THERMAL DATA ON ORGANIC COMPOUNDS.
X. FURTHER STUDIES ON THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF HYDROCARBONS[1]

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In four earlier papers[5] heat capacity data have been presented for about forty hydrocarbons and, in so far as possible, the corresponding entropies and free energies have been calculated. Certain pronounced regularities in these data have also been noted. In the present paper, which brings our studies on hydrocarbons to an end, we shall present similar thermal data for the following twenty compounds: propylene, n-butane, n-hexane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, methylcyclopentane, 1,2-dimethylcyclopentane, pseudocumene, durene, isodurene, prehnitene, p-cymene, n-butylbenzene, pentamethylbenzene, β-methylnaphthalene, anthracene and phenanthrene. Four of these (n-hexane, n-octane, n-nonane and n-decane) were studied to some extent in the first paper referred to above but our new heat capacity data, obtained with purer hydrocarbon samples, are much more nearly complete and reliable.

In general, our new entropy and free energy results confirm in a very satisfactory manner the conclusions reached in the earlier papers.

Materials

Propylene.—This hydrocarbon was very carefully prepared for us by Dr. Gerald van de Griendt of the Shell Development Company. Extremely pure isopropyl alcohol was dehydrated by phosphoric acid and the resulting propylene, when purified, was estimated to contain less than 0.1% impurities. The sample had an extremely sharp melting point at 88.2 °K.

n-Butane.—A large quantity of commercial n-butane (impurities guaranteed less than 1%) was obtained from the Carbide and Carbon Chemical Corporation. This material after three fractional distillations in a special still gave the product which was used in our measurements.

n-Hexane, n-Octane, n-Nonane, n-Decane, n-Undecane and n-Dodecane.—These samples constituted part of the materials prepared by Shepard, Henne and Midgley,

and for a full description of their preparation and properties the reader is referred to the recent paper[6] by these investigators. It is sufficient for us to say here that all of these samples showed very sharp melting points and were evidently of extreme purity. We likewise made measurements upon the samples of *n*-pentane and *n*-heptane prepared in the same series. However, as our earlier measurements upon these two compounds were also made with very pure materials and check the new values to better than 1%, we have omitted these data for *n*-pentane and *n*-heptane in preparing the present paper.

Methylcyclopentane and 1,2-Dimethylcyclopentane.—These two hydrocarbons were kindly loaned to us for our heat-capacity measurements by Professor G. Chavanne, in whose laboratory at the University of Brussels they had been prepared. The methylcyclopentane boiled at 71.5–71.7° (at 752.5 mm.) and had a very sharp melting point at −143.0°. The 1,2-dimethylcyclopentane (supposedly the *trans* form) boiled at 91.8°; it melted at −119.0° with considerable premelting.

Pseudocumene, Durene, Isodurene, Prehnitene and Pentamethylbenzene.—The samples of these five hydrocarbons were kindly loaned to us by Professor Lee Irvin Smith of the University of Minnesota. Details concerning them will not be given here, as their preparation and properties have been fully described elsewhere.[7] It is sufficient for us to add that all of these materials were of satisfactory purity for our measurements.

n-Butylbenzene and p-Cymene.—High grade Eastman materials were subjected to several fractional distillations in a special still. The final products had narrow boiling ranges: *n*-butylbenzene, 183.1–183.5°; *p*-cymene, 176.7–177.0°.

β-Methylnaphthalene.—This was a highly purified German material which was subjected to eight fractional crystallizations in our own laboratory. The melting point of the final product was 34.1°.

Anthracene.—The anthracene was obtained from Eastman's material (m. p. 213°) by six fractional crystallizations from benzene. The final product was very slightly yellow and had a melting point of 215.0°. Further attempts to purify the material were unsuccessful.

· Phenanthrene.—Kahlbaum's phenanthrene was subjected to fourteen crystallizations from ethyl alcohol. Our final sample melted at 97.7°.

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 other places.[8] 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 a hydrocarbon sample may cause premelting or otherwise influence the results.

