servation, the entropy difference between the PuO_2^+ and PuO_2^{+2} ions in molar perchloric acid at 25° has been found to be 9.5 e.u. in the present work. An interesting comparison of entropy changes for similar reactions of neptunium and plutonium in 1 M perchloric acid at 25° can be made. For the reactions $X^{+3} + H^+ \rightleftarrows X^{+4} + \frac{1}{2}H_2$ and $XO^{+2} + H^+ \rightleftarrows XO_2^{+2} + \frac{1}{2}H_2$, Cohen and Hindman[11] found −31.2 and 6.4 e.u. for neptunium ions, whereas for plutonium ions the values of the entropy differences have been found to be −30.2 and 6.0 e.u., respectively. However, for the reaction $X^{+4} + 2H_2O \rightleftarrows XO_2^+ + 3H^+ + \frac{1}{2}H_2$, the value of 62.3 e.u. has been reported[11] for neptunium and a value of 50.1 e.u. has been computed from the plutonium (III)–(IV) and (V)–(VI) couples together with the Pu(IV) disproportionation results.[1] It appears that the difference between these two ΔS values reflects a measure of the difference in the structure of the neptunium and the plutonium ions.

Complexing of PuO_2^{+2} by Chloride Ion.—From alterations in the absorption spectrum of plutonyl ion as the solvent is changed from perchloric to hydrochloric acid it has been concluded that a chloride complex is formed.[12] It has been observed that a color change visible to the unaided eye occurs upon the addition of hydrochloric acid to a perchloric acid solution of plutonyl ion. A solution of plutonyl ion was prepared by the ozonization of a perchloric acid solution of Pu^{+3}. At the completion of the oxidation period, the dissolved ozone was removed by bubbling helium through the solution,

then a weighed quantity of standardized hydrochloric acid was added to make the final concentration 0.50 M hydrochloric–0.50 M perchloric acid. The plutonyl ion was titrated with P^{+3} in acid of the same composition. The Pu^{+3}–Pu^{+4} formal potential in 0.50 M hydrochloric–0.50 M perchloric acid, −0.9750 volt, was used in the computation of the ratio, $\Sigma(Pu^{IV})/(Pu^{+3})$, thus the assumption that the $\Sigma(Pu^{IV}) = (PuO_2^+)$ is not invalidated by the chloride complexing of Pu^{+4}. A value of −0.9124 ± 0.0001 volt was obtained for the PuO_2^+–PuO_2^{+2} formal potential in this solvent at 25°. The more positive value of this couple in 0.50 M hydrochloric–0.50 M perchloric acid appears to indicate the formation of a plutonyl chloride complex. Since formal potential measurements yield only *differences* in the stabilities of the complex ions, it is necessary to use some other means to obtain the degrees of complexing of one of the ions directly.

Potentials of Plutonium Couples.—In Table IV are given the formal potentials of the plutonium couples in molar perchloric acid at 25.00°. The Pu^{+3}–Pu^{+4} and the PuO_2^+–PuO_2^{+2} potentials have been measured directly. The remainder of the potentials have been calculated from these values

TABLE IV

FORMAL POTENTIALS OF PLUTONIUM COUPLES AT 25°

(1)   1 M HClO₄ $Pu^{+3} \xrightarrow{\hspace{0.3cm}-0.9819\hspace{0.3cm}} Pu^{+4} \xrightarrow{\hspace{0.3cm}-1.1721\hspace{0.3cm}} PuO_2^+ \xrightarrow{\hspace{0.3cm}-0.9133\hspace{0.3cm}} PuO_2^{+2}$

         −1.0433

         −1.0228

and the Pu^{+4} disproportionation equilibrium quotient.

LOS ALAMOS, NEW MEXICO

(12) R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, "The Transuranium Elements," Natl. Nuclear Energy Ser., IV, 14-B McGraw–Hill Book Co., Inc., New York, N. Y., 1949, p. 559.

