

THE ENTROPIES AND RELATED PROPERTIES OF BRANCHED PARAFFIN HYDROCARBONS^{1,2}

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The status of the data on the entropies of branched paraffin hydrocarbons is reviewed. Experimental values come largely from low-temperature heat-capacity measurements calculated on the basis of the Third Law of Thermodynamics.

Entropy values calculated from statistical formulas and from semistatistical-semiempirical formulas are compared with experimental values. Revisions are made in the statistical formulas in view of recent spectral and other data.

For the branched-chain butane, pentanes, and hexanes, the revised statistical formulas are used to calculate values of the entropy, heat content, free-energy function, and heat capacity of the ideal gases over a range of temperatures.

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I. INTRODUCTION

The thermodynamic properties of paraffin hydrocarbons are of considerable importance for a variety of reasons. The isomers with branched chains, which received less attention in early work, have recently become of greater interest for practical fuels and have received corresponding attention in the laboratory. The entropy is a quantity of particular interest for chemical equilibrium calculations, and it has been obtained experimentally for certain isomers by low-temperature specific-heat measurements and the Third Law of Thermodynamics. In view of the multitude of branched paraffin isomers of higher molecular weight, simple methods of calculation, even though approximate, are very desirable. For isobutane and neopentane (tri- and tetramethylmethanes) relatively exact statistical mechanical calculations can be made. Revised calculations of this type are given in Section III. The methods for these statistical

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calculations have been discussed fully elsewhere (21, 28) and will not be considered in detail here.

II. NORMAL PARAFFINS

Since the straight-chain or normal paraffins are frequently used as a basis of comparison for branched isomers, the status of the data for them will be mentioned. For methane, ethane, and propane relatively detailed statistical calculations have been made and compared with experimental entropies. For butane, pentane, hexane, and heptane, more approximate statistical methods are used which, however, give reasonably good agreement with the experimental values. Table 1 gives the comparison of entropy values. A more detailed discussion of these calculations and tables of related properties may be found in a recent paper (20).

TABLE 1
Entropies of normal paraffins

PARAFFIN	T	S ⁰		REFERENCES FOR EXPERIMENT
		Calculated (reference 20)	Experimental	
	°K.			
Methane.....	298.16	44.50	44.3 ± 0.3	(11)
Ethane.....	298.16	(54.85)	54.85 ± 0.15	(29)
Propane.....	231.09	(60.46)	60.46 ± 0.1	(12)
<i>n</i> -Butane.....	272.66	(72.06)	72.05 ± 0.2	(6)
<i>n</i> -Pentane.....	298.16	83.27	83.13 ± 0.2	(15)
<i>n</i> -Hexane.....	298.16	92.45	92.87 ± 0.3	(9)
<i>n</i> -Heptane.....	298.16	101.64	102.32	(3, 18)
	371.5	111.5	111.77 ± 0.3	(18)

III. ISOBUTANE AND NEOPENTANE

These two molecules, which may also be described as trimethylmethane and tetramethylmethane, respectively, have rigid carbon skeletons and highly symmetrical structures. Consequently, relatively detailed analyses are possible. In each case the experimental entropy is available from the work of Aston and collaborators (5, 7), and several rough vibrational assignments have been proposed. Since further spectral studies have been made recently, it is now possible to make much better vibrational assignments. These revised calculations are discussed in the following paragraphs.

Table 2 shows, for isobutane, all the Raman lines observed in the important range below 1500 cm.⁻¹ together with the infrared bands. The polarization of Raman lines is also given.

In the degenerate symmetry class *E*, one very low skeletal bending band is expected and three in the range 800 to 1250 cm.⁻¹ which may be classified as one carbon-carbon bond stretching and two methyl group wagging motions. The selection of 371, 921, 965, and 1180 cm.⁻¹ is definite, in view of the observations.

The 921 infrared band shows clearly a contour characteristic of this class, while the others are fixed by the Raman polarization data. The higher frequencies in this class include a wagging motion of the C—H group expected near 1300 cm^{-1} on the basis of results for the series CHX_3 . Also, there will be the usual CH_3 symmetrical bending at about 1375 cm^{-1} and unsymmetrical bending (in this case two modes) near 1460 cm^{-1} .