As liquid propylene has a vapor pressure of 7 or 8 atm. at room temperature, the filling of our thin-walled calorimeter can and its subsequent installation in our apparatus in the usual fashion was hardly feasible in this case. Accordingly we first installed an empty calorimeter can, which

[6] Shepard, Henne and Midgley, THIS JOURNAL, **53**, 1948 (1931).

[7] Smith and Lux, *ibid.*, **51**, 2994 (1929); Smith and MacDougall, *ibid.*, **51**, 3001 (1929); Smith and Lund, *ibid.*, **52**, 4144 (1930).

[8] Parks, *ibid.* **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

was equipped with a German-silver entry tube, about 1.0 mm. inside diameter and 100 cm. long. This entry tube ran outside of the calorimeter system and was connected through a valve system to a monel-metal bomb of about 40-cc. capacity. The bomb was equipped with a vacuum- and pressure-tight valve so that it could be disconnected and weighed with its contents. By connecting the bomb filled with propylene to the entry tube and opening the valve, any desired quantity of propylene could be distilled into the calorimeter can and condensed by the maintenance of liquid-air temperatures around the calorimeter system. For emptying the calorimeter after a series of heat capacity determinations, this distillation process was easily reversed. Thus the weight of hydrocarbon used could be determined before, and checked after, a series of measurements with an accuracy of 0.05%.

The specific heats and the fusion data, expressed in terms of the 15° calorie[9] and with all weights reduced to a vacuum basis, appear in Tables I and II. For comparison with these values the literature contains only

TABLE I

SPECIFIC HEATS

PROPYLENE: Crystals

Temp., °K.	68.9	72.0	73.5	76.5	76.7	81.6		
C_p per g.	0.273	0.280	0.286	0.296	0.295	0.317		

Liquid

Temp., °K.	93.1	93.5	98.6	108.7	125.2	144.8	153.9	165.3
C_p per g.	0.523	0.522	0.516	0.504	0.494	0.490	0.490	0.492
Temp., °K.	189.5	210.3						
C_p per g.	0.502	0.512						

n-BUTANE: Crystals I

Temp., °K.	69.1	74.9	83.0	89.5	92.5	95.6	97.0	
C_p per g.	0.212	0.226	0.238	0.252	0.256	0.264	0.267	

Crystals II

Temp., °K.	114.3	119.9						
C_p per g.	0.35	0.37						

Liquid

Temp., °K.	139.7	150.2	152.5	170.2	187.0	190.1	230.0	261.8
C_p per g.	0.467	0.469	0.472	0.474	0.484	0.483	0.506	0.533

n-HEXANE: Crystals

Temp., °K.	93.4	99.0	115.0	131.4	145.5	154.8	163.5	
C_p per g.	0.219	0.227	0.251	0.274	0.295	0.309	0.328	

Liquid

Temp., °K.	188.8	217.8	275.4	276.2	293.5	
C_p per g.	0.472	0.482	0.521	0.523	0.536	

[9] The factor 0.2390 has been used in converting the joule to the 15° calorie.

TABLE I   (*Continued*)

n-OCTANE: Crystals

Temp., °K.	92.4	97.3	110.8	140.2	170.3	179.2	188.7	197.7
C_p per g.	0.198	0.207	0.226	0.263	0.300	0.312	0.327	0.346

Liquid

Temp., °K.	227.0	250.9	275.0	286.6	298.3
C_p per g.	0.483	0.490	0.508	0.517	0.526

n-NONANE: Crystals

Temp., °K.	92.8	97.6	113.8	136.8	150.1	163.1	179.3	187.7
C_p per g.	0.195	0.203	0.227	0.256	0.271	0.288	0.309	0.322

Liquid

Temp., °K.	228.3	233.7	245.0	259.4	275.3	282.8	289.9	297.9
C_p per g.	0.489	0.489	0.491	0.498	0.508	0.514	0.518	0.523

n-DECANE: Crystals

Temp., °K.	91.3	96.8	102.2	107.0	113.9	120.7	130.1	139.5
C_p per g.	0.188	0.196	0.204	0.210	0.219	0.228	0.239	0.250
Temp., °K.	150.0	159.6	170.1	180.2	190.6	200.2	210.5	220.6
C_p per g.	0.262	0.273	0.285	0.297	0.310	0.323	0.338	0.355