Thermodynamic Functions of Alkylnaphthalenes from 298 to 1500°K.[1]

BY DOLPHUS E. MILLIGAN, EDWIN D. BECKER AND KENNETH S. PITZER

The values of the heat content function, free energy function, heat capacity and entropy of the dimethylnaphthalenes (except 1,8-dimethylnaphthalene), of the 1-n-alkylnaphthalenes and 2-n-alkylnaphthalenes and of three methylethylnaphthalenes have been calculated by the method of increments. The functions are tabulated from 298 to 1500°K. The barriers to internal rotation of the methyl group in 1- and 2-methylnaphthalenes have been determined to be approximately 3.8 and 2.3 kcal./mole, respectively. The entropy uncertainty of approximately 0.5 cal./deg. mole yields ranges 2.5–5.6 and 0.9–3.5 kcal./mole for the potential barriers.

Values of the thermodynamic functions of naphthalene in the ideal gas state have recently been calculated on the basis of a complete vibrational assignment for this molecule.[2] These functions, together with the previously published functions of paraffins[3,5] and alkylbenzenes,[4,5] furnish the basis

for a calculation of the thermodynamic properties of various alkylnaphthalenes.

We have used the method of increments[6] to calculate values of the heat content function, free energy function, heat capacity and entropy of all dimethylnaphthalenes (except 1,8-dimethylnaphthalene), all 1-n-alkylnaphthalenes and 2-n-alkylnaphthalenes and 2-methyl-3-ethyl-, 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene. In certain cases the potential barriers to internal rotation are ex-

(1) This research was a part of the program of Research Project 50 of the American Petroleum Institute.

(2) A. L. McClellan and G. C. Pimentel, J. Chem. Phys., 23, 245 (1955).

(3) K. S. Pitzer, Ind. Eng. Chem., 36, 829 (1944).

(4) Taylor, Wagman, Williams, Pitzer and Rossini, J. Research Natl. Bur. Standards, 37, 95 (1946).

(5) "Selected Values of Physical and Thermodynamic Properties of

Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

(6) For a discussion of this method see, for example, reference 5.

pected to differ from the values found for the benzene series. Entropy values for 1- and 2-methylnaphthalenes[7] are used to evaluate potential barriers for the naphthalene series.

1- and 2-Methylnaphthalenes.—Experimental thermodynamic data are available for only these two alkylnaphthalenes. In each case we have the entropy of the liquid[7] at temperatures up to 360°K. and precise vapor pressure measurements[8] in the range 410–520°K. This leaves a gap of about 50° across which an interpolation must be made if we are to obtain thermodynamic functions for these substances in the gaseous state. We used several methods based upon independent assumptions for this interpolation but will describe only the simplest here.[9] The others yielded concordant results.

In the absence of other information as to the functional form of the liquid heat capacity–temperature relation, straight lines with the equations

$$C_p = 22.52 + 0.1044T \text{ (1-methylnaphthalene)} \quad (1)$$
$$C_p = 23.66 + 0.0997T \text{ (2-methylnaphthalene)} \quad (2)$$

were fitted to the experimental points between the melting point and 360°K., and these lines were used for extrapolation of the liquid heat capacity to higher temperatures and calculation of the entropies of the liquids at temperatures above 360°K. These heat capacity extrapolations were checked in a manner to be described below.

The values of the entropy of vaporization at several temperatures were calculated from the vapor pressure equations of Camin and Rossini[8] on the assumption that the vapor volumes follow the Berthelot equation of state with critical constants $T_c = 773°K.$ and $P_c = 38$ atm. These values were estimated from the known values for naphthalene[10] ($T_c = 753°K.$, $P_c = 41$ atm.) by the use of the approximate increment for the addition of a CH_2 group found for the paraffins and alkylbenzenes. The correction of the entropy to the ideal gas state was made with the aid of the Berthelot equation and the entropy of compression was then added to yield the values shown in Tables I and II for the entropies of the ideal gases at the standard pressure of one atmosphere.