TABLE 2
Spectra of isobutane

RAMAN (4, 15)	INFRARED (1)	ASSIGNMENT
371 (4b) <i>D</i>		<i>E</i>
437 (2) <i>P</i>	{ 422 m. 437	A_1
795 (10) <i>P</i>	{ 784 799 s. 816	A_1
	{ 913 930 v.s.	<i>E</i>
965 (4b) <i>D</i>		<i>E</i>
1098 (1b)	1095 w.	A_1
1172 (4sb) <i>D</i>	1180 v.s.	<i>E</i>
	1210 1225 w. 1240	(437 + 795), (A_1)
1322 to (3b) <i>D</i> 1355	1335 s.	<i>E</i>
	1377 v.s.	$E + A_1$
1452 (7b) <i>D</i>	1475 v.s.	{ <i>E</i> $E + A_1$

The totally symmetric class A_1 (polarized in the Raman) includes a low, skeletal bending frequency, clearly 437 cm^{-1} , and a carbon-carbon stretching motion, 799 cm^{-1} . In addition, there will be one methyl wagging motion somewhere below 1200 cm^{-1} . The 1095 band seems by far the most probable selection, although the band contour is doubtful. The Raman data independently favor this selection. In addition, there must be lines near 1375 and 1460, although these are not separated.

The three vibrations in the remaining symmetry class, A_2 , are forbidden in both the Raman and infrared spectra, so they must be assigned on other bases. Fortunately, all modes but one can be readily and reliably estimated. The final uncertain mode in this class is the methyl wagging motion. It would be expected to be in the general range 900–1200 cm^{-1} . The top value, 1200 cm^{-1} , gives best agreement with the specific-heat data for the gas (8) and is adopted for that reason.

Table 3 shows the complete assignment of the vibration frequencies of isobutane.

The moments of inertia were calculated from the dimensions: C—C, 1.54 Å.; C—H, 1.09 Å.; tetrahedral angles. The product of the principal moments is then 2113×10^{-117} (g.cm.^2)³. By comparison with the Third Law entropy at the boiling point (5) the barrier to internal rotation was found to be 3620 cal. per mole.

TABLE 3
Vibration frequencies of isobutane

	SKEL- ETAL	C—C STRETCHING	CH ₃ WAG- GING	CH ₃ SYM- MET- RICAL δ	CH ₃ UNSYM- MET- RICAL δ	CH δ	CH ₃ SYM- METRICAL STRETCHING	CH ₃ UNSYM- METRICAL STRETCHING	CH STRETCHING	INTERNAL ROTATION	ACTIVITY
A_1	437	799	1098	1377	1460		2950	2950	2950		$IR, R(p)$
A_2			(1200)		1460			2950		?	i.a.
E	371	921	965	1377	1460	1335	2950	2950		?	$IR, R(dp)$
				1172		1460			2950		

Table 4 shows, for neopentane, the Raman lines and the important infrared bands, together with their assignments. Table 5 shows the complete vibrational assignment of neopentane.

The two Raman lines at 335 cm^{-1} and 414 cm^{-1} are undoubtedly due to the E and T_2 skeletal deformation frequencies, respectively. The A_1 and T_2 C—C stretching modes should be well separated, the former below 1000 cm^{-1} and the latter above, because of the difference in reduced mass involved in the motions. In the A_1 mode, the central carbon does not move and so is effectively an infinite mass. In the T_2 mode, however, a considerable displacement of this carbon atom is to be expected. The frequencies 733 cm^{-1} and 1250 cm^{-1} have been assigned, therefore, to the A_1 and T_2 C—C stretching modes.

The infrared band at 925 cm^{-1} is probably due to T_2 methyl wagging. The other two methyl wagging frequencies do not appear in the spectrum. The one with the symmetry T_1 is forbidden in both infrared and Raman spectra, while the other with the symmetry E may appear in the Raman spectrum only. The values 950 and 1150 cm^{-1} have been estimated for T_1 and E , respectively.

The infrared band at 1370 cm^{-1} has been selected for T_2 symmetric CH₃ bending and 1360 cm^{-1} estimated for the same motion with the symmetry A_1 .

The value 1470 cm.^{-1} has been assigned to E , T_2 , and T_1 unsymmetrical methyl bending.

