooth.

TABLE III

THE MOLAL HEAT CAPACITIES, $C_{sat.}$, IN CAL./DEGREE, AT INTEGRAL TEMPERATURES

T, °K.	1-Pentene	*cis*-2-Pentene	*trans*-2-Pentene	2-Methyl-1-butene	3-Methyl-2-butene	2-Methyl-2-butene
12	0.70		0.50	0.70		0.64
13	.88	0.75	.64	.88	0.89	.78
14	1.08	.89	.80	1.08	1.09	.94
15	1.29	1.06	.97	1.31	1.30	1.13
20	2.52	2.13	2.03	2.55	2.47	2.27
25	3.93	3.40	3.24	3.91	3.79	3.56
30	5.30	4.73	4.50	5.20	5.06	4.88
35	6.65	6.04	5.75	6.38	6.25	6.16
40	7.86	7.28	6.93	7.48	7.34	7.35
45	8.97	8.44	8.04	8.46	8.33	8.49
50	9.99	9.53	9.08	9.36	9.23	9.55
55	10.94	10.54	10.07	10.20	10.05	10.57
60	11.78	11.49	11.00	11.00	10.83	11.52
65	12.58	12.40	11.92	11.74	11.57	12.44
70	13.33	13.23	12.75	12.44	12.27	13.30
75	14.08	14.04	13.55	13.11	12.94	14.12
80	14.80	14.82	14.32	13.77	13.61	14.92
85	15.48	15.59	15.08	14.41	14.26	15.71
90	16.14	16.32	15.79	15.03	14.89	16.45
95	16.79[a]	17.02	16.45	15.61	15.52	17.15
100	17.44[a]	17.71	17.08	16.18	16.14[a]	17.81
105	18.07[a]	18.38[a]	17.70	16.74	29.08	18.47
110	30.89	19.03[a]	18.30	17.31	29.08	19.13
115	30.82	19.68[a]	18.92	17.87[a]	29.08	19.79
120	30.77	20.34[a]	19.52[a]	18.42[a]	29.11	20.44
125	30.75	31.99	20.14[a]	18.98[a]	29.17	21.10[a]
130	30.74	31.85	20.74[a]	19.54[a]	29.26	21.76[a]
135	30.76	31.73	30.51	20.10[a]	29.35	22.42[a]
140	30.79	31.62	30.60	31.80	29.46	31.58
150	30.87	31.48	30.79	31.81	29.69	31.58
160	30.97	31.40	31.01	31.87	29.96	31.58
170	31.13	31.38	31.25	31.99	30.27	31.65
180	31.34	31.44	31.53	32.16	30.62	31.79
190	31.60	31.55	31.85	32.38	31.00	31.96
200	31.90	31.72	32.20	32.66	31.42	32.17
210	32.24	31.95	32.59	32.97	31.87	32.41
220	32.65	32.23	33.01	33.33	32.35	32.69
230	33.09	32.57	33.47	33.74	32.86	33.05
240	33.57	32.98	33.96	34.19	33.41	33.45
250	34.08	33.46	34.49	34.68	33.98	33.90
260	34.64	33.98	35.06	35.22	34.59	34.37
270	35.23	34.53	35.67	35.80	35.23	34.87
280	35.87	35.11	36.31	36.40	35.93	35.41
290	36.55	35.73	36.97	37.04	36.67	36.00
298.16	37.12	36.26	37.52	37.57	37.30	36.52
300	37.25	36.38	37.64	37.69	37.44	36.64

[a] These values taken from extrapolated curve after making allowance for premelting.

Two or more heats of fusion were determined for each of these compounds. In the cases when there were significant amounts of premelting the specific-heat curves were corrected for this, and the excess energy was included in the heat of fusion. While this procedure may involve some error because of the uncertainty in determining the true heat-capacity curve it will have no sig-

TABLE IV

THE MOLAL HEATS OF FUSION OF THE PENTENES

ΔH, in calories

Substance	Expt. 1	Expt. 2	Expt. 3	Mean
1-Pentene	1388	1389[a]	1386	1388 ± 1.8[b]
cis-2-Pentene	1700.3	1698.4	1700.4	1699.7 ± 1.3
trans-2-Pentene	1994.9	1997.0		1996.0 ± 1.0
2-Methyl-1-butene	1891.1	1889.5[a]	1891.3	1890.6 ± 1.0
3-Methyl-1-butene	1281.8	1280.0		1280.9 ± 1.0
2-Methyl-2-butene	1815.9	1815.6		1815.8 ± 1.0

[a] This value was obtained from data taken during the determination of the melting point. [b] Estimated precision uncertainty.