TABLE I

CALCULATION OF THE BARRIER TO INTERNAL ROTATION IN 1-METHYLNAPHTHALENE

Temp., °K.	425	440	450	470	500
S_T(liq)	82.08	84.43	85.97	89.05	93.57
ΔS_v (at T)	29.38	27.88	26.93	25.20	22.85
S(ideal gas) − S(real gas)	0.02	0.03	0.04	0.06	0.11
S(1 atm.) − S(v.p.)	−5.08	−4.08	−3.46	−2.31	−0.80
S_T°	106.40	108.26	109.48	112.00	115.73
S_T° (freely rotating methylnaphthalene)	107.60	109.42	110.65	113.09	116.76
$(S_f - S)_T$	1.20	1.16	1.17	1.09	1.03
V_0/RT	4.39	4.26	4.27	4.01	3.81
V_0(cal./mole)	3710	3720	3820	3740	3790

(7) Private communication from Dr. G. Waddington, U. S. Bureau of Mines, Bartlesville, Oklahoma.

(8) D. L. Camin and F. D. Rossini, *J. Phys. Chem.*, **59**, 1173 (1955).

(9) Some other methods are discussed in an American Petroleum Institute Project 50, Report of September 26, 1955. Copies may be obtained from the authors.

(10) E. Schroer, *Z. physik. Chem.*, **B49**, 271 (1941).

TABLE II

CALCULATION OF THE BARRIER TO INTERNAL ROTATION IN 2-METHYLNAPHTHALENE

Temp., °K.	425	440	450	470	500
S_T(liq)	82.83	85.15	86.68	89.69	94.15
ΔS_v(at T)	28.99	27.47	26.61	24.90	22.57
S(ideal gas) − S(real gas)	0.02	0.03	0.04	0.07	0.12
S(1 atm.) − S(v.p.)	−4.88	−3.89	−3.28	−2.14	−0.64
S_T°	106.96	108.76	110.05	112.52	116.20
S_T° (freely rotating methylnaphthalene)	107.60	109.42	110.65	113.09	116.76
$(S_f - S)_T$	0.64	0.66	0.60	0.57	0.56
V_0/RT	2.70	2.74	2.58	2.49	2.48
V_0(cal./mole)	2280	2395	2306	2325	2463

The values shown in Tables I and II for a freely rotating methylnaphthalene were obtained by the following equation

$$S = S(\text{naphthalene}) + S(\text{toluene}) - S(\text{benzene})$$
$$- R \ln 3/2 + (S_f - S)(750 \text{ cal. barrier}) \quad (3)$$

The first three terms give a base value for a methylnaphthalene which must be corrected by the fourth term for symmetry and the fifth term for the 750 cal./mole potential barrier which was employed in the toluene calculations.

The lower parts of Table I and II show the calculations of the apparent potential barriers to methyl group rotation in the methylnaphthalenes. The tables of Pitzer and Gwinn[11] were used together with a moment of inertia of 5.52×10^{-40} g.cm.[3]

The uncertainty in the entropy values may be estimated to be about 0.5 cal./mole. This leads to ranges of 2.5–5.6 and 0.9–3.5 kcal./mole for the potential barriers. Thus we may safely conclude that a substantial barrier exists in 1-methylnaphthalene, and this is very reasonable in view of the interference between the methyl group hydrogen atoms and that in ring position 8.

The apparent value found for 2-methylnaphthalene seems high in comparison with the value of 750 cal./mole in toluene and in *m*- and *p*-xylene, but the lower limit of the range of uncertainty for the barrier is below 1 kcal./mole. Also, it should be remembered that naphthalene is much less symmetrical than benzene. Consequently there may remain a threefold barrier in 2-methylnaphthalene, whereas in toluene the threefold terms must cancel and leave a sixfold symmetry for the barrier. Indeed the 1–2 bond is known to be[12] about 0.04 Å. shorter than the 2–3 bond in naphthalene, and the simplest resonance picture yields $1^2/_3$ bond in 1-2 location and only $1^1/_3$ bond in the 2-3 position.

