

Charles L. Rose of the Lilly Research Laboratories, Indianapolis, Indiana. A preliminary report of this work is given in the following table.

1-Substituent	PHARMACOLOGICAL DATA						
	Average duration of anesthesia, minutes	Subcutaneous toxicity to white mice (mg./kg.)			Intravenous toxicity to white rats (mg./kg.)		
		M. T. D.	M. L. D.	No. of mice used	M. T. D.	M. L. D.	No. of rats used
Cyclohexyl	42	300	400	11	12.5	15	8
Benzyl	19	200	300	9	25	30	7

It will be seen from the table that 1-cyclohexyl-4-piperidyl benzoate hydrochloride has a lower subcutaneous and a higher intravenous toxicity than the 1-benzyl-4-piperidyl benzoate hydrochloride. Neither of these products shows any unusual anesthetic properties.

### Summary

1. The preparation and properties of 1-phenyl- and 1-benzyl-4-piperidones have been described.
2. The catalytic reduction of these piperidones has been studied.
3. Two local anesthetics, 1-cyclohexyl and 1-benzyl-4-piperidyl benzoate hydrochlorides, have been prepared from the reduction products.

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## THERMAL DATA ON ORGANIC COMPOUNDS. VI. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF SOME SATURATED, NON-BENZENOID HYDROCARBONS<sup>1</sup>

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In five earlier papers<sup>5</sup> the entropies and free energies of nineteen compounds of carbon, hydrogen and oxygen were calculated from heat capacity data by means of the third law of thermodynamics. These results indicated that the entropy and free energy of an organic compound are related to its constitution in a simple additive manner. The present in-

<sup>1</sup> This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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<sup>5</sup> Parks, *THIS JOURNAL*, **47**, 338 (1925); Parks and Kelley, *ibid.*, **47**, 2094 (1925); Parks and Anderson, *ibid.*, **48**, 1506 (1926); Parks and Huffman, *ibid.*, **48**, 2788 (1926); Parks, Kelley and Huffman, *ibid.*, **51**, 1800 (1929).

vestigation represents essentially a continuation of the past work and deals exclusively with compounds of carbon and hydrogen. This particular paper contains heat capacity data for the following fourteen saturated, non-benzenoid hydrocarbons: 2-methylbutane, *n*-hexane, *n*-heptane, 2-methylhexane, *n*-octane, 2,2,4-trimethylpentane, hexamethylethane, *n*-nonane, *n*-decane, di-*iso*-amyl, eicosane, pentacosane, tritriacontane and cyclohexane. In so far as it has been possible, we have utilized these data to calculate, by the third law of thermodynamics, the corresponding entropies and free energies. The latter values are especially interesting in view of the recent paper by Francis<sup>6</sup> in the same field.

### Materials

For our work we have found it rather difficult to obtain compounds of sufficient purity, especially in the case of aliphatic hydrocarbons. A material which would be satisfactory to the organic chemist for the study of reactions, or of properties characteristic of the liquid state, may contain a few per cent. of isomers, the presence of which produces very erratic results when the specific heats in the crystalline state and the heat of fusion are measured. For this reason we have come to place little reliance upon the density of the sample or even upon the narrowness of the distillation range. From our own experience we feel that the sharpness of the melting point is by far the best criterion of purity, as even small amounts of impurity ordinarily cause very marked premelting. The details as to the source and character of the fourteen hydrocarbons employed are given in the following paragraphs.

**2-Methylbutane.**—This was a very pure Kahlbaum chemical, b. p. 28.0°. The product of a careful fractional distillation gave an extremely sharp melting point at 112.6°K.

***n*-Hexane, *n*-Nonane and *n*-Decane.**—These compounds were very carefully synthesized for us by Mr. R. E. Marker of Yonkers, N. Y. They gave distillation ranges of from 0.2 to 0.5° at the accepted boiling points. However, only the hexane sample proved entirely satisfactory in our measurements. The other two materials gave a very irregular curve for the specific heats in the crystalline phase and showed marked premelting, which phenomena we took as evidence that the samples probably contained appreciable amounts of the isomers of the normal compounds. In view of the increasing number of isomers as we proceed up the series of paraffin hydrocarbons, it is extremely difficult to synthesize really pure compounds containing more than eight carbon atoms. However, isomeric impurities cannot affect appreciably the accuracy of specific heat determinations for the liquid state and, therefore, we shall present our data for liquid *n*-nonane and *n*-decane.

