[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

Thermodynamic Properties and the Characteristic CH_2 Frequencies of *n*-Paraffins

BY WILLIS B. PERSON AND GEORGE C. PIMENTEL

RECEIVED JULY 22, 1952

A revision of the calculations of Pitzer on the thermodynamic properties of normal paraffins is presented. Reconsideration of the characteristic CH_2 frequencies has been made. Values of the parameters have been reviewed and, in some cases, revised. Results of the new calculations are compared with the available experimental data. Tables are given which present the calculations of the thermodynamic properties, $-(F^\circ - H_0^\circ/T)$, $H^\circ - H_0^\circ/T$, S° and C_p°, for normal paraffins from butane through heptane, and a table of increments is given which will permit the calculation of these thermodynamic properties of normal paraffins at least through *n*-eicosane.

Several years ago Pitzer[1] developed an approximate statistical method for calculating the thermodynamic properties of the *n*-paraffins and related compounds. In the meantime many precise investigations have made available more accurate experimental data. Consequently, a need has arisen to revise Pitzer's calculations,[2] both by the introduction of more precise methods where feasible, and by the adjustment of parameters to the present best values. Therefore, re-examination and revision of the calculations made by Pitzer have been undertaken, using the same general method of calculation, but selecting a more appropriate type of average in certain cases. Also, the assignment of vibration frequencies for the infinite paraffin chain has been placed on a more secure basis.

New Data.—Very accurate calorimetric measurements giving liquid phase standard entropies at 25° of the normal paraffins from C_6H_{14} through $C_{16}H_{34}$ were completed by Huffman, Waddington, *et al.*, at the Petroleum Experiment Station of the Bureau of Mines.[3] These were coupled with entropies of vaporization obtained by Osborne and Ginnings[4] and the vapor pressure measurements of the A.P.I. Research Project 6[5] to give reliable values of the standard entropies at 25° for the normal paraffins through $C_{16}H_{34}$ in the ideal gas state. These values are shown in Table I. The experimental CH_2 increment becomes relatively constant at 9.31 ± 0.06 cal./deg./mole between successive homologs above C_7H_{16}, whereas the calculated increment was 9.183 cal./deg./mole.

TABLE I

EXPERIMENTAL ENTROPIES IN CAL./DEG./MOLE OF GASEOUS *n*-PARAFFINS AT 298.16°K.

	$S^\circ_{298.16}$ K.	$\Delta S/CH_2$		$S^\circ_{298.16}$ K.	$\Delta S/CH_2$
CH_4	44.50		C_9H_{20}	121.01	9.36
C_2H_6	54.85	10.35	$C_{10}H_{22}$	130.29	9.28
C_3H_8	64.51	9.66	$C_{11}H_{24}$	139.57	9.28
C_4H_{10}	74.10	9.59	$C_{12}H_{26}$	148.86	9.29
C_5H_{12}	83.43	9.33	$C_{13}H_{28}$	158.14	9.28
C_6H_{14}	92.90	9.47	$C_{14}H_{30}$	167.51	9.37
C_7H_{16}	102.26	9.36	$C_{15}H_{32}$	176.75	9.24
C_8H_{18}	111.65	9.39	$C_{16}H_{34}$	186.01	9.26

Vapor phase heat capacity measurements have also been completed for *n*-hexane,[6] *n*-heptane[7] and *n*-octane.[8] These values differ from the computed values by about 1%, as shown in Table V of reference 8. In addition to the new calorimetric data, a large amount of spectral data on the *n*-paraffins has become available. These spectral data are discussed in the following section.

Vibrational Frequencies of the CH_2 Group.—In view of the abundance of new spectral data of normal paraffins, it seemed desirable to investigate the validity of the assignment of fundamental frequencies used earlier.[1,2] Some data have appeared since the review of the assignment published by Barrow[9]: *e.g.*, infrared spectra of deuterated derivatives of propane,[10] additional polarization measurements of the Raman spectra of *n*-hexane and *n*-heptane,[11] the low temperature infrared spectra of solid *n*-pentane, *n*-hexane and *n*-heptane,[12] and the infrared spectra of even-numbered *n*-paraffins in solid and liquid states from *n*-octane to *n*-tetradecane.[13] These data were considered in detail and they provide basis for minor changes in the assignments made by Barrow. Disregarding permutations among symmetry classes, the present assignment differs from that of Barrow by the substitution of a frequency at 1440 cm.$^{-1}$ for one of the two frequencies Barrow assigned at 1242 cm.$^{-1}$. The detailed arguments comparing the several alternate assignments in the light of the recent data are included in Appendix I.

Several attempts to interpret the spectra of long chain hydrocarbons based on calculations by the method of Whitcomb, Nielsen and Thomas[14] have recently appeared.[15-17] This method consists of calculating the vibrational frequencies of

---

[1] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940), hereafter cited as I.

[2] The values in reference 1 were revised and extended in (a) K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944), and in (b) "Selected Values of Properties of Hydrocarbons," Circular of the National Bureau of Standards C461, U. S. Government Printing Office, Washington, D. C., 1947.

[3] Private communication from F. D. Rossini.

[4] N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947); reference 1, Table 20m.

[5] See reference 2b, Table 20k.

[6] G. Waddington and D. R. Douslin, THIS JOURNAL, **69**, 2275 (1947).

[7] G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947).

[8] G. Barrow, *ibid.*, **73**, 1824 (1951).

[9] G. Barrow, *J. Chem. Phys.*, **19**, 345 (1951).

[10] (a) H. L. McMurry, V. Thornton and F. E. Condon, *ibid.*, **17**, 918 (1949); (b) H. L. McMurry and V. Thornton, *ibid.*, **18**, 1515 (1950); (c) H. L. McMurry and V. Thornton, *ibid.*, **19**, 1014 (1951).