We are now able to calculate the heat capacity of gaseous 1- and 2-methylnaphthalenes by the equation equivalent to (3) but with correction for the potential barriers just determined. Also, each ΔC_p of vaporization is available from the vapor pressure equation and the equation of state for the vapor. Thus we are able to check our extrapolations of the liquid heat capacities. The comparisons are made in Table III. In view of the uncertainties involved in the calculations, the agreement

(11) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

(12) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

TABLE III

CHECK ON EXTRAPOLATION OF THE HEAT CAPACITY OF LIQUID 1- AND 2-METHYLNAPHTHALENES

T, °K.	1-Methyl Eq. 1	Calcd.	2-Methyl Eq. 2	Calcd.
425	66.9	68.1	66.0	67.1
440	68.5	69.1	67.5	68.1
450	69.5	69.8	68.5	68.8
470	71.6	71.2	70.5	70.5
500	74.7	73.8	73.5	73.1

of the liquid heat capacity and the treatment of the gas imperfection are more uncertain. Consequently the good agreement in the middle range suffices as a check on the extrapolation.

Calculated Properties of Gaseous Alkylnaphthalenes.—The heat capacity, heat content, entropy and free energy of the alkylnaphthalenes were calculated by the use of the following incremental equations together with corrections for the potential barrier specified.[13]

TABLE IV

FREE ENERGY FUNCTION OF ALKYLNAPHTHALENES IN THE IDEAL GAS STATE $(-F° - H_0°)/T$, (CAL./DEG. MOLE)

Alkyl-naphthalenes	298.16	300	400	500	600	700	Temperature (°K.) 800	900	1000	1100	1200	1300	1400	1500
Naphthalene	63.36	63.46	69.11	74.65	80.08	85.40	90.56	95.56	100.40	105.07	109.58	113.93	118.14	122.20
1-Methyl	70.34	70.44	77.05	83.54	89.89	96.14	102.16	107.99	113.66	119.06	124.33	129.37	134.27	138.98
1-Ethyl	76.62	76.74	84.45	91.98	99.31	106.50	113.42	120.11	126.60	132.79	138.81	144.58	150.18	155.55
1-n-Propyl	82.43	82.59	91.5	100.1	108.4	116.5	124.3	131.8	139.1	146.1	152.8	159.3	165.6	171.6
1-n-Butyl	88.41	88.59	98.5	108.1	117.3	126.3	135.0	143.3	151.4	159.1	166.6	173.7	180.7	187.4
1-n-Amyl	94.51	94.71	105.7	116.3	126.4	136.3	145.8	155.0	163.8	172.3	180.5	188.3	196.0	203.3
2-Methyl	70.71	70.81	77.49	84.00	90.39	96.60	102.59	108.41	114.02	119.43	124.69	129.71	134.62	139.29
2-Ethyl	76.99	77.11	84.89	92.44	99.81	106.96	113.85	120.56	126.96	133.16	139.17	144.92	150.54	155.86
2-n-Propyl	82.79	82.97	91.9	100.5	108.9	117.0	124.8	132.2	139.5	146.4	152.2	159.7	165.9	172.0
2-n-Butyl	88.79	88.92	98.9	108.6	117.8	126.9	135.4	143.7	151.8	159.5	167.0	174.1	181.0	187.7
2-n-Amyl	94.89	95.09	106.1	116.7	126.9	136.8	146.3	155.3	164.2	172.6	180.9	188.7	196.3	203.6
Increment per CH₂ group	5.979	5.999	7.061	8.043	8.970	9.856	10.705	11.516	12.299	13.053	13.781	14.477	15.151	15.798
1,2-Dimethyl	74.56	74.66	82.23	89.68	96.95	104.13	111.01	117.67	124.17	130.30	136.33	142.06	147.65	153.01
1,3-Dimethyl 1,6-Dimethyl 1,7-Dimethyl	74.94	75.04	82.68	90.14	97.45	104.59	111.44	118.09	124.53	130.67	136.69	142.40	148.00	153.32
1,4-Dimethyl 1,5-Dimethyl 2,3-Dimethyl	73.19	73.29	80.86	88.31	95.58	102.76	109.64	116.30	122.80	128.93	134.96	140.69	146.28	151.64
1,5-Dimethyl 2,3-Dimethyl	73.86	74.01	81.98	89.63	97.01	104.17	111.05	117.70	124.11	130.28	136.24	141.96	147.53	152.87
2,6-Dimethyl 2,7-Dimethyl	74.12	74.22	82.04	89.60	97.02	104.16	111.02	117.69	124.09	130.26	136.27	141.98	147.60	152.90
2-Methyl-3-ethyl	81.52	81.69	90.7	99.4	107.8	116.0	123.6	131.2	138.5	145.4	152.1	158.6	164.8	170.8
2-Methyl-6-ethyl 2-Methyl-7-ethyl	81.78	81.89	91.6	100.2	108.5	116.6	123.6	131.7	138.5	145.4	152.1	158.6	164.8	170.9