***n*-Heptane, 2-Methylhexane, *n*-Octane, 2,2,4-Trimethylpentane and Hexamethylethane.**—These compounds were prepared in the Research Laboratory of the Ethyl Gasoline Corporation under the direction of Dr. Graham Edgar. The details of the preparation of the two heptanes and the 2,2,4-trimethylpentane have been given in other places.<sup>7</sup> All five hydrocarbons had been synthesized very carefully and showed

<sup>6</sup> Francis, *Ind. Eng. Chem.*, 19, 277 (1928).

<sup>7</sup> Edgar, Calingaert and Marker, *THIS JOURNAL*, 51, 1483 (1929); Edgar, *Ind. Eng. Chem.*, 19, 146 (1927).

a narrow distillation range, usually less than  $0.2^\circ$ . The melting point was fairly sharp in every case.

**Di-iso-amyl.**—This material was a Kahlbaum preparation, supposedly of high grade, showing a boiling range of  $0.8^\circ$ . However, like the *n*-nonane and *n*-decane previously described, it did not give a satisfactory melting point and specific heat curve for the crystalline state. Nevertheless, we believe that our data for this compound in the liquid state are fairly reliable.

**Eicosane, Pentacosane and Trtriacontane.**—These were straight-chained hydrocarbons which had been carefully recovered from paraffin wax in the Research Laboratory of the Standard Oil Company of Indiana. Their properties as well as their preparation by fractional distillation and fractional crystallization have been fully described elsewhere.<sup>8</sup> Throughout our measurements these substances gave every indication of excellent purity. The melting points were  $36.4^\circ$  ( $C_{20}H_{42}$ ),  $53.3^\circ$  ( $C_{25}H_{52}$ ) and  $71.1^\circ$  ( $C_{33}H_{68}$ ).

**Cyclohexane.**—This was an Eastman product, m. p.  $4.5^\circ$ . It was subjected to twelve fractional crystallizations. The resulting material gave a very sharp melting point at  $6.2^\circ$  and an extremely sharp transition point at  $185.9^\circ K$ . It was undoubtedly one of the purest hydrocarbons that we have studied.

### Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in the first paper of this series. In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except in so far as impurities in the various samples may cause premelting or otherwise influence the results.

The specific heats and the fusion data, expressed in terms of the  $15^\circ$  calorie and with all weights reduced to a vacuum basis, appear in Tables I and II. For comparison with these values the literature contains only very meager data. Mabery and Goldstein<sup>9</sup> have studied the heat capacities between 0 and  $50^\circ$  of a number of hydrocarbons, including *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane and *isodecane*. They used an ice calorimeter and worked on materials derived from petroleum. Their result for *n*-octane at  $25^\circ$  is 3% below our curve; for the other compounds their values deviate by from 1.2 to 4.0% from our curves. The heat of fusion of only one of these compounds has been previously measured; Padoa<sup>10</sup> obtained 5.87 cal. per g. for cyclohexane as against our value of 7.41 cal.

Hexamethylethane and cyclohexane were found to exist in two crystalline forms with fairly definite transition temperatures at 148.1 and  $185.9^\circ K$ ., respectively, and the corresponding heats of transition were measured by the same procedure used in the fusion determinations. The data thus obtained are recorded in Table III. In this connection it is noteworthy

<sup>8</sup> Buchler and Graves, *Ind. Eng. Chem.*, **19**, 718 (1927).

<sup>9</sup> Mabery and Goldstein, *Am. Chem. J.*, **28**, 69 (1902).

<sup>10</sup> Padoa, *Atti. Accad. Lincei*, [5] **28**, 239 (1919).

that the heat of transition of cyclohexane is quite large, while its heat of fusion is extremely small.