[11] F. F. Cleveland and P. Porcelli, *ibid.*, **18**, 1459 (1950).

[12] D. W. E. Axford and D. H. Rank, *ibid.*, **18**, 51 (1950).

[13] J. K. Brown, N. Sheppard and D. M. Simpson, *Disc. Faraday Soc.*, **9**, 261 (1950).

[14] S. E. Whitcomb, H. H. Nielsen and L. H. Thomas, *J. Chem. Phys.*, **8**, 143 (1940).

[15] L. Kellner, *Nature*, **163**, 877 (1949).

[16] (a) T. Simanouti and S. Mizushima, *J. Chem. Phys.*, **17**, 1102 (1949); (b) T. Simanouti, *ibid.*, **17**, 734 (1949).

[17] W. E. Deeds and W. H. Shaffer, Vibrational Analysis of Normal Paraffins, presented at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June 14, 1951.

an infinite paraffin chain in terms of the motions of individual CH_2 groups, each group vibrating with a particular phase relation to adjacent groups. The published normal coördinate analyses based on this method have previously calculated only the frequencies at phase angles of $\lambda = 0$ and π except for the original treatment[14] in which the force field seems open to question. Barrow[9,18] carried out the analysis for these values of λ, substituting a valence force field. We have repeated the analysis of Barrow, extending it to intermediate values of λ for several of the symmetry classes. The frequencies at these intermediate values are important to the present problem, for frequencies at all values of λ contribute to the thermodynamic properties of hydrocarbons. An average frequency for thermodynamic calculations should be weighted in accordance with these intermediate values.

In the course of our analysis, two errors were found in the treatment of Barrow: a typographical error and a numerical error which had only a slight effect on the calculated frequencies. The interaction force constant, $f_{CC,HCC}$, actually used by Barrow in his calculations had a value of 0.4×10^5 dynes/cm.[19] This interaction force constant enters into the calculation of only one class of frequencies (B_{1g}) for $\lambda = \pi$. However, it has a value as large as the principal bending force constants used. It was felt that such a large interaction force constant casts significant doubt on the frequency assignment. Good agreement with the calculated frequencies could be obtained with an alternate assignment. The force constants used are given below in units of 10^5 dynes/cm.

$$f_{CC} = 3.6 \qquad f_{HCH} = 0.42 \qquad f_{CCC} = 0.2$$
$$f_{CH} = 4.55 \qquad f_{HCC} = 0.61 \qquad f_{CC,HCC} = 0.15$$

TABLE II

CALCULATED FREQUENCIES OF THE NORMAL VIBRATIONS OF AN INFINITE CH_2 CHAIN FOR $\lambda = 0$ OR π, AND PROPOSED ASSIGNMENTS

Class	Description	Present calculations	Present assignment	B.[a]	S. and M.[b]	B.S.S.[c]
Raman active	"C–C stretch"	948	890	890	1135	?
A_{1g}	"H–C–H bend"	1490	1471	1440 1471	1471	1462
	C–H stretch	2837	2878	2862	2846 2878	2846
A_{2g}	"CH_2 twist"	1241	1296	1242[d]	978[d]	?
B_{1g}	"C–C stretch"	957	1060	1060	1058	1135
	"CH_2 wag"	1480	1440	1296	1442	1295
B_{2g}	"CH_2 rock"	1113	1135	1135	1295	?
	C–H stretch	2939	2950	2950	2934 2963	2934
Infrared active	"H–C–H bend"	1459	1467	1475	1475	1462
A_{1u}	C–H stretch	2847	2853	2853	2853	2853
A_{2u}	"CH_2 twist"	1241	1241[d]	1242[d]	978[d]	?
B_{1u}	"CH_2 wag"	1342	1375	1375	1375	1309
B_{2u}	"CH_2 rock"	734	732	728	728	721
	C–H stretch	2922	2926	2926	2926	2925

[a] Assignment by Barrow, ref. 9. [b] Assignment by Simanouti and Mizushima, ref. 16. [c] Assignment by Brown, Sheppard and Simpson, ref. 13. [d] Calculated, but not observed.

The results of this calculation for $\lambda = 0$ and π are compared in Table II to the proposed assignment and to several earlier assignments. The variation of frequencies as a function of λ may be seen in Table III for the motions antisymmetric to the plane of the molecule.

TABLE III

FREQUENCIES AS A FUNCTION OF PHASE ANGLE λ. DETERMINATION OF THE THERMODYNAMIC FREQUENCIES

Vibrations antisymmetric to the plane of the molecule[a]

Mode		B_{2g}–B_{2u} "CH_2 rock"	B_{2g}–B_{2u} C–H stretch	A_{2u}–A_{2g} "CH_2 twist"
Frequency	$\lambda = 0$	1135	2950	1296
Observed	$\lambda = \pi$	732	2926	
Frequency	$\lambda = 0$	1113	2939	1241
Calculated	$\lambda = \pi/4$	993	2934	1295
	$\lambda = \pi/2$	911	2925	1303
	$\lambda = 3\pi/4$	758	2922	1270
	$\lambda = \pi$	734	2922	1241
Average of obs. frequencies		933	2938	1268
Δ		−21	−2	+29
Thermodynamic frequency		912	2936	1297

[a] We should like to thank Mr. I. C. Hisatsune for his help in the calculations in this table.

Evaluation of Thermodynamic Properties.—In the reconsideration of the calculations of the thermodynamic properties of normal paraffins, the terms given in Table IV of paper I must be examined to see which need revision. The revised terms are given in Table VI. The considerations made for those terms which were altered are given below. Further details and further explanation of the nomenclature may be obtained by reference to paper I.

