agent, $CF_3CH_2CH_2MgCl$, was converted to $CF_3CH_2CH_3$ by hydrolysis, to $CF_3CH_2CH_2OH$ by oxygen and hydrolysis, and to $CF_3CH_2CH_2CO_2H$ by carbon dioxide and hydrolysis. The alcohol was found to be identical to the one prepared by Scherer[4] following another procedure. The γ,γ,γ-trifluorobutyric acid is a new compound.

The $CF_3CH_2CH_2Cl$, used in the preparation of the Grignard reagent, was prepared by the vapor-phase chlorination of $CF_3CH_2CH_3$ following an improved synthesis which gives a preponderance of monochlorides.

Experimental

Chlorination of 1,1,1-Trifluoropropane.—Chlorinations were carried out at 110° in a 2-liter round-bottom flask surrounded by three 200-watt incandescent lamps. The lamps served a dual purpose of furnishing light for the photochemical reaction and heat to maintain the temperature. Chlorine and trifluoropropane were introduced at predetermined rates through calibrated flow meters. The products were led from the reaction flask to the bottom of a countercurrent water scrubber to remove hydrogen chloride. Gases leaving the scrubber were dried and collected in a receiver cooled by Dry Ice. The organic material was separated by rectification.

In a typical experiment, 1,1,1-trifluoropropane and chlorine were introduced into the reactor at a rate of 45 l./hr. and 11.5 l./hr., respectively. After 14.7 moles of trifluoropropane had been introduced, the system was purged with air and the product was rectified to strip out unreacted trifluoropropane for recycling. This procedure was continued until 10.4 moles had reacted. Upon rectification of the final product, there was obtained 2.2 moles of $CF_3CHClCH_3$, 5.8 moles of $CF_3CH_2CH_2Cl$, and 1.7 moles of $CF_3CH_2CHCl_2$ or a yield of chlorinated product of 93%. This is a different ratio of products than obtained by Henne using a different technique,[2] although the preferential path of chlorination is still substitution of hydrogen beta to the trifluoromethyl group.

Synthesis of 3,3,3-Trifluoropropanol.—A 1-liter, 3-necked flask was equipped with a mercury-sealed stirrer, a dropping funnel and a reflux condenser the top of which contained a calcium chloride tube. Magnesium turnings (0.8 mole) was placed in the flask and the system was flushed with dry nitrogen. A solution of 3-chloro-1,1,1-trifluoropropane (0.8 mole) in dry ethyl ether (300 ml.) was added from the dropping funnel. The reaction was slow in starting and had to be catalyzed with a crystal of iodine. Once started, the reaction was very vigorous. Dry oxygen was introduced into the flask until no more was absorbed. Then 200 ml. of 25% sulfuric acid was added. The water phase was continuously extracted with ether for five hours. The ether extract was dried over Drierite and then rectified to give 36 g. of 3,3,3-trifluoropropanol, b. p. 100°, d^{25}_4 1.2937, n^{25}_{D} 1.3200.

Anal. Calcd. for $C_3H_5F_3O$: F, 50.0. Found: F, 50.0.

Synthesis of γ,γ,γ-Trifluorobutyric Acid.—The Grignard reagent was prepared as before starting with 0.4 mole of $CF_3CH_2CH_2Cl$ and small lumps of solid carbon dioxide were dropped into the ether solution. The resulting mixture was then treated with 100 ml. of dilute sulfuric acid. The layers were separated and the aqueous layer was extracted several times with fresh portions of ether. The combined ether layers were dried over anhydrous calcium chloride and the ether was then boiled away. The residue was transferred to a 50-ml. side arm distilling flask fitted with an air condenser. The fraction boiling in the range 162–176° was collected as $CF_3CH_2CH_2CO_2H$ (24 g., 0.17 mole). The $CF_3CH_2CH_2CO_2H$ was dissolved in (30–60°) petroleum ether, decolorized with Norite and recrystallized twice to give a white solid (m. p. 33.2°, b. p. 166.6°) having an odor similar to that of butyric acid. Neutral equivalent calcd. for $C_4H_5F_3O_2$: 142.1. Found: 141.4.

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Summary

A Grignard reagent containing fluorine was obtained by treating $CF_3CH_2CH_2Cl$ in diethyl ether with magnesium turnings to give $CF_3CH_2CH_2MgCl$. The latter was converted to $CF_3CH_2CH_3$, $CF_3CH_2CH_2OH$ and $CF_3CH_2CH_2CO_2H$ by reactions common to Grignard reagents.