TABLE 4
Spectra of neopentane

RAMAN (24, 25)	INFRARED (2)	ASSIGNMENT
335 (10)		E
414 (3)		T_2
733 (20)		A_1 2×414
	822 } (0) 835 }	
	917 } 926 } (2) 937 }	T_2
925 (15B)		
	990 (0) 1148 (0) ~ 1200 (1s)	414 + 733
1252 (20B)	1257 (9)	T_2
	1364 } 1376 } (10) 1385 }	T_2
1455 (15)	1460 } 1475 } (10) 1488 }	$E + T_2$

TABLE 5
Vibration frequencies of neopentane

	SELETEL	C-C STRETCHING	CH ₃ WAGGING	CH ₃ SYMMETRI- CAL δ	CH ₃ UNSYMMET- RICAL δ	CH STRETCHING	INTER- NAL RO- TATION	ACTIVITY
A_1		733		(1360)		2913		$R(p)$
A_2							?	i.a.
E	335		(1150)		(1470)	(2950)		$R(dp)$
T_2	414	1250	925	1370	1470	(2900, 2950)		$IR, R(dp)$
T_1			(950)		(1470)	(2950)	?	i.a.

The spectral region around 2900 cm.^{-1} is very complicated, as is usual in molecules containing several methyl groups. However, the Raman line at 2913 cm.^{-1} was chosen for the A_1 C—H stretching motion, 2950 cm.^{-1} for the motion with the symmetry E , 2900 and 2950 cm.^{-1} for T_2 , and 2950 cm.^{-1} for the inactive T_1 motion.

The four internal rotations combine to give one mode with the symmetry A_2 and one triply degenerate mode of symmetry T_1 . Both of these are inactive.

The product of the principal moments was calculated to be 6726×10^{-117} (g.cm.²)³. By comparison with the Third Law entropy (7), the barrier to internal rotation was found to be 4300 cal. per mole.

IV. ISOPENTANE AND THE BRANCHED HEXANES

These molecules have internal rotations within their carbon skeletons and are consequently more complex for theoretical treatment. However, we now have available accurate experimental entropies for all except 3-methylpentane. This last substance has never been frozen and hence has not been handled by the Third Law method. The value in table 6 is obtained from the equilibrium with 2-methylpentane (10, 14) and the heat of isomerization (23).

Two approximate methods of calculation will be considered. The first is the very simple, partly empirical formula of Pitzer and Scott (22), which is given in equation 1.

$$S = S_n + R \ln 2 + R \ln (I/\sigma_e \sigma_i) - 3.5B \quad (1)$$

S_n is the entropy of the normal isomer and $R \ln 2$ a correction for its symmetry number, I is the number of optical or other isomeric forms included in the structural isomer being considered, σ_e and σ_i are the symmetry numbers for external rotation and for the internal rotation of the carbon skeleton, respectively, and B is the number of chain branchings. The constant 3.5 cal. per degree is an empirical factor for all effects of branching not included in detail. This method will be designated the "simplified" method and is particularly appropriate for still more complex molecules. In the hexanes we are testing its accuracy.

The second method is a modification of the approximate statistical formulas for the n -paraffins (19). Its character is indicated in equation 2.

$$S = S_0 + N_1(\text{C—C stretching}) + N_2(\text{C—C bending}) + N_3(\text{internal rotation}) \\ + S_{\text{steric}} + R \ln I/\sigma_e + N_4(\text{CH}_3) + N_5(\text{CH}_2) + N_6(\text{CH}) + N_7(\text{C})$$

$$S_{\text{steric}} = R(\ln Q + T d \ln Q/dT)$$

$$Q = \sum_i e^{-E_i/RT} \quad (2)$$

With occasional exceptions all terms are functions of temperature. N_1 , N_2 , N_3 are the numbers of C—C stretching and bending motions and the number of skeletal internal rotations, respectively. $N_4 \dots N_7$ are the numbers of CH_3 , CH_2 , CH , and C groups in the molecule. In the equation for Q the quantity E_i is the steric strain energy of the molecule in a particular configuration. This has been expressed in terms of a parameter a from the n -paraffins whose value is 800 cal. per mole. This formula has been derived and explained elsewhere (19). More recently, revised sets of vibration frequencies have been recommended for the (CH_3) and (CH_2) terms (20). This will be called the "statistical" method.

Table 6 contains a comparison of experimental and calculated entropies for these molecules. The previous calculations contained certain errors in the assignment of steric energies. To be consistent with isopentane and the *n*-paraffins that for 2-methylpentane should be two positions at 0 energy, two at *a*, one at *2a*, and four at ∞ . Then 3-methylpentane should probably have two positions at 0 energy, one at *a*, four at *2a*, and two at ∞ . The latter set is still rather arbitrary but is more consistent than the previous assignment. 2,3-Dimethylbutane also involves steric positions different from those for simpler molecules and no definite assignment can be made. It clearly consists of one lowest position and two of higher energy. While the previous difference of *2a* seems somewhat more reasonable structurally, a value of *a* is needed to fit the experimental entropy closely. The revised values are shown in table 6. While

TABLE 6
The entropies of isopentane and the branched hexanes
Ideal gas state, $T = 298.16^\circ\text{K}$.