(1) **Term in $F_0(T)$.**—The only term in the expressions for $F_0(T)$ which requires consideration is the value of the effective CH_2 mass, *m*. This mass should be the geometric mean of the effective CH_2 mass in each degree of freedom. The value used in I, $m = 18.6$, was obtained by equating the value of the product $(M^3I_1I_2I_3)$ for propane to the value of this product calculated for the carbon skeleton using point masses of value *m* at each carbon. This gives the geometric mean of the effective CH_2 mass for the translational and rotational degrees of freedom, but neglects the vibrational and internal rotational masses. It is difficult to estimate the effective CH_2 mass for the latter degrees of freedom. An argument is presented in Appendix II which gives the same effective CH_2 mass, 18,6, an agreement which is fortuitous but which indicates that no major change is needed. However, this argument indicates that for short chains the effective CH_2 mass may be a function of the chain length. In calculating the thermodynamic properties of normal paraffins shorter than *n*-heptane the value of *m* for these paraffins has been adjusted in the ratio of their effective rotational masses.

(2) **Term in C–$C_{str.}$.**—The assignment of the "C–C stretch" frequencies requires a small change in the average frequency from $\nu_1 = 1000$ cm.$^{-1}$ to $\nu_1 = 975$ cm.$^{-1}$. The latter value is also used

---

[18] G. Barrow, Ph.D. Thesis, University of California, 1951.

[19] Not 0.2×10^5 dynes/cm. as given in references 9 and 18 Barrow has indicated in a private communication that this value (0.2) was a misprint.

in equation 5 of I to evaluate $2\,(m/k_1)^{1/2}$ in the term in $-(F^\circ - H_0^\circ)/T$.

(3) **Term in C–C_{bend}.**—The only deviation from the earlier calculation is a small adjustment of the value of k_2 in accordance with the small change in k_1. Pitzer's estimate of the ratio, $\epsilon = k_2/k_1$, was used in preference to that obtained in the present normal coördinate analysis since k_2 is not important in any of the modes calculated and hence is not accurately known from the present treatment.

(4) **Term in CH_2.**—As mentioned above, the thermodynamic frequency to be used for a given motion in thermodynamic calculations should be a representative average of the frequencies for this motion over all values of λ. Such a representative average was obtained by averaging the values of the frequencies calculated at 0, $\pi/4$, $\pi/2$, $3\pi/4$ and π. It was assumed that the calculated frequency variation with phase angle in Table III gave a reasonable approximation of the deviation from a linear dependence on λ, even when the normal coördinate analysis did not exactly fit the assigned values of the optically active frequencies. The difference, Δ, between the average of the five calculated frequencies including intermediate values of λ, and the average of the two *calculated* frequencies at $\lambda = 0$ and π, was then added to the average of the *observed* frequencies at $\lambda = 0$ and π, and the resultant frequency used in the thermodynamic calculations. This is shown in Table III.

Using the thermodynamic frequencies given in the last line of Table III, or, for frequencies not given in Table III, the arithmetic average of the values at $\lambda = 0$ and π, the contributions to the thermodynamic functions were computed.[20]

The spectroscopic data available at present do not permit us to choose between our assignment and that of Barrow. Since the agreement of calculated with experimental thermodynamic quantities was slightly poorer with Barrow's assignment, the present assignment was used.

(5) **Term in CH_3.**—When all the changes mentioned above were made, the calculated entropies were still about 0.1–0.2 entropy unit below the observed values for *n*-hexane, *n*-heptane and *n*-octane, although the CH_2 increment was correct, and the calculated heat capacities were in agreement with experiment. Therefore, attention was given to the term in CH_3, a term which does not depend on the chain length. This term is a function of I_R, the effective moment of inertia of the CH_3 group, and V_0, the barrier restricting internal rotation of the methyl group. Pitzer took I_R and V_0 from propane, which might not have the same values of these parameters as long chain hydrocarbons. I_R is defined by Pitzer and Gwinn.[21] Their equation 1a indicates that the value of I_R should be a function of chain length. Based on this equation, an approximate expression for I_R as a function of the number of carbon atoms, n, (n greater than six) is

$$I_R = 5.40(1 - 5.40/30n)10^{40}$$

With this value of I_R, the value of V_0 was adjusted until a fit between experimental and calculated entropies for *n*-heptane was obtained. These calculations, together with those of the following section, were made using the methods presented in reference 21 with graphical interpolation. Agreement was obtained using the reasonable value of $V_0 = 3480$ cal./mole. For simplicity in the calculation of the thermodynamic properties of normal paraffins from *n*-hexane to *n*-eicosane ($C_{20}H_{42}$) $I_R = 5.319 \times 10^{40}$ was used, a weighted average value corresponding roughly to $n = 12$.

(6) **Terms in I.Rot. and F_{steric}.**—In these terms the values of V_0', 3260 cal./mole, and a, 500 cal./mole, were chosen to give agreement between the calculated and experimental entropies of *n*-hexane and *n*-octane. This value of V_0' compares favorably with the earlier estimate of 3300 cal./mole for this potential hindering the rotation of the CH_2 group.[2] The manner of determining the steric interaction energy, a, causes it to absorb any errors in the approximations made in this calculation. Therefore it is gratifying that this value of a (500 cal./mole) agrees exactly with the value found spectroscopically by Sheppard and Szasz[22] for *n*-pentane and *n*-hexane. The spectroscopic value for butane is 760 cal./mole, but the 500 cal. value was used in the calculation of the thermodynamic properties of butane.

Comparison with Experiment.—The comparison of the calculated with the experimental entropies at 298.16°K. for *n*-hexane, *n*-heptane and *n*-octane is given in Table IV. It is seen that the agreement is very good at this temperature for these hydrocarbons. Since the calculated increment (9.309) agrees with the average experimental entropy increment (9.31), the calculated and experimental entropies for higher paraffins at 298.16°K. agree well within experimental error.