TABLE I  
SPECIFIC HEATS

2-METHYLBUTANE: Crystals								
Temp., °K.	80.4	83.0	86.7	89.2	92.4	92.5	97.1	102.0
$C_p$ per g.	0.217	0.222	0.230	0.236	0.244	0.243	0.260	0.279
Liquid								
Temp., °K.	120.5	125.3	140.3	169.5	186.1	200.6	215.8	
$C_p$ per g.	0.409	0.413	0.421	0.437	0.447	0.458	0.468	
Temp., °K.	230.5	245.3	260.5	275.0	275.2	275.7	275.8	
$C_p$ per g.	0.480	0.492	0.507	0.519	0.518	0.519	0.521	
<i>n</i> -HEXANE: Crystals								
Temp., °K.	89.7	91.8	93.8	95.8	102.3	109.3		
$C_p$ per g.	0.218	0.221	0.223	0.226	0.236	0.247		
Temp., °K.	115.0	122.7	129.7	135.3	141.1	153.9		
$C_p$ per g.	0.256	0.267	0.279	0.288	0.302	0.331		
Liquid								
Temp., °K.	183.5	187.4	217.4	237.0	255.5	275.0	288.5	295.1
$C_p$ per g.	0.468	0.471	0.480	0.487	0.502	0.516	0.527	0.531
<i>n</i> -HEPTANE: Crystals								
Temp., °K.	90.1	90.5	96.0	96.0	102.6	109.8		
$C_p$ per g.	0.205	0.206	0.216	0.215	0.226	0.236		
Temp., °K.	122.2	128.5	134.6	140.5	145.3	150.9		
$C_p$ per g.	0.254	0.263	0.271	0.280	0.287	0.295		
Liquid								
Temp., °K.	188.0	200.0	217.4	235.8	240.4	258.0	262.5	
$C_p$ per g.	0.480	0.480	0.484	0.489	0.491	0.500	0.504	
Temp., °K.	275.4	276.0	279.5	287.5	291.3	294.2	299.2	
$C_p$ per g.	0.513	0.514	0.517	0.522	0.525	0.527	0.530	
2-METHYLHEXANE: Crystals								
Temp., °K.	85.9	87.6	89.8	92.5	94.1	101.4	107.4	
$C_p$ per g.	0.202	0.206	0.212	0.217	0.219	0.229	0.237	
Temp., °K.	108.6	114.4	115.5	122.8	129.7	135.9		
$C_p$ per g.	0.239	0.249	0.250	0.262	0.281	0.306		
Liquid								
Temp., °K.	160.2	166.0	180.3	195.2	211.0	225.0		
$C_p$ per g.	0.427	0.430	0.439	0.449	0.460	0.469		
Temp., °K.	240.3	255.4	275.8	280.6	286.2	292.4		
$C_p$ per g.	0.480	0.491	0.507	0.517	0.519	0.523		
<i>n</i> -OCTANE: Crystals								
Temp., °K.	85.5	90.8	96.9	103.0	109.5	122.2	128.7	134.8
$C_p$ per g.	0.188	0.196	0.209	0.219	0.227	0.244	0.252	0.258
Temp., °K.	146.6	152.7	161.2	171.6	176.9	181.6	186.4	195.9
$C_p$ per g.	0.274	0.282	0.292	0.308	0.317	0.326	0.338	0.372

TABLE I (Continued)