TABLE V

HEAT CONTENT FUNCTION OF ALKYLNAPHTHALENES IN THE IDEAL GAS STATE $(H° - H_0°)/T$, (CAL./DEG. MOLE)

Alkylnaphthalenes	298.16	300	400	500	600	700	Temperature (°K.) 800	900	1000	1100	1200	1300	1400	1500
Naphthalene	17.07	17.16	22.34	27.47	32.28	36.68	40.67	44.27	47.54	50.50	53.19	55.64	57.89	59.94
1-Methyl	19.87	19.99	26.19	32.18	37.73	42.83	47.43	51.61	55.40	58.81	61.91	64.77	67.36	69.75
1-Ethyl	23.32	23.45	30.46	37.23	43.50	49.26	54.43	59.13	63.40	67.24	70.74	73.97	76.89	79.60
1-n-Propyl	27.12	27.26	34.9	42.3	49.2	55.6	61.3	66.5	71.3	75.5	79.5	83.1	86.3	89.4
1-n-Butyl	30.42	30.57	39.0	47.1	54.7	61.6	67.9	73.7	78.9	83.6	88.0	92.0	95.6	98.9
1-n-Amyl	33.75	33.92	43.0	51.9	60.1	67.7	74.6	80.9	86.6	91.8	96.5	100.9	104.8	108.5
2-Methyl	20.12	20.25	26.35	32.26	37.71	42.75	47.35	51.45	55.23	58.63	61.71	64.55	67.13	69.53
2-Ethyl	23.57	23.71	30.62	37.31	43.48	49.18	54.35	58.97	63.23	67.03	70.54	73.75	76.66	79.38
2-n-Propyl	27.37	27.52	35.1	42.5	49.3	55.5	61.2	66.4	71.1	75.4	79.3	82.9	86.1	89.1
2-n-Butyl	30.67	30.83	39.2	47.2	54.7	61.6	67.8	73.5	78.8	83.5	87.8	91.8	95.3	98.7
2-n-Amyl	34.00	34.18	43.2	52.0	60.1	67.6	74.5	80.2	86.4	91.6	96.4	100.7	104.6	108.3
Increment per CH₂ group	3.330	3.344	4.063	4.774	5.439	6.062	6.643	7.176	7.663	8.112	8.528	8.908	9.258	9.582
1,2-Dimethyl	22.67	22.82	30.04	36.89	43.18	48.98	54.19	58.95	63.26	67.12	70.63	73.90	76.83	79.56
1,3-Dimethyl 1,6-Dimethyl 1,7-Dimethyl	22.92	23.08	30.20	36.97	43.16	48.90	54.10	58.79	63.09	66.94	70.43	73.68	76.60	79.34
1,4-Dimethyl 1,5-Dimethyl	22.67	22.82	30.04	36.89	43.18	48.98	54.19	58.95	63.26	67.12	70.63	73.90	76.83	79.56
2,3-Dimethyl	24.36	24.48	31.16	37.58	43.58	49.10	54.14	58.72	62.91	66.73	70.21	73.39	76.32	79.01
2,6-Dimethyl 2,7-Dimethyl	23.56	23.72	30.74	37.39	43.44	49.10	54.25	58.84	63.11	66.82	70.39	73.61	76.51	79.24
2-Methyl-3-ethyl	27.81	27.95	35.4	42.7	49.4	55.5	61.1	66.2	70.9	75.1	79.1	82.6	85.9	88.9
2-Methyl-6-ethyl 2-Methyl-7-ethyl	27.01	27.18	35.0	42.5	49.2	55.5	61.2	66.4	71.1	75.4	79.3	82.8	86.0	89.1

within 0.5 cal./deg. mole is entirely satisfactory in the middle temperature range. At the lowest temperatures the vapor pressure equation can hardly be expected to yield an accurate value of the second derivative which is required for ΔC_p. At the highest temperatures both the extrapolation