In Table V the comparison between calculated and experimental heat capacities of the ideal gases,

TABLE IV

COMPARISON OF CALCULATED AND OBSERVED ENTROPIES IN CAL./DEG./MOLE AT 298.16°K. OF IDEAL GASEOUS *n*-PARAFFINS

	$S^\circ_{298.16}$		$\Delta S/CH_2$	
Paraffin	Calcd.	Exptl.[a]	Calcd.	Exptl.[b]
n-Hexane	92.83	92.90	...	..
n-Heptane	102.24	102.26	9.309	9.31
n-Octane	111.55	111.65	9.309	9.31

[a] From Table I. [b] Average value of the entropy increment calculated from the data in Table I.

TABLE V

COMPARISON OF CALCULATED AND EXPERIMENTAL HEAT CAPACITIES IN CAL./DEG./MOLE OF IDEAL GASEOUS *n*-PARAFFINS

	C_p° at 400°K.		C_p° at 500°K.	
Paraffin	Calcd.	Exptl.	Calcd.	Exptl.
n-Hexane	43.47	43.38[a]	51.83	52.15[a]
n-Heptane	50.42	50.29[b]	60.07	60.13[b]
n-Octane	57.36	57.1[c]	68.32	68.3[c]

[a] Determined from the equation for C_p° for *n*-hexane given in reference 6. [b] Determined from the equation for C_p° for *n*-heptane given in reference 7. [c] Interpolated from the values given for C_p° in reference 8.

---

(20) "Contributions to Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Washington, D. C., July, 1949.

(21) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **7**, 428 (1942).

(22) N. Sheppard and G. J. Szasz, *ibid.*, **17**, 86 (1949).

TABLE VI

FORMULAS FOR CALCULATING THERMODYNAMIC FUNCTIONS OF NORMAL PARAFFINS

	$-(F^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	C_p°
$F_0(T)$	$R\ln\frac{64\pi^5 m^3 r_0^3 k^3 \sin\gamma R}{h^6 N_0} + 4R\ln T$ $= 4.235 + 4R\ln T$	$4R$	$4R$
C–C$_{\text{Str}}$	$R\ln(2\pi\nu_1(m/k_1)^{1/2}) + \text{Ein } h\nu_1/kT = 0.689 + \text{Ein } (hc\,975/kT)$	$\text{Ein } h\nu_1/kT$ $\nu_1/c = 975$ cm.$^{-1}$	$\text{Ein } h\nu_1/kT$
C–C$_{\text{Bend}}$	$R\ln(2\pi k m^{1/2}/hk_2^{1/2}) + R\ln T + \frac{R}{2}(h\nu_2/kT) - \frac{R}{24}(h\nu_2/kT)^2$ $= -11.296 + R\ln T + \frac{413}{T} - \frac{14{,}200}{T^2}$	$R - \frac{R}{2}(h\nu_2/kT) + \frac{R}{12}(h\nu_2/kT)^2$ $= R - \frac{413}{T} + \frac{28{,}400}{T^2}$	$R - \frac{R}{12}(h\nu_2/kT)^2$ $= R - 28{,}400/T^2$ $(T > 250)$
I.Rot.	$R[-1.275 + {}^1/_2\ln T + {}^1/_2\ln(mr_0^2\sin^2\gamma \times 10^{40}) - \ln 3]$ $-\frac{(F - F_f)}{T}\left(V_0'/RT, \frac{1}{Q_f} = 0\right) + \frac{h\nu_3}{2T} =$ $= {}^1/_2 R\ln T - 0.568 + \frac{170}{T} - \frac{(F - F_f)}{T}\left(\frac{3260}{RT}\right)$	$\frac{H}{T}\left(\frac{V_0'}{RT}, \frac{1}{Q_f} = 0\right) - \frac{h\nu_3}{2T}$ $= \frac{H}{T}\left(\frac{3260}{RT}\right) - \frac{170}{T}$	$C\left(\frac{V_0'}{RT}, \frac{1}{Q_f} = 0\right)$ $= C\left(\frac{3260}{RT}\right)$
F_{Steric}	$R\ln Q$ $Q = \sum_i e^{-E_i/kT}$ $(a = 500$ cal./mole$)$	$R(Q'/Q)$ $Q' = \sum_i \left(\frac{E_i}{kT}\right) e^{-E_i/kT}$	$R\left[\frac{Q''}{Q} - \left(\frac{Q'}{Q}\right)^2\right]$ $Q'' = \sum_i \left(\frac{E_i}{kT}\right) e^{-E_i/kT}$
$F(\sigma)$	$-R\ln\sigma = -R\ln 2$	0	0
CH$_3$	$\sum_i \text{Ein } (h\nu_i/kT) + R(-1.275 + {}^1/_2\ln T + {}^1/_2\ln I_R \times 10^{40} - \ln 3)$ $-\frac{(F - F_f)}{T}\left(\frac{V_0}{RT}\right) = -3.077 + {}^1/_2 R\ln T + \sum_i \text{Ein } \frac{h\nu_i}{kT} - \frac{(F - F_f)}{T}\left(\frac{V_0}{RT}\right)$ $\nu/c = (3)\ 2950, (2)\ 1460, 1375, 1170, 827$	$\sum_i \text{Ein }\left(\frac{h\nu_i}{kT}\right) + \frac{H}{T}\left(\frac{V_0}{RT}\right)$ $V_0 = 3480$	$\sum_i \text{Ein } \frac{h\nu_i}{kT} + C\left(\frac{V_0}{RT}\right)$ $I_R = 5.211 \times 10^{-40}$
CH$_2$	$\sum_i \text{Ein } h\nu_i/kT$ $\nu_i/c = 2936, 2865, 1469, 1407, 1297, 912$	$\sum_i \text{Ein } h\nu_i/kT$	$\sum_i \text{Ein } h\nu_i/kT$

n-hexane, n-heptane and n-octane is given. It is felt that there is enough uncertainty in the experimental values that an adjustment of the calculated values to remove the discrepancies is not justified. In particular, the value of the heat capacity of n-octane at 400°K. may be low by as much as 0.1–0.2 cal./deg./mole just due to the correction for gas imperfection.