Liquid

Temp., °K.	251.2	262.1	275.2	281.3	288.8	297.7
C_p per g.	0.495	0.500	0.509	0.512	0.517	0.523

n-UNDECANE: Crystals

Temp., °K.	92.0	97.5	112.4	140.2	158.1	190.1	208.4
C_p per g.	0.188	0.196	0.215	0.250	0.271	0.310	0.338

Liquid

Temp., °K.	258.5	274.9	283.4	290.8	298.0
C_p per g.	0.503	0.511	0.515	0.520	0.524

n-DODECANE: Crystals

Temp., °K.	93.3	99.5	106.3	113.7	124.1	136.4	148.0	159.3
C_p per g.	0.184	0.194	0.202	0.212	0.225	0.239	0.252	0.264
Temp., °K.	171.0	186.3	197.6	211.4	224.0	234.0	243.5	
C_p per g.	0.277	0.295	0.309	0.326	0.344	0.362	0.380	

Liquid

Temp., °K.	275.1	282.9	289.7	297.7
C_p per g.	0.510	0.514	0.518	0.521

METHYLCYCLOPENTANE: Crystals

Temp., °K.	92.2	97.0	103.3	110.6	117.4	123.3
C_p per g.	0.183	0.190	0.198	0.208	0.218	0.230

Liquid

Temp., °K.	139.0	169.5	189.2	210.3	230.0	251.3	275.1	293.7
C_p per g.	0.352	0.357	0.365	0.376	0.388	0.404	0.424	0.447

TABLE I (*Continued*)

1,2-DIMETHYLCYCLOPENTANE: Crystals

Temp., °K.	93.4	99.4	107.0	114.8	122.3	129.3		
C_p per g.	0.191	0.200	0.211	0.221	0.232	0.263		

Liquid

Temp., °K.	161.5	175.2	195.0	210.0	244.6	275.4	284.1	294.2
C_p per g.	0.364	0.371	0.385	0.393	0.414	0.439	0.446	0.456

PSEUDOCUMENE: Crystals

Temp., °K.	93.7	100.0	115.1	123.7	140.8	163.0	180.7	205.1
C_p per g.	0.158	0.166	0.185	0.195	0.214	0.240	0.259	0.307

Liquid

Temp., °K.	239.5	246.9	260.5	277.0	277.4	283.6	297.3	
C_p per g.	0.388	0.392	0.400	0.412	0.411	0.415	0.422	

DURENE: Crystals

Temp., °K.	92.2	98.7	106.4	114.4	123.2	137.2	154.2	170.1
C_p per g.	0.156	0.166	0.176	0.186	0.197	0.214	0.233	0.251
Temp., °K.	189.5	202.3	219.5	242.1	257.2	277.3	284.4	297.1
C_p per g.	0.271	0.285	0.302	0.324	0.338	0.361	0.369	0.383

ISODURENE: Crystals

Temp., °K.	92.4	103.3	121.7	140.4	160.2	189.3	200.3	210.7
C_p per g.	0.162	0.176	0.199	0.222	0.245	0.275	0.287	0.302

Liquid

Temp., °K.	255.3	275.7	281.6	288.6	297.1			
C_p per g.	0.401	0.414	0.417	0.422	0.428			

PREHNITENE: Crystals

Temp., °K.	91.0	95.5	100.1	122.4	145.8	177.5	208.3	223.6
C_p per g.	0.149	0.154	0.160	0.185	0.212	0.252	0.296	0.328

Liquid

Temp., °K.	276.5	281.8	286.5	291.9				
C_p per g.	0.416	0.417	0.418	0.420				

p-CYMENE: Crystals

Temp., °K.	92.2	96.9	103.8	111.3	120.3	139.8	158.9	179.8
C_p per g.	0.156	0.162	0.170	0.179	0.190	0.212	0.233	0.269

Liquid

Temp., °K.	210.8	215.9	228.2	243.3	259.6	280.7	291.0	297.1
C_p per g.	0.367	0.370	0.376	0.384	0.393	0.409	0.417	0.421

n-BUTYLBENZENE: Crystals

Temp., °K.	94.0	99.6	105.6	115.3	127.5	139.2	151.3	161.0
C_p per g.	0.154	0.160	0.166	0.177	0.192	0.205	0.218	0.231