$G(n\text{-alkylnaphthalene}) = G(\text{naphthalene}) + G(n\text{-alkylbenzene}) - G(\text{benzene}) - R \ln 3/2$

(13) The barrier for the rotation of the ethyl group in ethylbenzene is 1080 instead of 750 for toluene. The effect of this difference is so small that the same correction terms were used for ethyl as for methyl rotation.

TABLE VI

ENTROPY OF ALKYLNAPHTHALENES IN THE IDEAL GAS STATE $S°$ (CAL./DEG. MOLE)

Alkyl-naphthalenes	298.16	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	500
Naphthalene	80.43	80.63	91.44	102.11	112.36	122.07	131.22	139.83	147.93	155.56	162.77	169.57	176.03	182.14
1-Methyl	90.21	90.43	103.24	115.72	127.62	138.97	149.59	159.60	169.06	177.87	186.24	194.14	201.63	208.73
1-Ethyl	99.94	100.19	114.91	129.21	142.81	155.76	167.85	179.24	190.00	200.03	209.55	218.55	227.07	235.15
1-n-Propyl	109.55	109.85	126.4	142.4	157.6	172.1	185.6	198.3	210.4	221.6	232.3	242.4	251.9	261.0
1-n-Butyl	118.83	119.16	137.5	155.2	172.0	188.0	202.9	217.0	230.3	242.7	254.4	265.7	276.3	286.3
1-n-Amyl	128.26	128.63	148.7	168.2	186.5	204.0	220.4	235.8	250.4	264.0	277.0	289.2	300.8	311.8
2-Methyl	90.83	91.06	103.84	116.26	128.10	139.35	149.94	159.86	169.25	178.06	186.40	194.26	201.75	208.82
2-Ethyl	100.56	100.82	115.51	129.75	143.29	156.14	168.20	179.50	190.19	200.19	209.71	218.67	227.21	235.24
2-n-Propyl	110.18	110.50	127.0	142.96	158.2	172.4	186.0	198.6	210.6	221.8	232.4	242.5	252.0	261.1
2-n-Butyl	119.46	119.81	138.1	155.8	172.5	188.3	203.3	217.2	230.5	242.9	254.7	265.8	276.4	286.4
2-n-Amyl	128.89	129.28	149.30	168.7	187.10	204.4	220.7	236.0	250.6	264.2	277.1	289.3	300.9	311.9
Increment per CH_2 group	9.309	9.343	11.12_4	12.81_7	14.40_9	15.91_8	17.34_8	18.69_2	19.96_2	21.16_5	22.30_9	23.38_5	24.40_9	25.38_0
1,2-Dimethyl	97.23	97.48	112.27	126.57	140.13	153.11	165.20	176.62	187.43	197.42	206.96	215.96	224.48	232.57
1,3-Dimethyl / 1,6-Dimethyl / 1,7-Dimethyl	97.86	98.12	112.88	127.11	140.61	153.49	165.55	176.88	187.62	197.61	207.12	216.08	224.60	232.66
1,4-Dimethyl / 1,5-Dimethyl	95.86	96.11	110.90	125.20	138.76	151.74	163.83	175.25	186.06	196.05	205.59	214.59	223.11	231.20
2,3-Dimethyl	98.22	98.49	113.14	127.21	140.59	153.27	165.19	176.42	187.02	197.01	206.45	215.35	223.85	231.88
2,6-Dimethyl / 2,7-Dimethyl	97.68	97.94	112.78	126.99	140.46	153.26	165.27	176.53	187.20	197.18	206.66	215.59	224.11	232.14
2-Methyl-3-ethyl	109.33	109.64	126.2	142.1	157.2	171.5	184.8	197.4	209.3	220.5	231.2	241.2	250.7	259.7
2-Methyl-6-ethyl / 2-Methyl-7-ethyl	108.79	109.07	125.9	141.9	157.0	171.4	184.9	197.6	209.5	220.8	231.4	241.4	250.9	260.0