TABLE VII

NUMERICAL VALUES FOR THE TERMS IN TABLE VI WHICH CONTRIBUTE TO $-(F^\circ - H_0^\circ)/T$

T, °K.	$[F_0(T)]$ C$_7$ and above[a]	[C–C$_{\text{Str}}$]	[C–C$_{\text{Bend}}$]	[I.Rot.][c]	$[F_{\text{Steric}}]$[b] A	B	[CH$_3$]	[CH$_2$]
298.16	49.524	0.707	1.252	2.951	4.320	1.037	0.882	0.032
300	49.573	.707	1.258	2.960	4.335	1.040	0.898	.033
400	51.860	.749	1.554	3.444	4.997	1.195	1.399	.118
500	53.634	.813	1.823	3.849	5.425	1.295	1.932	.263
600	55.083	.890	2.065	4.189	5.724	1.365	2.487	.460
700	56.308	.976	2.284	4.482	5.944	1.416	3.055	.698
800	57.370	1.067	2.482	4.736	6.113	1.456	3.630	.965
900	58.306	1.158	2.663	4.954	6.246	1.487	4.203	1.254
1000	59.143	1.250	2.830	5.151	6.354	1.512	4.773	1.557
1100	59.901	1.340	2.984	5.326	6.443	1.533	5.335	1.870
1200	60.593	1.428	3.128	5.486	6.518	1.550	5.895	2.189
1300	61.229	1.514	3.262	5.625	6.582	1.565	6.440	2.511
1400	61.818	1.598	3.388	5.753	6.637	1.578	6.978	2.834
1500	62.366	1.679	3.506	5.868	6.685	1.589	7.503	3.156

For a normal paraffin of N carbon atoms

$$-(F^\circ - H_0^\circ)/T = [F_0(T)] + (N-1)[\text{C–C}_{\text{Str}}] + (N-2)\,[\text{C–C}_{\text{Bend}}] + (N-3)[\text{I.Rot.}] + [F_{\text{Steric}}] + F(\sigma) + 2[\text{CH}_3] + (N-2)[\text{CH}_2]$$

$$F(\sigma) = -R\ln 2$$

$$\Delta - (F^\circ - H_0^\circ/T) \text{ per CH}_2 = [\text{C–C}_{\text{Str}}] + [\text{C–C}_{\text{Bend}}] + [\text{I.Rot}] + [B] + [\text{CH}_2]$$

[a] $F_0(T)$ is decreased by 0.064 for hexane, 0.162 for pentane and 0.195 for butane, for all temperatures. [b] For heptane and above, $[F_{\text{Steric}}] = A + (N - 7)B$; for each of the paraffins, butane, pentane and hexane, this term was calculated individually. [c] [I.Rot.] was decreased by 0.033 for hexane, 0.054 for pentane, and 0.049 for butane, at all temperatures.

TABLE VIII

NUMERICAL VALUES FOR THE TERMS IN TABLE VI WHICH CONTRIBUTE TO $(H^\circ - H_0^\circ)/T$

T, °K.	$[F_0(T)]$	[C–C$_{\text{Str}}$]	[C–C$_{\text{Bend}}$]	[I.Rot.]	$[F_{\text{Steric}}]^a$ A	B	[CH$_3$]	[CH$_2$]
298.16	7.949	0.085	0.921	1.572	2.524	0.592	1.432	0.159
300	7.949	.087	0.926	1.577	2.515	.589	1.443	.164
400	7.949	.215	1.132	1.766	2.083	.487	2.075	.462
500	7.949	.359	1.275	1.864	1.762	.411	2.735	.865
600	7.949	.496	1.378	1.895	1.522	.355	3.382	1.315
700	7.949	.620	1.455	1.896	1.337	.312	4.004	1.778
800	7.949	.730	1.515	1.886	1.191	.278	4.594	2.234
900	7.949	.825	1.563	1.865	1.074	.250	5.147	2.672
1000	7.949	.909	1.603	1.835	0.977	.228	5.669	3.089
1100	7.949	.982	1.635	1.804	.896	.209	6.160	3.482
1200	7.949	1.047	1.663	1.775	.828	.193	6.621	3.851
1300	7.949	1.104	1.686	1.743	.769	.179	7.053	4.196
1400	7.949	1.155	1.707	1.711	.718	.167	7.455	4.518
1500	7.949	1.201	1.724	1.681	.673	.157	7.825	4.819

For a normal paraffin of N carbon atoms

$$H^\circ - H_0^\circ/T = [F_0(T)] + (N - 1)[\text{C–C}_{\text{Str}}] + (N \quad 2)[\text{C–C}_{\text{Bend}}] + (N - 3)[\text{I.Rot.}] + [F_{\text{Steric}}] + 2[\text{CH}_3] + (N - 2)[\text{CH}_2]$$

$$\Delta(H^\circ - H_0^\circ/T) \text{ per CH}_2 \text{ group} = [\text{C–C}_{\text{Str}}] + [\text{C–C}_{\text{Bend}}] + [\text{I.Rot.}] + [\text{B}] + [\text{CH}_2]$$

[a] See footnote b on Table VII.