PARAFFIN	<i>S</i> SIMPLIFIED	<i>S</i> STATISTICAL	<i>S</i> EXPERIMENTAL FROM 14°K.	REFERENCE FOR EXPERIMENT
2-Methylbutane.....	81.2	81.98	82.01 ± 0.55	(27)
2-Methylpentane.....	90.3	90.65	90.89 ± 0.17	(3,9)*
3-Methylpentane.....	90.3	90.77	91.0 ± 1.0	
2,2-Dimethylbutane.....	84.6	85.7	{ 85.55 ± 0.17	(3,9)
			{ 85.72 ± 0.2	(13)
2,3-Dimethylbutane.....	85.4	87.30	87.39 ± 0.17	(3,9)

* The references (3,9) indicate the entropy of the liquid from reference 9 with vaporization data from reference 3.

these steric assignments are very unsatisfactory in that they are somewhat subjective, nevertheless the magnitude of error from this source is limited to about 1 cal. per degree.

Fortunately 2,2-dimethylbutane has only a single type of steric position, so that no uncertainty arises from that source. Equation 2 gives essentially exact agreement with the experimental value in this case. A more detailed statistical treatment has also been published for 2,2-dimethylbutane (13) in which potential barriers are adjusted to fit the entropy. Values from this source are included in Section VI.

V. BRANCHED HEPTANES AND OCTANES

In the range of paraffins heavier than the hexanes the experimental data are fragmentary. Parks and collaborators (17) have measured by the Third Law method the entropies of most of the heptanes and of a few octanes. Their experimental measurements are reliable but extend only down to 90°K., which leaves a very large extrapolation to 0°K. While this extrapolation appears to have been about correct for the normal paraffins, in the case of 2,2,4-trimethyl-

pentane it is too small by over 3 cal. per degree. Thus the entropy values based on measurements only to 90°K. (see table 7) are probably from one to four units too small and in any case subject to considerable uncertainty. For two trimethylpentanes we have accurate Third Law values (based on measurement to 14°K.).

TABLE 7
The entropies of branched heptanes and octanes
Ideal gas state, $T = 298.16^\circ\text{K}$.

	S° SIMPLIFIED (22)	S° STATISTICAL (19)	S° EXPERIMENTAL FROM 14°K. (18, 22)	S° EXPERIMENTAL FROM 90°K. (17)
<i>Heptanes:</i>				
2-Methylhexane.....	99.4	99.5		98.4
3-Methylhexane.....	100.8	101.3		
3-Ethylpentane.....	97.2	98.3		97.7
2,2-Dimethylpentane.....	93.7	93.4		90.2
2,3-Dimethylpentane.....	97.3	98.8		
2,4-Dimethylpentane.....	94.5	94.7		92.0
3,3-Dimethylpentane.....	94.5	95.4		92.2
2,2,3-Trimethylbutane.....	90.2	92.3		86.5
<i>Octanes:</i>				
2-Methylheptane.....	108.5	108.6		
3-Methylheptane.....	109.9	110.1		
4-Methylheptane.....	108.5	108.1		
3-Ethylhexane.....	108.5	109.3		
2,2-Dimethylhexane.....	102.8	102.9		
2,3-Dimethylhexane.....	106.4	105.9		
2,4-Dimethylhexane.....	106.4	106.3		
2,5-Dimethylhexane.....	103.6	104.7		
3,3-Dimethylhexane.....	105.0	104.5		
3,4-Dimethylhexane (meso).....	105.0	105.5		
3,4-Dimethylhexane (<i>dl</i>).....	105.0	104.2		
2-Methyl-3-ethylpentane.....	105.0	105.2		
3-Methyl-3-ethylpentane.....	102.8	103.3		
2,2,3-Trimethylpentane.....	100.7	101.4		
2,2,4-Trimethylpentane.....	99.3	101.4	101.15	97.95
2,3,4-Trimethylpentane.....	101.5	102.8	102.31	
2,3,3-Trimethylpentane.....	101.5	102.9		
2,2,3,3-Tetramethylbutane.....	92.3	94.1		88.6

Calculated values are available from both the "simplified" and the "statistical" formulas. The "statistical" calculations are subject to the same revisions of vibration frequencies and steric energies which were made for the hexanes. However, the changes would be well within the uncertainty which must be allowed until further experimental values are obtained. Consequently, it seems hardly worthwhile to repeat the calculations now. (For 2-methylhexane there was a small but definite error previously; this is corrected.)