TABLE V

THE MOLAL ENTROPIES OF THE PENTENES, CAL./DEGREE

0°C. = 273.16° K.

Compound	Debye			$\Delta S_{12°}-T_{\text{T.P.}}$[e] crystals	$\Delta S T_{\text{T.P.}}$ fusion	$\Delta S T_{\text{T.P.}-298.16}$ sat. liq.	$S_{298.16°}$ sat. liq.	$T_{\text{T.P.}}$ °K.
	°Freedom	Θ	$S_{12°}$					
1-Pentene	5	123.0	0.238	16.93	12.86	32.72	62.75 ± 0.20	107.9[a]
cis-2-Pentene	5	132.4	.242[b]	18.592[c]	13.955	29.019	61.81 ± .12	121.80
trans-2-Pentene	6	146.2	.171	19.657	15.013	26.466	61.31 ± .12	132.95
2-Methyl-1-butene	5	122.5	.241	20.243	13.941	26.272	60.70 ± .12	135.62
3-Methyl-1-butene	5	123.1	.300[b]	15.209[c]	12.232	32.796	60.54[d] ± .12	104.72
2-Methyl-2-butene	5	129.1	.206	21.808	13.024	24.966	60.00 ± .12	139.42

[a] This value from reference 5. [b] Debye entropy at 13°K. [c] $\Delta S_{13°}-T_{\text{T.P.}}$. [d] Above normal boiling point. [e] $_{\text{T.P.}}T$ = triple point temp.

nificant effect on the experimentally determined entropy. The effect of impurity on the measurement of the heat of fusion has been discussed above. The calculated heats of fusion for these compounds are given in Table IV. The uncertainties listed are precision uncertainties.

The experimental data have been utilized to calculate the entropies of these compounds. These calculations are summarized in Table V.

Discussion

It should be noted that under the conditions of the measurements the quantity actually measured is the heat capacity of the saturated liquid ($C_{\text{sat.}}$). All of these compounds boil in the neighborhood of room temperature, and at the higher temperatures the difference between $C_{\text{sat.}}$ and C_p may be barely significant. The calculated entropies for the liquid state are also for the saturated liquid.

In some of the measurements at low temperatures the temperature rise is rather large. An estimate of the error produced by not allowing for the curvature showed that it was less than the experimental error so no correction has been applied for curvature. At the higher temperatures a small correction, less than 0.1%, has been applied for vaporization into the gas space. In the case of 2-methyl-2-butene the measurements of Parks and Huffman[3] agree with those of this research within the 1% limit of error of the former workers.

Acknowledgment.—The authors wish to express their thanks to Mr. D. R. Douslin who assisted with the measurements and calculations. Grateful acknowledgment is also made to the American Petroleum Institute and to the National Bureau of Standards for the loan of the samples measured.

Summary

Heat-capacity data on the six pentenes have been given over the temperature range 12 to 300° K.

Values of the triple points and heats of fusion have been given.

Entropy values for the liquid state at 298.16° K. were calculated.

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[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY, OFFICE OF NAVAL RESEARCH, WASHINGTON 20, D. C.]

Ethylene Adsorption Isotherms at −183°

BY ROBERT L. BURWELL, JR.,[1] P. ALLEN SMUDSKI[2] AND THOMAS P. MAY

In connection with corrosion problems, it was desired to measure surface areas of sheet metal. The specific surface of smooth metal foil is too low to permit application of the Brunauer, Emmett and Teller equation[3] to nitrogen adsorption isotherms. The use of much lower pressures would permit the measurement of smaller quantities of gas and reduce the effect of dead space. The method of Wooten and Brown,[4] adsorption of ethylene at the temperature of liquid oxygen, was adapted to this purpose. Some unusual features of the adsorption isotherms have been found which are apparently occasioned by the temperature of the adsorption isotherms lying 14° below that of the freezing point of ethylene.

Experimental

Adsorbents.—Aluminum foil from the J. T. Baker Chemical Co. was 28 μ thick and about 99.5% pure. Spectroscopically there was about 0.25% silicon, an equal quantity of iron, and a little copper. Before use the foil was carefully solvent cleaned.

Foil was subjected to one or more of the following treatments: fifteen seconds in a 5% solution of sodium carbonate at 86° (I); two minutes in a solution of 30 g. of chromic anhydride and 100 cc. of concentrated sulfuric acid in 900 cc. of water at 90° (II); anodizing in 15%

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(2) Present address: Department of Chemistry, Cornell University, Ithaca, New York.

(3) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

(4) Wooten and Brown, *ibid.*, **65**, 113 (1943).