Liquid								
Temp., °K.	223.0	232.7	244.8	255.7	275.3	279.3	284.8	293.7
$C_p$ per g.	0.482	0.483	0.487	0.493	0.504	0.508	0.513	0.518
2,2,4-TRIMETHYLPENTANE: Crystals								
Temp., °K.	87.9	91.9	98.2	105.5	113.2	123.2		
$C_p$ per g.	0.181	0.190	0.201	0.217	0.232	0.250		
Temp., °K.	129.4	135.2	140.9	147.7	152.8			
$C_p$ per g.	0.260	0.271	0.285	0.303	0.325			
Liquid								
Temp., °K.	169.6	173.4	177.8	188.3	194.4	213.8	218.5	230.2
$C_p$ per g.	0.388	0.390	0.393	0.399	0.403	0.420	0.422	0.432
Temp., °K.	255.2	275.0	278.4	283.1	287.6	292.0	295.2	
$C_p$ per g.	0.452	0.471	0.475	0.477	0.482	0.487	0.489	
HEXAMETHYLETHANE: Crystals I								
Temp., °K.	88.8	92.4	98.3	105.8	113.5	122.7	129.8	136.4
$C_p$ per g.	0.166	0.172	0.183	0.198	0.213	0.234	0.255	0.279
Crystals II								
Temp., °K.	161.3	173.0	178.8	188.4	194.3	204.4	209.5	223.8
$C_p$ per g.	0.308	0.326	0.332	0.345	0.353	0.369	0.374	0.394
Temp., °K.	229.1	242.5	250.5	259.7	275.5	281.0	291.2	295.4
$C_p$ per g.	0.400	0.417	0.427	0.438	0.458	0.466	0.481	0.486
<i>n</i> -NONANE: Liquid								
Temp., °K.	224.5	251.3	255.3	276.4	284.8	290.0	293.9	299.1
$C_p$ per g.	0.484	0.492	0.493	0.506	0.512	0.517	0.521	0.524
<i>n</i> -DECANE: Liquid								
Temp., °K.	242.3	254.9	275.1	277.6	287.7	295.5		
$C_p$ per g.	0.483	0.487	0.503	0.506	0.514	0.520		
DI-ISO-AMYL: Liquid								
Temp., °K.	223.2	227.5	244.5	275.0	278.2	283.3	289.4	295.0
$C_p$ per g.	0.453	0.455	0.467	0.492	0.493	0.498	0.501	0.507
<i>n</i> -EICOSANE: Crystals								
Temp., °K.	93.6	99.1	123.9	143.3	163.0	179.0	195.4	
$C_p$ per g.	0.175	0.182	0.212	0.234	0.258	0.276	0.298	
Temp., °K.	210.1	224.5	236.5	250.5	262.7	279.1		
$C_p$ per g.	0.319	0.340	0.360	0.389	0.414	0.512		
<i>n</i> -PENTACOSANE: Crystals								
Temp., °K.	91.3	97.8	122.7	152.0	180.3	194.5	199.9	
$C_p$ per g.	0.168	0.176	0.205	0.237	0.273	0.292	0.300	
Temp., °K.	223.5	240.7	256.9	275.1	279.4	284.4	294.5	
$C_p$ per g.	0.334	0.361	0.391	0.430	0.446	0.467	0.521	
<i>n</i> -TRITRIACONTANE: Crystals								
Temp., °K.	93.7	122.2	146.0	163.3	165.0	184.2		
$C_p$ per g.	0.168	0.201	0.227	0.248	0.249	0.272		
Temp., °K.	207.0	227.3	252.0	275.3	281.1	294.4		
$C_p$ per g.	0.303	0.331	0.368	0.412	0.426	0.463		

TABLE I (Concluded)  
 CYCLOHEXANE: Crystals I

Temp., °K.	91.8	97.6	105.1	112.8	125.6	132.1	137.7
$C_p$ per g.	0.157	0.164	0.173	0.181	0.196	0.203	0.209
Temp., °K.	144.1	150.0	162.9	166.0	168.4	177.5	
$C_p$ per g.	0.216	0.223	0.239	0.245	0.247	0.263	

## Crystals II

Temp., °K.	209.0	214.1	223.7	229.0	234.8	239.9	244.8	265.6
$C_p$ per g.	0.316	0.320	0.325	0.329	0.334	0.337	0.342	0.362

## Liquid

Temp., °K.	283.1	285.3	286.6	290.7	298.9		
$C_p$ per g.	0.422	0.423	0.425	0.430	0.440		

 TABLE II  
 FUSION DATA<sup>a</sup>

Substance	M. p., °K.	Heat of fusion (cal. per g.)		Mean
		1st result	2nd result	
2-Methylbutane	112.6	16.96	16.92	16.94
<i>n</i> -Hexane	178.6	34.88	34.90	34.89
<i>n</i> -Heptane	182.2	33.84	33.73	33.78
2-Methylhexane	154.0	21.17	21.16	21.16
<i>n</i> -Octane	215.6	41.90	42.17	42.04
2,2,4-Trimethylpentane	165.3	18.89	18.95	18.92
Eicosane	309.7	52.0	...	52.0
Cyclohexane	279.3	7.39	7.43	7.41

<sup>a</sup> In the calculation of these fusion values the marked rise in the specific heat of the solid as the melting point is approached was attributed to premelting, and the heat absorbed in this region in excess of that obtained by extrapolation of the specific-heat data at lower temperatures was added to the heat absorbed at the melting point.