TABLE VII

HEAT CAPACITY OF ALKYLNAPHTHALENES IN THE IDEAL GAS STATE C_p (CAL./DEG. MOLE)

Alkylnaphthalene	298.16	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500
Naphthalene	32.08	32.28	43.20	52.44	59.94	66.01	71.00	75.13	78.59	81.52	84.00	86.11	87.93	89.49
1-Methyl	38.13	38.37	50.74	61.25	69.79	76.76	82.48	87.19	91.21	94.63	97.51	99.97	102.08	103.93
1-Ethyl	44.02	44.30	58.25	70.06	79.65	87.47	93.91	99.24	103.79	107.67	110.96	113.77	116.19	118.31
1-n-Propyl	49.74	50.04	65.3	78.4	89.1	97.8	105.1	111.1	116.2	120.6	124.3	127.5	130.2	132.6
1-n-Butyl	55.18	55.51	72.2	86.6	98.4	108.1	116.1	122.8	128.5	133.4	137.6	141.1	144.2	146.9
1-n-Amyl	60.65	61.01	79.2	94.9	107.8	118.4	127.2	134.6	140.9	146.2	150.9	154.8	158.2	161.2
2-Methyl	38.19	38.42	50.50	60.87	69.31	76.28	82.03	86.81	90.86	94.28	97.21	99.71	101.86	103.72
2-Ethyl	44.08	44.35	58.01	69.68	79.17	86.99	93.46	98.86	103.44	107.32	110.66	113.51	115.97	118.10
2-n-Propyl	49.80	50.04	65.1	78.0	88.6	97.4	104.6	110.7	115.8	120.2	124.0	127.2	129.9	132.4
2-n-Butyl	55.24	55.56	72.0	86.2	97.9	107.7	115.7	122.4	128.1	133.1	137.3	140.9	143.9	146.7
2-n-Amyl	60.71	61.06	79.0	94.5	107.3	117.9	126.8	134.2	140.5	145.9	150.6	154.6	157.9	160.9
Increment per CH_2 group	5.466	5.494	6.94_1	8.24_6	9.34_2	10.27_6	11.06_5	11.74_6	12.33	12.84	13.28	13.66	13.98	14.27
1,2-Dimethyl	44.18	44.46	58.28	70.06	79.64	87.51	93.96	99.25	103.83	107.74	111.02	113.83	116.23	118.37
1,3-Dimethyl / 1,6-Dimethyl / 1,7-Dimethyl	44.24	44.51	58.04	69.68	79.16	87.03	93.51	98.87	103.48	107.39	110.72	113.57	116.01	118.16
1,4-Dimethyl / 1,5-Dimethyl	44.18	44.46	58.28	70.06	79.64	87.51	93.96	99.25	103.83	107.74	111.02	113.83	116.23	118.37
2,3-Dimethyl	44.41	44.65	57.49	68.75	78.18	86.02	92.58	98.10	102.78	106.76	110.16	113.07	115.59	117.75
2,6-Dimethyl / 2,7-Dimethyl	44.71	44.97	58.07	69.45	78.77	86.49	93.09	98.51	103.14	107.05	110.43	113.31	115.80	117.95
2-Methyl-3-ethyl	50.30	50.57	65.0	77.5	88.0	96.8	104.0	110.1	115.3	119.8	123.6	126.9	129.7	132.1
2-Methyl-6-ethyl / 2-Methyl-7-ethyl	50.60	50.90	65.6	78.2	88.7	97.3	104.4	110.6	115.7	120.2	123.8	127.2	130.0	132.3

with correction from $V_0 = 750$ to $V_0 = 3800$ for 1-series and to $V_0 = 2300$ for 2-series.