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[4] Scherer, Off. Pub. Bd. Report PB743, 1941.

[CONTRIBUTION NO. 11 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Heat Capacities, Heats of Transition, Heats of Fusion and Entropies of Cyclopentene and Cyclohexene

BY HUGH M. HUFFMAN, MARGARET EATON AND GEORGE D. OLIVER

As a part of the program of the Bureau of Mines to obtain thermodynamic data on petroleum hydrocarbons and related substances, low-temperature thermal investigations have been made on the two unsaturated alicyclics, cyclopentene and cyclohexene. Parks and Huffman[1] investigated cyclohexene over the temperature range of 90° K. to about room temperature. In general, their results agree with those of this research within their estimated error of 1%.

Materials.—These hydrocarbons were A.P.I.–N.B.S. "best" samples purified by A. P. I. Project 6 at the National Bureau of Standards.[2] An estimate of the mole per cent. impurity

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[1] Parks and Huffman, THIS JOURNAL, **52**, 4381 (1930).

[2] 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." These samples were purified at the National Bureau of Standards by the API Research Project 6 in the "Analysis, purification, and properties of hydrocarbons," under the supervision of Frederick D. Rossini, from materials supplied by the following laboratories: Cyclopentene, by the Atlantic Refining Company, Philadelphia, Pa., and the American Petroleum Institute Research Project 45 at The Ohio State University, under the supervision of C. E. Boord. Cyclohexene, by the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

as determined from melting point studies in this research is given in Table I.

TABLE I

MELTING POINT SUMMARY: 0° = 273.16°K.

Cyclopentene, $N_x = 0.0212\,\Delta T$ % Melted	T, °K. obs.	T, °K. calcd.	Cyclohexene, $N_x = 0.0138\,\Delta T$ % Melted	T, °K. obs.	T, °K. calcd.
26.1	138.109	138.105	25.0	169.653	169.652
45.2	.116	.116	45.3	.659	.659
70.8	.120	.121	70.7	.661	.662
89.9	.124	.123	91.1	.663	.663
100.0	.....	.124	100.0	.....	.663
Pure	.....	.130	Pure	.....	.667

Cyclopentene	Cyclohexene
Triple point, 138.13 ± 0.05° K.	Triple point, 169.67 ± 0.05° K.
Impurity, 0.018 ± 0.004 mole%	Impurity, 0.005 ± 0.003%

Apparatus.—The measurements were made in the calorimetric apparatus first described by Ruehrwein and Huffman,[3] which is briefly described as follows: Approximately 0.6 mole of the sample was contained in a sealed copper calorimeter, which was mounted in an adiabatic calorimetric system. The temperature of the environment was maintained at that of the calorimeter by means of an electrically heated shield and difference thermocouples, at all times, to prevent heat interchange. Typical heat capacity or fusion measurements were made by supplying a measured amount of electrical energy to the calorimeter and measuring the initial and final temperatures by means of a platinum resistance thermometer. The electrical measurements required to determine the temperature and electrical energy were made on a "White" double potentiometer in conjunction with a high-sensitivity galvanometer and accurately calibrated resistances. Time measurements were made with an electric stop clock driven by alternating current, the frequency of which was controlled to about 0.001%.

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%. The energy measurements were made in terms of the NBS international joule and were converted to calories by dividing by 4.1833.

Results

The melting-point study was made in the usual manner which has been adequately described in a previous publication.[4] The equilibrium temperatures, $T_{(\text{obs.})}$, for different liquid–crystal ratios are summarized in Table I. These temperatures were plotted against $1/F$, the reciprocal of the fraction melted, and then the curve was extrapolated to $1/F = 0$ to obtain the triple point of the pure material. These experimental data were used in the simplified relation $N_x = K\Delta T^5$ to calculate the mole fraction of impurity present in each sample on the assumption that the solutions obeyed Raoult's law.

Heat-capacity measurements were made on each compound from 12 to 300°K. These experimental results, listed in Table II, are the molal heat capacities of the saturated crystals and liquid, C_{sat}. The molal heat-capacity values at integral temperatures, as read from a smooth curve drawn through the experimentally determined points, are listed in Table III.