 TABLE III  
 TRANSITION DATA

Substance	Transition temperature	Heat of transition (cal. per g.)		Mean
		1st result	2nd result	
Hexamethylethane	148.1°K.	4.20	...	4.20
Cyclohexane	185.9°K.	19.07	19.07	19.07

## Discussion

**Entropies of the Compounds.**—Using the data contained in Tables I, II and III in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for all the hydrocarbons except *n*-nonane, *n*-decane and di-*iso*-amyl. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman<sup>11</sup> for estimating the entropy increases for the crystals, Col. 2 of Table IV, from 0 to 90°K. The various entropy increments from 90 to 298.1°K., which appear in Cols. 3, 4 and 5 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading " $S_{298}$  experimental" in

<sup>11</sup> Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

the sixth column. In the case of the four hydrocarbons which are normally crystalline at 298°K. and 1 atm. pressure, we have also calculated the entropy of fusion at 298° so as to obtain a value for the entropy of each liquid, even though the liquid state may be unstable at this temperature. For this calculation of the entropy of fusion we have employed unpublished data, obtained by Parks and Todd, for the specific heats and heat of fusion of hexamethylethane, pentacosane and tritriacontane.

In the previous studies an entropy increase of 7.8 E. U. per CH<sub>2</sub> increment was found for the normal alcohol series and of 8.0 E. U. for the normal aliphatic acid series, when all the compounds involved were in the liquid state. In the present case we have found an average increase of 7.7 units per CH<sub>2</sub> increment for the normal liquid hydrocarbons. In other words, the entropy of a normal hydrocarbon in the liquid state at 298°K. can be calculated by the equation,  $S_{298} = 25.0 + 7.7 n$ , where  $n$  is the number of carbon atoms in the straight chain. By this method the values of " $S_{298}$  predicted" in the last column of Table IV were obtained for *n*-hexane, *n*-heptane, *n*-octane, eicosane, pentacosane and tritriacontane, all in the liquid state. They are in excellent agreement with the experimental results.

TABLE IV  
ENTROPIES OF THE HYDROCARBONS PER MOLE

Substance	Crystals			Liquid	$S_{298}$ experimental	$S_{298}$ predicted
	0-90°K.	Above 90°K.	Fusion			
2-Methylbutane	13.74	4.28	10.84	31.90	60.8	59.0
<i>n</i> -Hexane	15.64	16.70	16.84	21.90	71.1	71.2
<i>n</i> -Heptane	16.97	18.80	18.58	24.51	78.9	78.9
2-Methylhexane	16.74	13.81	13.75	30.86	75.2	74.4
<i>n</i> -Octane	18.45	26.93	22.27	18.33	86.0	86.6
2,2,4-Trimethylpentane	15.90	17.30	13.06	28.90	75.2	73.1
Hexamethylethane (solid)	15.46	45.97 <sup>a</sup>	...	...	61.4	...
Hexamethylethane (liquid)	15.46	45.97 <sup>a</sup>	4.0	...	65.4	68.6
Eicosane (solid)	40.50	93.00	...	...	133.5	...
Eicosane (liquid)	40.50	93.00	47.0	...	180.5	179.0
Pentacosane (solid)	49.2	111.2	...	...	160.4	...
Pentacosane (liquid)	49.2	111.2	56.6	...	217.0	217.5
Tritriacontane (solid)	63.8	146.0	...	...	209.8	...
Tritriacontane (liquid)	63.8	146.0	70.3	...	280.1	279.1
Cyclohexane	12.08	32.53 <sup>u</sup>	2.23	2.35	49.2	...

<sup>a</sup> This value includes the entropy increase for both crystalline forms as well as the entropy effect for the transition between them.