Liquid

Temp., °K.	191.9	195.8	210.6	224.8	255.0	275.5	287.9	298.2
C_p per g.	0.369	0.371	0.377	0.383	0.400	0.411	0.420	0.428

TABLE I (*Concluded*)

PENTAMETHYLBENZENE: Crystals I

Temp., °K.	91.7	105.2	113.1	122.6	141.2	149.9	159.2	174.8
C_p per g.	0.169	0.182	0.188	0.197	0.213	0.222	0.230	0.245
Temp., °K.	189.4	205.0	213.0	231.9	242.4	258.4	265.0	283.8
C_p per g.	0.261	0.277	0.286	0.304	0.316	0.334	0.341	0.405

Crystals II

Temp., °K.	303.6
C_p per g.	0.447

β-METHYLNAPHTHALENE: Crystals

Temp., °K.	93.8	107.1	135.5	157.1	196.6	225.2	253.3	272.4
C_p per g.	0.121	0.133	0.157	0.175	0.210	0.238	0.268	0.299

Liquid

Temp., °K.	310.4
C_p per g.	0.383

ANTHRACENE: Crystals

Temp., °K.	94.4	102.4	110.8	118.4	124.8	142.4	158.2	173.3
C_p per g.	0.095	0.101	0.107	0.113	0.117	0.131	0.146	0.159
Temp., °K.	193.2	210.2	228.4	244.6	254.4	275.8	282.5	297.2
C_p per g.	0.177	0.194	0.211	0.227	0.236	0.257	0.264	0.278

PHENANTHRENE: Crystals

Temp., °K.	93.4	100.1	116.7	127.5	137.9	157.9	179.7	190.5
C_p per g.	0.097	0.102	0.114	0.122	0.130	0.147	0.166	0.176
Temp., °K.	210.4	232.0	252.2	277.4	283.9	290.6	297.5	304.4
C_p per g.	0.195	0.216	0.236	0.265	0.277	0.300	0.313	0.325

very meager data. Mabery and Goldstein[10] have studied the heat capacities between 0 and 50° of a number of hydrocarbons, including *n*-hexane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane. They used an ice calorimeter and worked on materials derived from petroleum. Their result for *n*-octane at 25° is 4% below our curve; for the other compounds their values deviate by from 2.0 to 4.5% from our curves. Referring to our own previous work, we find that these new values for normal hydrocarbons are in good agreement with our earlier data as far as the liquid state is concerned. On the other hand, the new values for the *n*-hexane and *n*-octane crystals are for the most part considerably lower than the older ones, which were apparently affected by premelting to a greater extent than we at first realized. Conversely, our new fusion values for *n*-hexane and *n*-octane are 3.5 and 2.7% higher than the corresponding earlier data.

The specific heat values for liquid propylene show rather abnormal behavior. There is a 7% decrease as we proceed up the temperature scale from 93 to 125°K., whereas for most liquids there is a small but definite

[10] Mabery and Goldstein, *Am. Chem. J.*, **28**, 69 (1902).

TABLE II

FUSION DATA[a]

Substance	M. p., °K.	Heat of fusion (cal. per g.)		
		1st result	2d result	Mean
Propylene	88.2	16.62	16.75	16.67
n-Butane	134.1	17.98	...	17.98
n-Hexane	177.9	36.14	...	36.14
n-Octane	215.8	43.21	...	43.21
n-Nonane	219.2	41.24	41.19	41.22[b]
n-Decane	243.1	48.34	48.34	48.34
n-Undecane	247.2	34.24	34.00	34.12
n-Dodecane	263.5	51.33	...	51.33
Methylcyclopentane	130.1	19.52	19.58	19.55
1,2-Dimethylcyclopentane	154.1	15.66	...	15.66
Pseudocumene	228.6	25.15	...	25.15
Isodurene	248.6	23.06	23.02	23.04[b]
Prehnitene	265.4	20.01	19.99	20.00
p-Cymene	204.2	17.21	17.20	17.20
n-Butylbenzene	184.6	19.55	19.55	19.55
β-Methylnaphthalene	307.2	20.09	20.12	20.11

[a] In the calculation of these fusion values, the marked rise in the specific heat of the crystals 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.