TABLE II

MOLAL HEAT CAPACITIES, $C_{\text{sat.}}$: 0° = 273.16° K.

Cyclopentene, molecular weight = 68.114

T, °K.	ΔT	Cal./degree	T, °K.	ΔT	Cal./degree
	Crystals I		71.06	6.353	12.827
12.09	1.416	0.766	77.07	6.722	14.157
13.56	1.575	1.029	78.95	5.757	14.738
15.26	1.518	1.416	80.95	1.986	15.400
15.28	1.923	1.398	82.73	4.584	16.324
16.90	1.802	1.779	82.89	1.885	16.329
17.78	3.130	2.024	83.42	5.103	16.810
19.12	2.682	2.348	84.71	1.764	17.622
21.15	3.591	2.898	86.00	.820	19.19
22.14	3.236	3.174		Crystals II	
22.37	3.848	3.223	91.99	4.968	18.516
24.79	3.693	3.875	95.02	6.637	18.410
25.72	3.920	4.124	97.83	6.711	18.355
26.21	3.833	4.239	99.43	8.974	18.346
28.90	4.539	4.932	108.32	8.818	18.368
29.82	4.285	5.160	116.51	7.546	18.560
30.03	3.824	5.200	124.49	8.419	18.864
33.36	4.377	5.983	130.06	8.239	19.151
34.07	4.224	6.133	131.77	6.149	19.299
37.72	4.332	6.886		Liquid	
38.00	3.648	6.951	140.85	5.101	23.738
38.51	3.587	7.042	144.93	6.744	23.671
41.72	3.798	7.636	146.85	6.914	23.653
41.92	3.237	7.673	150.32	7.844	23.618
42.05	4.332	7.689	154.61	8.600	23.598
45.27	3.457	8.241	158.14	7.800	23.578
45.58	3.921	8.288	163.61	9.402	23.578
46.40	4.359	8.411	172.56	8.483	23.624
48.60	3.194	8.777	180.65	7.706	23.721
48.68	2.276	8.793	188.32	7.642	23.845
50.60	1.551	9.151	195.92	7.570	24.026
50.75	4.356	9.184	199.55	8.560	24.113
52.02	1.487	9.520	203.99	8.558	24.238
52.11	1.484	9.532	208.06	8.460	24.366
53.48	1.417	9.959	212.50	8.451	24.516
54.87	1.370	10.263	216.99	9.389	24.677
54.88	4.162	10.177^a	226.82	10.267	25.091
55.32	4.787	10.295^a	236.99	10.082	25.553
56.22	1.339	10.438	246.98	9.894	26.072
57.63	1.470	10.644	256.77	9.700	26.634
58.91	5.166	10.827^a	266.38	9.522	27.171
59.08	1.431	10.862	275.82	9.339	27.765
59.51	5.095	10.932^a	284.61	8.255	28.332
64.26	5.527	11.670	292.80	8.112	28.900
64.97	5.821	11.785	300.84	7.981	29.436
70.37	6.692	12.686			

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[3] Ruehrwein and Huffman, THIS JOURNAL, **65**, 1620 (1943).

[4] Todd, Oliver and Huffman, *ibid.*, **69**, 1519 (1947).

[5] Mair, Glasgow and Rossini, *J. Research Natl. Bur. Standards*, **26**, 594 (1941).

TABLE II (*Continued*)