Compared with the normal compound, isomers with branches on the chain have a lower entropy, which depends upon the amount of the branching. From the study of a number of branched compounds, both hydrocarbons and alcohols, we have found an average decrease of 4.5 E. U. on substituting a CH<sub>3</sub> branch for a CH<sub>2</sub> group in the chain. Thus the

entropy of a branched hydrocarbon in the liquid state is given by the equation,  $S_{298} = 25.0 + 7.7n - 4.5r$ , where  $n$  is the total number of carbon atoms in the molecule and  $r$  represents the number of methyl branches on the straight chain. In this way we have obtained the predicted values for 2-methylbutane, 2-methylhexane, 2,2,4-trimethylpentane and liquid hexamethylethane. On the whole these values agree fairly well with the experimental results.

Thus we are justified in concluding that  $S_{298}$  for any aliphatic saturated hydrocarbon in the liquid state can be predicted to within a few per cent. from the constitutional formula of the substance.

The experimentally determined entropy of cyclohexane (49.2 E. U.) is much smaller than that of  $n$ -hexane; and, in general, it seems certain that the entropy effect of a carbon ring is much less than that of the same number of atoms in a straight chain. However, at present we do not possess any means of predicting the entropies of such ring compounds.

**The Free Energies of Nine Hydrocarbons.**—To the chemist the free energy of formation of a compound is of greater interest than its entropy. Accordingly we have also calculated the free energies of nine of these hydrocarbons by means of the third law of thermodynamics and the fundamental thermodynamic equation,  $\Delta F = \Delta H - T\Delta S$ .

The essential data are given in Table V. For obtaining the figures for the  $\Delta H$  of formation of eight of the compounds we have used the heats of combustion given in the "International Critical Tables,"<sup>12</sup> converted to 25° for our present purpose. The heat of combustion of pentacosane was computed from the result of Richards and Davis<sup>13</sup> for "hard paraffin." The literature contains no reliable values for  $C_{20}H_{42}$  and  $C_{33}H_{68}$ . The  $\Delta H_{298}$  values were then calculated from these data by use of 68,330 cal.,<sup>14</sup> and 94,270 cal.<sup>15</sup> for the heats of combustion of hydrogen and graphite carbon, respectively. Column 4 contains the entropy of formation of each compound, which is simply the difference between its  $S_{298}$  and the corresponding values for the entropies of the elements contained therein. For this purpose the respective entropies of carbon and hydrogen were taken as 1.3<sup>16</sup> and 14.8<sup>17</sup> E. U. per gram atom.

<sup>12</sup> "International Critical Tables," Vol. V, p. 163.

<sup>13</sup> Richards and Davis, *THIS JOURNAL*, **39**, 352 (1917).

<sup>14</sup> The value in the "International Critical Tables," Vol. V, p. 176, is 286.2 kJ. at 18°; this is equivalent to 68,330 cal. at 25°.

<sup>15</sup> Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925).

<sup>16</sup> Lewis and Gibson, *THIS JOURNAL*, **39**, 2581 (1917).

<sup>17</sup> Giauque and Wiebe, *ibid.*, **50**, 121 (1928). In a recent paper Giauque and Johnston [*ibid.*, **50**, 3221 (1928)] consider that this value for the entropy of hydrogen should be increased by 2.2 E. U. per gram atom at 298.1°K. However, their new value is larger than any result obtained experimentally, either by a direct or indirect application of the third law of thermodynamics, and they now believe that only 0.8 E. U. of this increase need be considered for chemical reactions (Johnston, personal communi-



The molal free energies appear in the last column of the table. The results for hexamethylethane and pentacosane refer to the solid state. According to our estimate, based upon the unpublished data of Parks and Todd, the free energies of the corresponding liquids at 298°K. will be algebraically greater than these results by about 300 cal. and 1600 cal., respectively. For comparative purposes the accuracy of the free energy data is largely limited by the accuracy of the combustion data employed. In the case of the two heptanes and three octanes these combustion values were obtained recently by the U. S. Bureau of Standards and are probably accurate to about a thousand calories. For the other four compounds the errors may easily be twice this figure.

TABLE V  
THERMAL DATA AT 298.1°K.