[b] This value includes the heat effect for a solid transition taking place a few degrees below the melting point.

TABLE III

TRANSITION DATA

Substance	Transition point, °K.	Heat of transition (cal. per g.)		
		1st result	2d result	Mean
n-Butane	107.0	8.7	..	8.7
n-Undecane	236.1	9.67	9.71	9.69
Pentamethylbenzene	296.8	3.19	..	3.19

increase in heat capacity with rising temperatures. For this reason we at first feared that the use of our special calorimeter can with its long entry tube was affecting our results in some unaccountable manner. However, a second series of determinations made on n-butane with the special calorimeter yielded values which were in excellent agreement with earlier data obtained in the usual way. Thus the propylene behavior is apparently real.

Five of the hydrocarbons, n-butane, n-nonane, n-undecane, isodurene and pentamethylbenzene exhibited definite transitions in the solid state with quite appreciable heat effects. In three instances these heats of transition were directly measured, and the data thus obtained are recorded in Table III. In the case of n-nonane the transition came only 2.5° below the melting point. The situation is illustrated graphically in Fig. 1, where we have plotted the time–temperature curve for the transition and fusion processes. It is noticeable that the horizontal steps for the

two processes stand roughly in the ratio of 2 to 5.   However, it was hardly practical to determine accurately the heats of transition and fusion apart from one another.   Therefore, the two quantities are lumped together in the fusion value given in Table II.   For most practical purposes, such as entropy calculations, there is no real objection to such a procedure. We have acted similarly in the case of the isodurene transition, which came about 10° below the melting point.   In this case the ratio between the transition heat and the fusion heat was about 2 to 9, and our heat of fusion is therefore about 2500 cal. per mole.   This result is in satisfactory agreement with the estimate (2550 cal. per mole) obtained by Smith and MacDougall from freezing point measurements on the durene–isodurene system.[7]
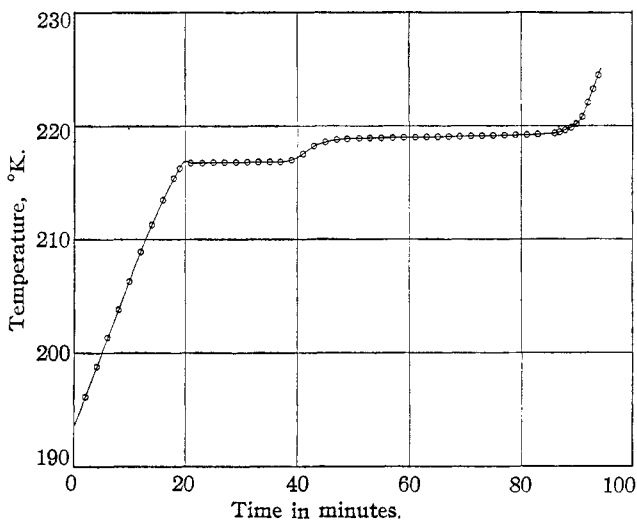

Fig. 1.—The time–temperature curve for the transition and fusion of n-nonane.

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 the various hydrocarbons. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[11] for estimating the entropy increase 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 the sixth column.

[11] Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

Two of these hydrocarbons, propylene and n-butane, are gases at 298°K. and 1 atm. pressure. Accordingly, in compiling the table, we have estimated their entropies of vaporization at the respective boiling points (225.3 and 273.7°K.) by use of the corresponding vapor pressure data of Burrell and Robertson.[12] The entropy increases in the gaseous state from the boiling points to 298.1°K. were then estimated on the assumption of $C_p = 14.0$ cal. per mole for propylene and $C_p = 22.3$ cal. per mole for n-butane. While these assumptions are rather arbitrary guesses, they cannot involve us in serious errors, as the magnitude of these increments is small.