TABLE 8

Heat capacity, C_p^o

Units: calories per degree mole

<i>T</i>	<i>n</i> -BUTANE	ISO-BUTANE	<i>n</i> -PENTANE	2-METHYL-BUTANE	2,2-DI-METHYL-PROPANE	<i>n</i> -HEXANE	2-METHYL-PENTANE	3-METHYL-PENTANE	2,2-DI-METHYL-BUTANE	2,3-DI-METHYL-BUTANE
^o K.										
298.16	23.61	23.14	29.30	28.83	29.07	35.06	34.46	35.14	34.25	34.64
300	23.77	23.25	29.51	28.97	29.21	35.32	34.63	35.31	34.43	34.84
400	29.80	29.77	36.91	37.05	37.55	44.04	44.0	44.6	44.2	44.3
500	33.54	35.62	43.96	44.23	45.00	52.39	52.5	52.9	53.0	52.8
600	40.42	40.62	49.88	50.28	51.21	59.38	59.6	59.9	60.4	60.0
700	44.61	44.85	54.98	55.41	56.40	65.35	65.7	65.9	66.5	65.9
800	48.23	48.89	59.37	59.80	60.78	70.51	70.8	71.0	71.7	71.1
900	51.42	51.65	63.21	63.60	64.55	75.01	75.3	75.4	75.9	75.5
1000	54.20	54.40	66.57	66.90	67.80	78.94	79.2	79.3	79.9	79.4
1100	56.60	56.81	69.46	69.80	70.62	82.32				
1200	58.72	58.89	72.01	72.29	73.04	85.30				
1300	60.55	60.71	74.22	74.47	75.15	87.89				
1400	62.15	62.29	76.14	76.37	76.99	90.12				
1500	63.51	63.67	77.76	78.01	78.60	92.02				

TABLE 9

Entropy, S^o

Units: calories per degree mole

<i>T</i>	<i>n</i> -BUTANE	ISO-BUTANE	<i>n</i> -PENTANE	2-METHYL-BUTANE	2,2-DI-METHYL-PROPANE	<i>n</i> -HEXANE	2-METHYL-PENTANE	3-METHYL-PENTANE	2,2-DI-METHYL-BUTANE	2,3-DI-METHYL-BUTANE
^o K.										
298.16	74.10	70.42	83.27	81.98	73.23	92.45	90.65	90.77	85.72	87.33
300	74.25	70.55	83.44	82.15	73.40	92.67	90.88	91.00	85.92	87.53
400	81.91	78.13	92.95	91.58	83.00	104.03	102.1	102.4	97.2	98.8
500	89.20	85.45	101.94	100.65	92.17	114.75	112.9	113.3	108.1	109.7
600	96.11	92.40	110.48	109.23	100.94	124.91	123.1	123.6	118.4	120.0
700	102.66	98.98	118.56	117.40	109.23	134.52	132.7	133.3	128.1	129.7
800	108.87	105.21	126.19	125.11	117.07	143.60	141.9	142.4	137.4	138.8
900	114.74	111.11	133.41	132.37	124.45	152.16	150.5	151.0	146.0	147.4
1000	120.31	116.69	140.26	139.24	131.41	160.29	158.6	159.2	154.3	155.6
1100	125.59	121.99	146.74	145.76	138.00	167.97				
1200	130.60	127.03	152.89	151.95	144.26	175.27				
1300	135.37	131.82	158.74	157.82	150.20	182.20				
1400	139.91	136.37	164.31	163.41	155.84	188.79				
1500	144.22	140.67	169.60	168.67	161.19	195.03				

It may be noted from tables 6 and 7 that the statistical method gives values within a few tenths of a calorie per degree of all reliable experimental values (from 14°K.). However, in other cases the uncertainty should still be taken as 1½ cal. per degree. We believe that this is considerably less than the uncertainty

TABLE 10
The heat-content function, $(H^0 - H_0^0)/T$
 Units: calories per degree mole