T, °K.	ΔT	Cal./ degree	T, °K.	ΔT	Cal./ degree
Cyclohexene, molecular weight = 82.140					
Crystals I			111.41	8.086	14.634
12.77	2.176	0.506	119.20	9.565	15.351
12.89	2.133	0.515	119.30	7.698	15.348
14.87	2.086	0.789	126.83	7.362	16.064
15.24	2.587	0.847	127.62	7.282	16.146
16.87	1.930	1.134	134.10	7.178	16.827
17.94	2.830	1.349	134.75	6.976	16.907
18.73	1.808	1.508	Crystals II		
21.18	3.116	2.062	131.80	7.614	21.952[b]
21.77	4.835	2.202	139.29	7.362	22.702[b]
24.58	3.667	2.875	147.71	9.472	23.524
27.43	6.485	3.585	148.15	5.488	23.517
28.78	4.736	3.899	152.38	8.997	23.837
32.99	3.679	4.906	154.46	7.128	24.157
33.38	5.401	4.989	161.53	7.000	24.964
38.90	5.650	6.177	Liquid		
44.82	6.187	7.278	178.83	6.227	28.107
50.58	5.328	8.226	178.99	8.031	28.112
55.92	7.484	9.004	185.96	8.039	28.395
56.39	6.296	9.071	187.95	9.893	28.485
56.76	7.313	9.122	193.94	7.926	28.757
62.97	6.626	9.938	202.08	7.799	29.142
64.19	7.531	10.088	210.78	9.600	29.585
69.80	7.029	10.712	220.30	9.436	30.105
71.37	6.846	10.877	230.12	10.187	30.698
77.00	7.380	11.475	240.65	10.890	31.390
78.41	7.216	11.624	251.43	10.655	32.118
84.12	6.849	12.213	253.88	8.751	32.283
85.38	6.722	12.346	261.97	10.434	32.855
88.48	7.145	12.622	263.41	10.304	32.951
91.55	8.024	12.909	272.30	10.216	33.623
92.30	7.133	12.980	273.61	10.092	33.716
95.99	7.863	13.277	283.60	9.888	34.482
99.90	8.681	13.639	292.59	8.090	35.200
103.64	7.446	13.946	300.61	7.959	35.846
109.33	10.170	14.476			

[a] Large ΔT, were not used in plot. [b] Supercooled crystals II.

TABLE III

MOLAL HEAT-CAPACITY VALUES AT INTEGRAL TEMPERATURES

T, °K.	Cyclo- pentene	Cyclo- hexene	T, °K.	Cyclo- pentene	Cyclo- hexene
12	0.74	...	110	18.40	14.51
13	0.92	0.54	120	18.68	15.42
14	1.12	0.66	130	$\underline{19}.\underline{18}$	$\underline{16}.\underline{38}$
15	1.32	0.81	140	23.75	22.73
20	2.59	1.79	150	23.62	23.69
25	3.94	2.98	160	23.57	$\underline{24}.\underline{76}$
30	5.20	4.20	170	23.60	27.78
35	6.33	5.35	180	23.72	28.15
40	7.33	6.40	190	23.88	28.58
45	8.19	7.32	200	24.12	29.03
50	9.04	8.14	210	24.42	29.54
55	10.29	8.87	220	24.80	30.09
60	11.00	9.55	230	25.24	30.68
65	11.79	10.18	240	25.72	31.32
70	12.62	10.74	250	26.25	31.99
75	13.62	11.28	260	26.81	32.70
80	15.04	11.80	270	27.40	33.44
85	$\underline{17}.\underline{90}$	12.29	280	28.03	34.20
90	18.62	12.77	290	28.70	34.99
95	18.42	13.22	300	29.38	35.80
100	18.33	13.64			

Both compounds were found to have two crystalline forms. Observations were made of the equilibrium temperatures with different amounts of crystals I transposed to obtain the transition temperature. The results of these studies and the experimental values for the heats of transition are given in Table IV.

Two measurements of the heat of fusion were made for each compound and the results are tabulated in Table V. The uncertainties given are precision uncertainties.

TABLE IV

TRANSITION-DATA SUMMARY, ΔH, CAL./MOLE

Substance	Trans. temp., °K.	Expt. 1	Expt. 2	Expt. 3	Mean
Cyclopentene	87.07 ± 0.05	114.8	113.8	115.2	114.6 ± 0.5
Cyclohexene	138.7 ± 0.2	1016.0	1015.5	1016.2	1015.9 ± 1.0

TABLE V

FUSION-DATA SUMMARY, ΔH, CAL./MOLE

Substance	Expt. 1	Expt. 2	Mean
Cyclopentene	803.8	804.0	803.9 ± 0.4
Cyclohexene	787.3	786.9	787.1 ± 0.4

The above experimental data were used to calculate the entropies of these compounds in the liquid state at 298.16° K. The results of these calculations are summarized in Table VI. It may be noted that the entropy value, 51.8 e. u., for cyclohexene reported by Parks and Huffman[1] is in excellent agreement with that found in this research.