TABLE IX

NUMERICAL VALUES FOR THE TERMS IN TABLE VI WHICH CONTRIBUTE TO C_p°

T, °K.	$[F_0(T)]$	[C–C$_{\text{Str}}$]	[C–C$_{\text{Bend}}$]	[I.Rot.]	$[F_{\text{Steric}}]^a$ A	B	[CH$_3$]	[CH$_2$]
298.16	7.949	0.406	1.668	2.334	1.049	0.238	3.229	0.821
300	7.949	.413	1.672	2.336	1.037	.235	3.253	0.838
400	7.949	.779	1.810	2.309	0.595	.135	4.687	1.908
500	7.949	1.072	1.874	2.176	.383	.087	6.025	3.038
600	7.949	1.284	1.908	2.010	.262	.058	7.212	4.081
700	7.949	1.437	1.929	1.858	.196	.045	8.250	5.007
800	7.949	1.548	1.943	1.722	.150	.034	9.175	5.818
900	7.949	1.629	1.952	1.612	.119	.027	9.998	6.525
1000	7.949	1.691	1.959	1.521	.096	.022	10.726	7.140
1100	7.949	1.738	1.964	1.446	.079	.018	11.367	7.672
1200	7.949	1.776	1.967	1.385	.067	.015	11.931	8.133
1300	7.949	1.805	1.970	1.336	.057	.013	12.428	8.532
1400	7.949	1.829	1.973	1.292	.049	.011	12.864	8.878
1500	7.949	1.848	1.975	1.257	.043	.010	13.247	9.179

For a normal paraffin of N carbon atoms

$$C_p^\circ = [F_0(T)] + (N - 1)[\text{C–C}_{\text{Str}}] + (N - 2)[\text{C–C}_{\text{Bend}}] + (N - 3)[\text{I.Rot.}] + [F_{\text{Steric}}] + 2[\text{CH}_3] + (N - 2)[\text{CH}_2]$$

$$\Delta C_p^\circ \text{ per CH}_2 \text{ group} = [\text{C–C}_{\text{Str}}] + [\text{C–C}_{\text{Bend}}] + [\text{I.Rot.}] + [B] + [\text{CH}_2]$$

[a] See footnote b on Table VII.

Calculation of Thermodynamic Properties.—Table VI gives the expressions used in calculating the thermodynamic properties of normal paraffins, with the revised values of the parameters discussed above. The terms in Table VI are evaluated in Tables VII, VIII and IX. Using these tables and the formulas given in them, the thermodynamic properties of any n-paraffin from n-butane to n-eicosane may be calculated. Although the errors will tend to accumulate on extrapolation, the thermodynamic properties calculated from these tables should be fairly good approximations for even longer normal paraffins. For normal paraffins beyond n-heptane, the average value of F_{steric} presented in these tables should be used. For n-butane through n-heptane, F_{steric} is calculated for each molecule using the formulas in Table VI and using Table VI of paper I.

The thermodynamic properties of n-butane, n-pentane, n-hexane and n-heptane are presented in Tables X, XI, XII and XIII, respectively. In Table XIV the CH$_2$ increments of these thermodynamic properties are given. The thermody-

TABLE X

THERMODYNAMIC PROPERTIES OF NORMAL BUTANE

T, °K.	$-(F^\circ - H_0^\circ/T)$	$(H^\circ - H_0^\circ)/T$	S°	C_p°
298.16	58.54	15.58	74.12	23.29
300	58.65	15.63	74.27	23.40
400	63.51	18.35	81.86	29.60
500	67.91	21.19	89.10	35.34
600	72.01	23.96	95.97	40.30
700	75.91	26.60	102.50	44.55
800	79.63	29.08	108.71	48.23
900	83.18	31.39	114.57	51.44
1000	86.60	33.54	120.14	54.22
1100	89.90	35.53	125.43	56.64
1200	93.08	37.39	130.47	58.74
1300	96.14	39.11	135.25	60.58
1400	99.09	40.71	139.80	62.17
1500	101.95	42.18	144.13	63.57

TABLE XI

THERMODYNAMIC PROPERTIES OF NORMAL PENTANE

T, °K.	$-(F^\circ - H_0^\circ/T)$	$(H^\circ - H_0^\circ)/T$	S°	C_p°
298.16	64.52	18.88	83.40	28.73
300	64.65	18.94	83.58	28.87
400	70.57	22.38	92.95	36.53
500	75.94	25.94	101.88	43.58
600	80.96	29.38	110.34	49.64
700	85.74	32.64	118.38	54.83
800	90.31	35.71	126.02	59.30
900	94.67	38.55	133.23	63.18
1000	98.87	41.19	140.06	66.55
1100	102.92	43.63	146.56	69.48
1200	106.83	45.91	152.74	72.02
1300	110.58	48.01	158.60	74.24
1400	114.21	49.96	164.17	76.16
1500	117.72	51.75	169.47	77.83

TABLE XII

THERMODYNAMIC PROPERTIES OF NORMAL HEXANE

T, °K.	$-(+F^\circ - H_0^\circ/T)$	$(H^\circ - H_0^\circ)/T$	S°	C_p°
298.16	70.62	22.21	92.83	34.20
300	70.77	22.29	93.06	34.37
400	77.75	26.45	104.20	43.47
500	84.11	30.72	114.82	51.83
600	90.06	34.82	124.88	58.99
700	95.73	38.71	134.43	65.10
800	101.14	42.35	143.50	70.36
900	106.32	45.73	152.05	74.93
1000	111.31	48.85	160.16	78.89
1100	116.10	51.75	167.85	82.32
1200	120.74	54.44	175.18	85.30
1300	125.19	56.92	182.12	87.89
1400	129.49	59.22	188.71	90.14
1500	133.64	61.34	194.98	92.10

TABLE XIII

THERMODYNAMIC PROPERTIES OF NORMAL HEPTANE

T, °K.	$-(+F^\circ - H_0^\circ/T)$	$(H^\circ - H_0^\circ)/T$	S°	C_p°
298.16	76.80	25.54	102.34	39.67
300	76.97	25.63	102.60	39.86
400	84.91	30.51	115.42	50.42
500	92.25	35.49	127.74	60.07
600	99.13	40.26	139.39	68.33
700	105.68	44.77	150.45	75.38
800	111.95	49.00	160.95	81.43
900	117.93	52.91	170.84	86.68
1000	123.70	56.52	180.22	91.22
1100	129.25	59.86	189.11	95.16
1200	134.62	62.97	197.59	98.57
1300	139.76	65.83	205.59	101.55
1400	144.74	68.48	213.22	104.12
1500	149.54	70.92	220.46	106.37

namic properties for normal paraffins with more than seven carbons may be obtained by adding the correct number of CH_2 increments to the values of the properties for heptane.