<i>T</i>	#-BUTANE	ISOBUTANE	#-PENTANE	2-METHYL-BUTANE	2,2-DI-METHYL-PROPANE	#-HEXANE	2-METHYL-PENTANE	3-METHYL-PENTANE	2,2-DI-METHYL-BUTANE	2,3-DI-METHYL-BUTANE
°K.										
298.16	15.58	14.34	19.01	17.24	16.87	22.44	20.45	20.62	19.91	20.36
300	15.63	14.39	19.07	17.31	16.94	22.52	20.54	20.71	19.99	20.45
400	18.42	17.41	22.62	21.23	21.07	26.83	25.2	25.5	24.9	25.2
500	21.27	20.50	26.18	25.13	25.13	31.10	29.9	30.2	29.6	29.9
600	24.06	23.45	29.64	28.83	28.98	35.23	34.2	34.6	34.2	34.4
700	26.71	26.20	32.90	32.27	32.53	39.11	39.3	38.6	38.3	38.4
800	29.18	28.76	35.93	35.44	35.80	42.71	42.0	42.4	42.2	42.2
900	31.46	31.13	38.73	38.36	38.78	46.02	45.5	45.8	45.6	45.7
1000	33.58	33.31	41.34	41.03	41.51	49.11	48.7	48.9	48.9	48.8
1100	35.56	35.34	43.76	43.52	44.02	51.97				
1200	37.40	37.23	46.01	45.83	46.34	54.63				
1300	39.12	38.96	48.10	47.94	48.49	57.10				
1400	40.71	40.56	50.04	49.90	50.47	59.39				
1500	42.18	42.03	51.84	51.69	52.28	61.50				
ΔH_0^0 (calories per mole)	-23,332	-24,602	-27,270	-28,660	-31,300	-30,980	-32,080	-31,490	-34,610	-32,880

TABLE 11
The free-energy function, $-(F^0 - H_0^0)/T$
 Units: calories per degree mole

<i>T</i>	#-BUTANE	ISOBUTANE	#-PENTANE	2-METHYL-BUTANE	2,2-DI-METHYL-PROPANE	#-HEXANE	2-METHYL-PENTANE	3-METHYL-PENTANE	2,2-DI-METHYL-BUTANE	2,3-DI-METHYL-BUTANE
^o K.										
298.16	58.52	56.08	64.26	64.74	56.36	70.01	70.20	70.15	65.81	66.97
300	58.62	56.16	64.37	64.84	56.46	70.15	70.34	70.29	65.93	67.08
400	63.49	60.72	70.33	70.35	61.93	77.20	76.9	76.9	72.4	73.6
500	67.93	64.95	75.76	75.52	67.04	83.65	83.0	83.1	78.4	79.8
600	72.05	68.95	80.84	80.40	71.96	89.68	88.8	89.0	84.2	85.7
700	75.95	72.78	85.66	85.13	76.70	95.41	94.4	94.6	89.8	91.2
800	79.69	76.45	90.26	89.67	81.27	100.89	99.8	100.1	95.2	96.6
900	83.28	79.98	94.68	94.01	85.67	106.14	105.0	105.3	100.4	101.8
1000	86.73	83.38	98.92	98.21	89.90	111.18	110.0	110.3	105.4	106.8
1100	90.03	86.65	102.98	102.24	93.98	116.00	114.7	115.1	110.2	111.6
1200	93.20	89.80	106.88	106.12	97.92	120.64	119.3	119.7	114.8	116.0
1300	96.25	92.86	110.64	109.88	101.71	125.10	123.8	124.2	119.3	120.6
1400	99.20	95.81	114.27	113.51	105.37	129.40	129.1	128.5	123.6	125.0
1500	102.04	98.64	117.76	116.98	108.91	133.53	132.2	132.6	127.8	129.1
ΔH_f (calories per mole).....	-23,332	-24,602	-27,270	-28,660	-31,300	-30,980	-32,080	-31,490	-34,610	-32,880

in the extrapolation of the heat capacity below 90°K.; hence, the statistical values are recommended as more reliable than values based on experimental measurements from 90°K. Values from the simplified formula are naturally less accurate but are within 2 cal. per degree. This formula should give useful estimates for nonanes, decanes, etc.

VI. CALCULATED THERMODYNAMIC FUNCTIONS

In Sections III and IV, previous statistical entropy calculations for the branched butane, pentanes, and hexanes have been revised to take account of recent data. Several thermodynamic functions may be calculated by these same statistical methods. Values of these functions for a range of temperatures are presented in tables 8 to 11. Also included are values for the *n*-paraffins for comparison (20). As discussed above, the detailed statistical method was used for isobutane, neopentane, and neohexane (2,2-dimethylbutane). The approximate statistical method of equation 2 was used for isopentane and the remaining branched hexanes.

Values of ΔH_f° calculated from heat of formation data (23) are included for convenience in calculations.

VII. REFERENCES

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