In the cases of durene and β-methylnaphthalene, compounds which are normally crystalline at 298°K., it has seemed desirable for purposes of

TABLE IV

ENTROPIES OF THE HYDROCARBONS PER MOLE

Substance	Crystals 0-90°K.	Crystals Above 90°K.	Fusion	Liquid	S_{298}^o experimental	S_{298} predicted
Propylene (gas)	12.0[a]	...	7.96	19.26	63.1[b]	...
n-Butane (liquid)	11.7	12.31[c]	7.79	23.13	54.9	55.8
n-Butane (gas)	...	...	...	20.36	74.4[d]	...
n-Hexane	15.33	15.88	17.50	21.90	70.6	71.2
n-Octane	18.14	26.68	22.85	18.33	86.0	86.6
n-Nonane	19.86	30.23	24.10	19.69	93.9	94.3
n-Decane	22.00	37.56	28.27	14.65	102.5	102.0
n-Undecane	23.92	50.51	21.55	14.91	110.9	109.7
n-Dodecane	25.10	49.10	33.16	10.78	118.1	117.4
Methylcyclopentane	13.83	6.36	12.64	26.38	59.2	...
1,2-Dimethylcyclopentane	16.67	11.98	9.97	25.86	64.5	...
Pseudocumene	16.68	25.02	13.21	12.80	67.7	67.6
Durene (solid)	18.33	40.37	...	...	58.7	...
Durene (liquid)	...	...	13.13	...	71.8	75.3
Isodurene	19.25	32.35	12.43	10.03	74.1	75.3
Prehnitene	18.24	34.59	10.11	6.51	69.5	75.3
p-Cymene	19.12	23.16	11.30	19.70	73.3	75.3
n-Butylbenzene	18.87	18.60	14.20	25.10	76.8	75.3
Pentamethylbenzene (solid)	24.59	45.63[e]	...	...	70.3	...
β-Methylnaphthalene (solid)	15.74	33.00	...	...	48.7	...
β-Methylnaphthalene (liquid)	...	...	9.2	...	57.9	...
Anthracene (solid)	14.98	34.60	...	...	49.6	...
Phenanthrene (solid)	15.58	35.05	...	...	50.6	...

[a] The entropy of propylene crystals at the melting point (88.2°K.). [b] This value includes 20.0 E. U. for the entropy of vaporization of propylene at the normal boiling point (225.3°K.) and 3.9 E. U. for the entropy increase of the gas between this temperature and 298.1°K. [c] This value includes the entropy increase for both crystalline forms as well as the entropy effect (4.72 E. U.) for the transition between them. [d] This value includes the entropy of vaporization at the boiling point (20.44 E. U.) and 1.91 E. U. for the entropy increase of the gas between 273.7 and 298.1°K. [e] This value includes 1.85 E. U. for an entropy of transition at 297°K.

[12] Burrell and Robertson, THIS JOURNAL, 37, 2188 (1915).

comparison to have values for the entropy as a liquid, even though the liquid state is unstable at this temperature.   Accordingly we have roughly calculated their entropies of fusion at 298° by the method previously employed by Huffman, Parks and Daniels.[5]   For this purpose we have used the heat of fusion of durene recently obtained by Smith and Mac-Dougall[7] and our own result for β-methylnaphthalene.
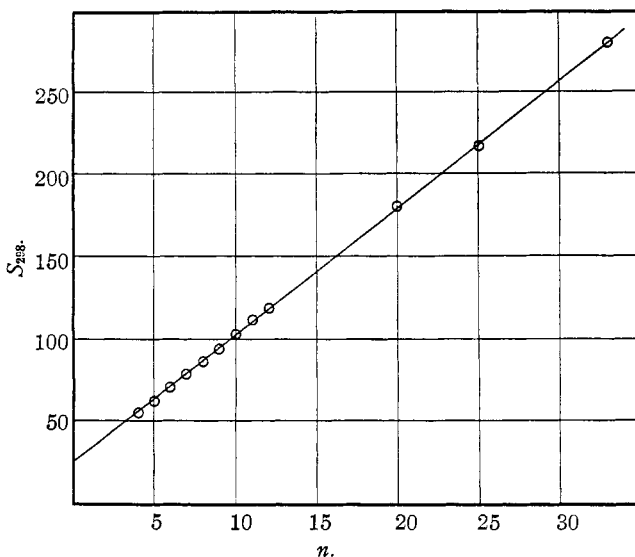

Fig. 2.—The molal entropies of some normal paraffins plotted against the number of carbon atoms in the molecule.