TABLE VI

SUMMARY OF MOLAL ENTROPY DATA

Cyclopentene	
$S_{12°}$ (Debye, 5°, θ = 120.88)	0.250
$\Delta S_{12°-87.07°}$ (graphical)	12.873
$\Delta S_{87.07°}$ (114.6/87.07)	1.316
$\Delta S_{87.07°-138.13°}$ (graphical)	8.616
$\Delta S_{138.13°}$ (803.9/138.13)	5.820
$\Delta S_{138.13°-298.16°}$ (graphical)	19.228
$S_{298.16°}$ liquid	48.10 ± 0.10
Cyclohexene	
$S_{13°}$ (Debye, 6°, θ = 155.21)	0.182
$\Delta S_{13°-138.7°}$ (graphical)	17.291
$\Delta S_{138.7°}$ (1015.9/138.7°)	7.324
$\Delta S_{138.7-169.67°}$ (graphical)	4.859
$\Delta S_{169.67°}$ (787.1/169.67°)	4.639
$\Delta S_{169.67°-298.16°}$ (graphical)	17.377
$S_{298.16}$ liquid	51 67 ± 0.10

Discussion

Molal heat capacity curves for both compounds are shown in Fig. 1. The curve for cyclopentene

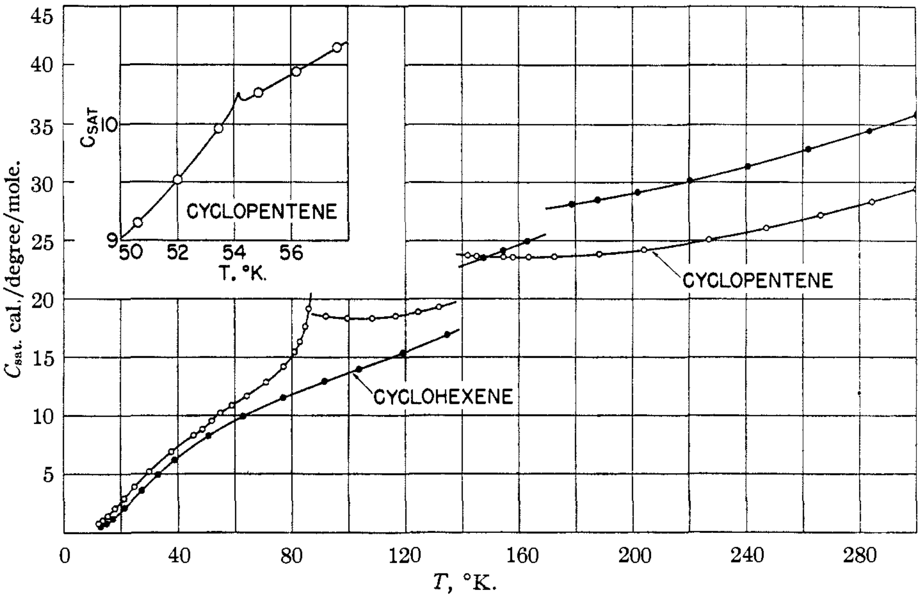

Fig. 1.—Molal heat capacity, $C_{sat.}$ of cyclopentene and cyclohexene.

shows an anomalous behavior in the region of 54° K. in that the heat capacity changes to a higher level in a very short temperature interval in a manner characteristic of organic glasses. This is shown in the large-scale plot of the heat capacity *versus* temperature in the insert of Fig. 1. This behavior may represent the release of a frozen in mode of motion over a short temperature interval.

Similar behavior in crystals has been observed in the study of cyclohexanol[6] and *cis*-1,2-dimethylcyclohexane.[7] In these two cases the anomaly occurred in an unstable crystalline modification which had been supercooled. In the case of *cis*-1,3-dimethylcyclohexane, the material showing the anomaly had a residual entropy of approximately 2.0 cal./degree/mole, whereas in cyclohexanol the entropy of the two forms was the same within experimental error. This apparent freezing in of a mode of motion may lead to a random orientation, hence a possibility of residual entropy. Therefore, the entropy calculated for cyclopentene may be uncertain by an amount greater than the experimental error.

During the measurement of the heat of transition of cyclohexene, the rate of transition was observed to be so slow that when energy was supplied part of it was used to raise the temperature of the sample instead of changing the phase composition. The approach to equilibrium was slow and precluded an accurate determination of the transition temperature.

Summary

Heat-capacity data on cyclopentene and cyclohexene have been given over the temperature range 12 to 300° K.

Values of the triple points, heats of fusion, transition temperatures and heats of transition were determined for these compounds.

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

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(6) Kelley, THIS JOURNAL, 51, 1400–6 (1929).

(7) Oliver, Todd and Huffman, unpublished observations.