The 15° cal. is used throughout and all weights have been reduced to a vacuum basis

Substance	Heat of combustion at constant pressure	$\Delta H_{298}$ , cal.	$\Delta S_{298}$ , E. U.	$\Delta F_{298}^{\circ}$ , cal.
2-Methylbutane	838,000	-43,300	-123.3	-6,600
<i>n</i> -Hexane	990,200	-53,300	-143.9	-10,800
<i>n</i> -Heptane	1,149,400	-57,100	-167.0	-7,300
2-Methylhexane	1,148,400	-58,100	-170.7	-7,200
<i>n</i> -Octane	1,304,500	-64,600	-190.8	-7,700
2,2,4-Trimethylpentane	1,303,400	-65,700	-201.6	-5,600
Hexamethylethane (s)	1,301,300	-67,800	-215.4	-3,600
Pentacosane (s)	3,941,500	-191,800	-641.7	- 500
Cyclohexane	938,700	-36,900	-136.2	+3,700

Even in view of these uncertainties the data serve to bring out two important points. First, there is evidence of a small but definite increase in molal free energy as we proceed up the series of normal paraffins. Thus between *n*-hexane and liquid pentacosane there is a free energy increase of 11,900 cal. or about 630 cal.<sup>18</sup> per CH<sub>2</sub> increment. This trend, being small, is easily masked over the range of a few CH<sub>2</sub> increments by experimental errors in the combustion values and, in fact, was overlooked by one<sup>5</sup> of us in an earlier study of the simpler normal alcohols. That it actually exists, however, can be demonstrated in another way. From studies on various series of normal aliphatic compounds, it has been demonstrated that a fairly definite increase of about 156,300 cal.<sup>19</sup> occurs in the heat of combustion per CH<sub>2</sub> increment. This means that the  $\Delta H_{298}$  of formation must decrease by 6300 cal. per CH<sub>2</sub> group. On the other hand, we find cation). Until the question has been investigated further, we shall use 14.8 E. U., as in preceding papers.

<sup>18</sup> Of course, it should be noted that if the entropy of hydrogen be increased by 0.8 E. U. per gram atom, as suggested in Ref. 17, this free energy increase per  $\Delta\text{CH}_2$  will become about 1100 cal.

<sup>19</sup> Kharasch and Sher, *J. Phys. Chem.*, **29**, 629 (1925); see also Verkade and Coops, *Rec. trav. chim.*, **46**, 911 (1927), and Verkade, Coops and Hartman, *ibid.*, **45**, 585 (1926).

that the  $T\Delta S$  term decreases by 6900 cal. and consequently  $\Delta F_{298}^{\circ}$  must increase by approximately 600 cal.

The data also indicate that the free energy of a branched isomer is probably somewhat higher than the value for the normal hydrocarbon and that the more extensive the branching, the larger becomes this difference. In other words, the branched isomers are thermodynamically unstable with reference to the normal compound. This point is now being more thoroughly investigated in our laboratory in a study of the free energies of the nine isomeric heptanes recently prepared by Edgar and co-workers.

It should be noted that cyclohexane has a free energy value about 14,000 cal. above that of normal hexane. Evidently the withdrawal of a mole of hydrogen and the formation of a ring are accompanied by a very appreciable free energy increase.

Before concluding, the authors wish to thank the Research Laboratory of the Ethyl Gasoline Corporation and the Standard Oil Company of Indiana for the loan of valuable hydrocarbon samples.

### Summary

1. The specific heats of fourteen saturated, non-benzenoid hydrocarbons have been measured over a wide range of temperatures.

2. The heats of fusion of eight of these compounds have also been determined. In the cases of hexamethylethane and cyclohexane, which exist in two crystalline forms at low temperatures, the heat of transition has been measured.

3. The entropies of eleven of the compounds have been calculated from these heat capacity data. Two empirical equations for the estimation of the entropies of aliphatic hydrocarbons have been tested with the results.

4. The free energies of nine of these hydrocarbons have also been calculated. Apparently there is a small free energy increase, about 600 cal., per  $\text{CH}_2$  increment in the normal hydrocarbons. In isomeric hydrocarbons the free energy level becomes higher with increased branching.

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