In the preceding papers[5] it has been shown that the entropy of a liquid paraffin or benzenoid hydrocarbon can be calculated quite accurately by the empirical equation, $S_{298} = 25.0 + 7.7n - 4.5r + 19.5p$.   Here n and p represent, respectively, the number of aliphatic carbon atoms and phenyl groups in the molecule, and r ordinarily refers to the number of methyl branches attached on the main aliphatic chain.   In the present study we have applied this equation, wherever possible, to obtain the values of "S_{298} predicted" in the last column of the table.   In the case of the normal paraffins these are in excellent agreement with the experimental results, as a comparison of the tabulated data will show.   This agreement is also shown graphically in Fig. 2, where the circles represent the experimental values of S_{298} for the various normal paraffins studied in this and in the preceding papers and the straight line represents the graph of our empirical entropy equation.   In the case of the benzenoid compounds the agreement between the experimental results and "predicted S_{298}" values is, in general, considerably poorer, although even here the

empirical equation serves to give a rough approximation of the entropy of any hydrocarbon.

The Free Energies of Fourteen Hydrocarbons.—We have also calculated the free energies of fourteen of these hydrocarbons by means of the third law of thermodynamics and the fundamental equation, $\Delta F = \Delta H - T \Delta S$.

The essential data are given in Table V. For obtaining the ΔH of formation of propylene we have used the heat of combustion reported in

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	ΔH_{298}, Cal.	ΔS_{298}, E. U.	ΔF_{298}° Cal.
Propylene (g)	492,200	+ 4,550	− 34.5	+14,800
n-Butane (g)	686,400	−32,110	− 87.0	− 6,200
n-Hexane	990,200	−53,410	−155.6	− 7,000
n-Octane	1,304,500	−64,210	−205.5	− 3,000
n-Decane	1,615,200	−78,610	−254.0	− 2,900
Methylcyclopentane	937,500	−37,800	−136.0	+ 2,700
1,2-Dimethylcyclopentane	1,090,200	−47,650	−163.2	+ 1,000
Pseudocumene	1,239,800	−18,220	−131.4	+21,000
Durene (s)	1,393,000	−27,570	−172.9	+24,000
p-Cymene	1,401,800	−18,770	−158.3	+28,400
n-Butylbenzene	1,401,900	−18,670	−154.8	+27,500
Pentamethylbenzene	1,553,400	−29,720	−193.8	+28,100
Anthracene (s)	1,693,100	+32,200	−124.7	+69,400
Phenanthrene (s)	1,692,200	+31,300	−123.7	+68,200

the early days by Thomsen,[13] and for anthracene and phenanthrene, Stohmann's values.[14] For pseudocume we have employed the result obtained by Richards and Barry and more recently revised by Swietoslawski and Bobinska;[15] and for n-butylbenzene we have adopted their corresponding result for n-propylbenzene increased by 156,300 cal. (the observed increase in the heat of combustion per CH_2 increment). In the absence of any reliable combustion values for n-butane and n-decane, we have substituted Thomsen's result for isobutane and that of Richards and Davis[15] for diisoamyl. Such a substitution seems entirely justifiable because the U. S. Bureau of Standards has recently shown that the nine isomeric heptanes have practically identical heats of combustion and that n-octane

[13] Thomsen (translation by Burke), "Thermochemistry," Longmans, Green and Co., London, 1908, p. 441.

[14] Landolt–Börnstein–Roth–Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 1590.

[15] Swietoslawski and Bobinska, THIS JOURNAL, 49, 2478 (1927). The values have been increased by 0.017%, as suggested by Verkade and Coops, Rec. trav. chim., 46, 910 (1927).

and a branched isomer, 2,2,4-trimethylpentane, differ in this particular by less than 0.1%.[16]   In the cases of the remaining seven compounds we have taken the heats of combustion as given in the "International Critical Tables."[17]   For our present purposes we have converted all these combustion data to 298.1°K.   The ΔH_{298} values were then calculated by use of 68,310[18] and 94,240[19] cal. for the heats of combustion of hydrogen and graphitic 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[20] and 15.62[21] E. U. per gram atom.