Acknowledgments.—We wish to express our appreciation to the American Petroleum Institute Research Project 44 for support of this research. We are very grateful to Dr. K. S. Pitzer for many helpful suggestions during the course of this research.

TABLE XIV

VALUES OF THE CH_2 INCREMENT FOR NORMAL PARAFFINS $N \geq 7$

T, °K.	$-(F^\circ - H_0^\circ/T)$	$(H^\circ + H_0^\circ)/T$	S°	C_p°
298.16	5.979	3.330	9.309	5.466
300	5.999	3.344	9.343	7.695
400	7.061	4.063	11.123	6.941
500	8.043	4.774	12.817	8.246
600	8.970	5.439	14.409	9.342
700	9.856	6.062	15.918	10.276
800	10.705	6.643	17.348	11.065
900	11.516	7.176	18.692	11.746
1000	12.299	7.663	19.963	12.333
1100	13.053	8.112	21.165	12.838
1200	13.781	8.528	22.309	13.276
1300	14.477	8.908	23.386	13.657
1400	15.050	9.258	24.409	13,983
1500	15.798	9.582	25.381	14.269

Appendix I

Assignment of Characteristic CH_2 Frequencies.—The work of Simanouti and Mizushima on the Raman spectra of long chain hydrocarbons[16] shows that only a very few Raman lines in n-butane persist through n-hexadecane. It is reasonable to assign most, if not all, these persisting lines to motions of the CH_2 group on the assumption that the relative intensities of CH_3 lines should decrease with respect to those of the CH_2 lines. This assumption is substantiated in part by the gradual disappearance in the longer chain hydrocarbons of some of the bands of n-butane (*e.g.*, the lines at 2950 and 2896 cm.$^{-1}$ in the Raman spectrum and the band at 1340 cm.$^{-1}$ in the infrared spectrum). Also, n-hexadecane is probably long enough that no effects due to the odd–even change in selection rules for shorter chains are expected. Therefore, the Raman lines in n-hexadecane from the data of Simanouti and Mizushima[16] were taken to be the same as the Raman-active CH_2 frequencies of the infinite chain. The infrared active CH_2 frequencies of the infinite chain are taken from the infrared active frequencies of polythene[23] (which do coincide with those of liquid n-hexadecane). It is to be noted that liquid n-hexadecane contains a considerable fraction of non-planar molecular configurations. Since polythene is probably in the planar form, it is gratifying that no large spectral differences are observed between the spectrum of solid polythene and liquid n-hexadecane.

Except for the present work, all assignments of the "C–C stretch" modes given in Table II were made before the work of McMurry and co-workers on deuteropropane cast doubt on the conventional assignments of these motions. These workers suggest that these modes interact strongly with other low-frequency rocking motions of the molecule. The presence of the two Raman lines at 890 and 1060 cm.$^{-1}$ which persist in the spectrum of hexadecane suggests that this interaction is the same for the series of molecules from n-hexane through n-hexadecane. Thus one "C–C stretch" is assigned at 890 cm.$^{-1}$ and the other is assigned at 1060 cm.$^{-1}$.

The assignment of the line observed near 1135 cm.$^{-1}$ in the Raman spectra of all normal paraffins presents a dilemma. Depolarization measurements in the liquid are available for two homologs, n-hexane and n-heptane; the measurements were made by Herz, Kahovec and Wagner,[24] and later by Cleveland and Porcelli.[11] The depolarization factors observed by the two groups were 0.57 and 0.46 for n-hexane, and 0.56 and 0.54 for n-heptane, clearly indicating a totally symmetric vibration. In view of the possibility of non-planar forms, there are several possible explanations of these measurements. For the planar infinite CH_2 chain there are only three A_{1g} vibrations, one of which is a C–H stretch near 3000 cm.$^{-1}$, and the other two are composed of contributions from the C–C stretch and the CH_2 symmetric deformation. It is expected that the C–C stretch

---

[23] H. W. Thompson and P. Torkington, *Proc. Roy. Soc.* (*London*), **A184**, 3 (1945).

[24] E. Herz, L. Kahovec and J. Wagner, *Monatsh.*, **76**, 100 (1946).

will dominate one of these motions and that it will be lower in frequency than in ethane (*i.e.*, 993 cm.$^{-1}$). The remaining vibration is expected to be characteristic of the CH_2 group, and the totally symmetric CH_2 deformations of several molecules are found near 1450 cm.$^{-1}$. To assign the 1135 cm.$^{-1}$ line to the A_{1g} class requires a choice between two undesirable alternatives: to omit the polarized and persisting line at 890 cm.$^{-1}$ and assign the 1135 cm.$^{-1}$ line as the "C–C stretch," or to omit the persistent (but not highly polarized) line at 1470 cm.$^{-1}$ and assign 1135 cm.$^{-1}$ as the "CH_2 deformation." Simanouti and Mizushima select the first alternative which merely shifts the difficulty to the assignment of the 890 cm.$^{-1}$ line and adds the problem of justification of an assignment which departs from predictions made from simpler molecules. The other alternative appears equally undesirable in view of conventional assignments.