The molal free energies appear in the last column of the table.   For the most part the accuracy of these values is largely limited by the accuracy of the combustion data employed.   In the case of n-octane, where the heat of combustion has been determined recently by the U. S. Bureau of Standards, the free energy value is probably good to 1000 or 1500 cal.   On the other hand, in the cases of durene, pentamethylbenzene, anthracene and phenanthrene, where the heats of combustion were determined by Stohmann and his co-workers in the early days, the combustion values may be in error by as much as four or five thousand calories; and therefore the free energies are uncertain to this extent.   For the remaining compounds the values are probably reliable to within two or three thousand calories.

On the whole these free energies are in excellent accord with the various conclusions presented in the preceding papers.   However, in making comparisons with the previous data it must be borne in mind that we are here employing different values for the heats of combustion of carbon and hydrogen and for the entropy of hydrogen.   Our new values for the combustion of carbon and hydrogen are 30 and 20 calories, respectively, below the former ones, and serve to increase (algebraically) the corresponding free energy values by 50 calories per CH_2 increment or, for example, by a total of only 420 calories in the case of n-octane.   On the other hand, the alterations in free energy produced by the use of Giauque's new entropy value for hydrogen are much more important, amounting to an increase of 243 calories for each gram atom of hydrogen involved.   This corresponds to 486 calories per CH_2 increment, or 4370 calories in the case of n-octane.   Fortunately the revision of our earlier data is very simple and may be easily made by any reader interested in a given free energy value.

[16] Kharasch, *Bureau of Standards Journal Research*, **2**, 373 (1929).

[17] "International Critical Tables," Vol. V, p. 163.

[18] Rossini, *Bureau of Standards Journal Research*, **6**, 34 (1931).

[19] Roth and Naeser, *Z. Electrochem.*, **31**, 461 (1925).   We here have reduced their value to a vacuum basis.

[20] Lewis and Gibson, THIS JOURNAL, **39**, 2581 (1917).

[21] Giauque, *ibid.*, **52**, 4816 (1930).

In the present study we have calculated a ΔF°_{298} value for one or more representatives of each of the four important classes of hydrocarbons. The numerical results serve to illustrate that the order of decreasing thermodynamic stability (*i. e.*, increasing free energy of formation) at room temperature is: (1) paraffin, (2) naphthene, (3) olefin, (4) aromatic hydrocarbons.

Before concluding, the authors wish to thank the Shell Development Company, Dr. Albert L. Henne, Professor G. Chavanne and Professor Lee Irvin Smith for the valuable hydrocarbons which made this research possible.

Summary

1. The specific heats of twenty hydrocarbons have been measured over a wide range of temperatures. Heats of fusion and of transition have also been determined in the case of seventeen of these compounds.

2. The entropies of the twenty hydrocarbons have been calculated from these heat capacity data. In general the results are in good agreement with the corresponding values calculated by an empirical equation developed in preceding papers.

3. The corresponding free energies for fourteen of these hydrocarbons have also been calculated. The order of decreasing thermodynamic stability at 298° K. is (1) paraffin, (2) naphthene, (3) olefin, (4) aromatic hydrocarbons.

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STUDIES ON PROTEINS IN LIQUID AMMONIA. I[1,2]

BY EVAN W. MCCHESNEY AND CLEMMY O. MILLER

During the last few years there has been an increasing interest in the study of proteins in non-aqueous media. Granacher[3] has studied the reactions of proteins and polypeptides in ethyl alcohol at 170°; Fodor and Epstein[4] have studied the decomposition of gelatin by acetic anhydride.

[1] This article is taken from the dissertation presented by Evan W. McChesney to the Graduate School of Northwestern University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] This is an abstract of two papers, one of which was presented before Section C of the American Association for the Advancement of Science, Cleveland, Ohio, and the other before the Organic Division of the American Chemical Society in Indianapolis, Indiana, April, 1931.

[3] Granacher, *Helv. Chim. Acta*, **8**, 784 (1925).

[4] Fodor and Epstein, *Z. physiol. Chem.*, **171**, 222 (1927); *Biochem. Z.*, **200**, 211 (1928); **228**, 310 (1930).