If this line arises from a planar form, a possible explanation for the polarization properties of the 1135 cm.$^{-1}$ line in *n*-hexane and *n*-heptane is that two vibrations are coincident at this frequency, one a totally symmetric CH_3 motion which causes the line to be polarized in the lower members of the series and the other a B_{2g} CH_2 motion which accounts for the persistence of this line in the Raman spectra of normal paraffins through hexadecane. Further polarization data are needed in the Raman spectra of higher normal paraffins or of polythene to check this assignment, since any CH_3 contributions should become relatively less intense. Another explanation for the polarization properties of this line which suggests itself is that the CH_3 frequencies are still quite intense in *n*-hexadecane, and that either the 890 or the 1135 cm.$^{-1}$ line is a line due to a motion of the CH_3 group. However, on the basis of existing data it seems that the 1135 cm.$^{-1}$ line should be assigned to a B_{2g} CH_2 motion, and the 890 cm.$^{-1}$ line is assigned to an A_{1g} CH_2 motion, in agreement with Barrow.

There has been some criticism[13] of the choice of 1375 cm.$^{-1}$ as a CH_2 fundamental. This band is one of the most intense in the infrared spectrum of *n*-hexadecane[25] and the ratio of the intensity of the 1375 cm.$^{-1}$ band to that of the 1470 cm.$^{-1}$ band in *n*-hexadecane is roughly the same as the ratio in *n*-hexane. If this band were due to a CH_3 deformation entirely, as claimed by Brown, Sheppard and Simpson, it seems that the relative intensity should drop off between *n*-hexane and *n*-hexadecane. The polarized infrared spectrum of polythene[26] is consistent with the assignment of this band as a "CH_2 wag," with the dipole moment change parallel to the chain. In polythene itself this band is very much more intense than any absorption near 1310 cm.$^{-1}$ which Brown, Sheppard and Simpson assign to the "CH_2 wag." It seems likely that the assignment of the 1375 cm.$^{-1}$ band as a B_{1u} fundamental is correct. (See Simanouti[16b] for further discussion in favor of this assignment.)

Since the line at 1296 cm.$^{-1}$ remains as one of the stronger Raman lines in the spectrum of *n*-hexadecane and falls close to the value calculated for the A_{2g} "CH_2 twist," it is so assigned in preference to the earlier assignments of unobserved frequencies.

The assignment of the A_{2u} "CH_2 twist" at 1241 cm.$^{-1}$ was selected to fit the normal coördinate analysis, since this frequency should be inactive. This choice is consistent with the assignment of the analogous A_{2g} motion at 1296 cm.$^{-1}$.

The assignment of the B_{1g} "CH_2 wag" at 1440 cm.$^{-1}$ was made on the basis of the normal coördinate analysis, as discussed above.

The several assignments agree in the selection of the remaining frequencies. Without reference to classes, our assignment differs from that of Barrow only by the replacement of a frequency at 1242 cm.$^{-1}$ by one at 1440 cm.$^{-1}$.

The present assignment seems to be consistent with all the data available at present, except for the polarization of the Raman line at 1135 cm.$^{-1}$. It is possible that the assignment of this line may be changed in the future, when more experimental data are available. In spite of this possibility and the uncertainty in the assignment of the "C–C stretch" fundamentals, this assignment seems to be a satisfactory basis for thermodynamic calculations. The assignment includes every Raman line in the spectrum of *n*-hexadecane except for two C–H stretching frequencies and one line which is approaching zero frequency as chain length increases. It also includes every band in the infrared spectrum of polythene except for one branch of the unexplained doublet at 732 cm.$^{-1}$.

Appendix II

The Effective CH_2 Mass.—Considering the mass of the CH_2 group to be concentrated at a point, then for a normal paraffin with n of these points, the degrees of freedom may be divided among 3 translations, 3 rotations, $n - 1$ stretching vibrations, and $2n - 5$ bending vibrations and internal rotations. Assigning an effective CH_2 mass to each of these degrees of freedom, the complete expression defining m, the average effective CH_2 mass, should be

$$m^{3n} = (m_{tr})^3(m_{rot})^3(m_{st})^{n-1}(m_{bend})^{2n-5}$$

The translational mass, m_{tr}, is 14.0. The rotational mass, m_{rot}, of the CH_2 group in a long chain has been evaluated by equating the exact product of inertia, $(I_1I_2I_3)$ to this product calculated using point masses at the carbons, and solving for the value of the mass needed to make these products equal. This was done for the series: $C_{2n}H_{4n+2}$; for n from 2 to 6. For long chains the value of m_{rot} approaches 18.5. The value of the stretching vibrational mass, m_{st}, is estimated to be close to that of a pure C–C stretching mode, 14.0. The value of the bending vibrational mass, m_{bend}, is expected to be higher because of the large contribution of the hydrogen atoms to the moments of inertia involved in the bending motions. Since the bending modes may be considered to be local rotations with moments of inertia close to those of the group CH_2–CH_2, two CH_2 units of the chain, m_{bend} may be approximated by equating the exact product of inertia $(I_1I_2I_3)$ for CH_2–CH_2 to that product calculated using point masses at the carbons. In this manner, m_{bend} is estimated to be 21.5. Thus

$$m^{3n} = (14.0)^3\,(18.5)^3\,(14.0)^{n-1}\,(21.5)^{2n-5}$$

and for large n

$$m = 18.6$$

While the argument given above is certainly not conclusive, and the exact agreement with the earlier choice is fortuitous, the argument does justify the empirical choice of $m = 18.6$ as a reasonable value.

BERKELEY, CALIF.

---

[25] Catalog of Infrared Spectral Data, issued by the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

[26] A. Elliott, E. J. Ambrose and R. B. Temple, *J. Chem. Phys.*, **16**, 877 (1948).