G(1,2-dimethylnaphthalene) $= 2G$(1-methylnaphthalene) $- G$(naphthalene) $- R \ln 4$

G(1,4-dimethylnaphthalene) $= G$(1,5-dimethylnaphthalene) $= 2G$(1-methylnaphthalene) $- G$(naphthalene) $- R \ln 8$

G(1,3-dimethylnaphthalene) $= G$(1,6-dimethylnaphthalene) $= G$(1,7-dimethylnaphthalene) $= G$(1-methylnaphthalene) $+ G$(2-methylnaphthalene) $- G$(naphthalene) $- R \ln 4$.

G(2,3-dimethylnaphthalene) $= G$(naphthalene) $+ G$(o-xylene) $- G$(benzene) $- R \ln 3$;

G(2,6-dimethylnaphthalene) $= G$(2,7-dimethylnaphthalene) $= G$(naphthalene) $+ G$(m-xylene) $- G$(benzene) $- R \ln 3$

with correction from $V_0 = 750$ to $V_0 = 2300$.

G(2-methyl-3-ethylnaphthalene) $= G$(naphthalene) $+ G$(1-methyl-2-ethylbenzene) $- G$(benzene) $- R \ln 3$;

G(2-methyl-6-ethylnaphthalene) $= G$(2-methyl-7-ethylnaphthalene) $= G$(naphthalene) $+ G$(1-methyl-3-ethylbenzene) $- G$(benzene) $- R \ln 3$

with correction from $V_0 = 750$ to $V_0 = 2300$ for both internal rotations about bonds adjacent to the aromatic ring system.

In these equations G represents $C_p°$, $S°$, $(H° - H_0°)/T$ or $-(F° - H_0°)/T$. The logarithm term applies only to $S°$ and $-(F° - H_0°)/T$. The component values come from sources mentioned above.[2,4,5,11]

The calculated values are listed in Tables IV–VII. The increments per CH_2 group given in the tables can be used to calculate the functions for n-

alkylnaphthalenes higher than amylnaphthalene. The values of McClellan and Pimentel[2] for naphthalene are included for convenience. These authors estimate that their values are probably accurate to ±0.5 cal. per degree mole. The values for the substituted naphthalenes are subject to additional uncertainty. We estimate the uncertainty

to range from 0.5 for the simpler derivatives at the lower temperatures to 1.0 for the larger molecules at the higher temperatures.

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An Electron Diffraction Investigation of the Molecular Structure of Trifluoroethanol[1]

BY R. L. LIVINGSTON AND G. VAUGHAN

The molecular structure of trifluoroethanol has been investigated by electron diffraction using the visual correlation procedure. The structural parameters as determined by this investigation are as follows: C–F = 1.34 ± 0.02 Å., C–C = 1.52 ± 0.05 Å., C–O = 1.41 ± 0.05 Å., $\angle$FCF = 108.5 ± 1.5°, and $\angle$CCO = 110 ± 4°.

Introduction

There has been considerable interest in the effect of halogen atoms on the carbon–carbon bond distances in simple organic halides. Early results[2] gave a C–C distance of about 1.45 Å. in C_2F_6 and CF_3CH_3 but more recent work indicates that these distances are considerably longer, probably between 1.50 and 1.54 A.[3,4] The determination of the structure of trifluoroethanol was undertaken to determine further the effect of fluorine atoms on the C–C distance and, in addition, to determine any effects on the C–O bond length and the CCO angle.

Experimental

The sample of trifluoroethanol used in this work was purchased from the Minnesota Mining and Manufacturing Company. A 60-ml. sample was rectified in a glass helices packed column which was equivalent to fifteen theoretical plates. Ten milliliters of the middle fraction, b.p. 77.7 ± 0.1° (uncorrected), was collected for use in preparing the diffraction photographs. The infrared spectrum of this fraction showed no spurious features when compared with the spectrum from a sample with a known purity greater than 99%.

The diffraction photographs were obtained in the usual manner[5] using a camera designed and constructed by Professor H. J. Yearian of the Purdue Physics Department. Twelve satisfactory photographs of varying density were obtained from the sample described above, using a camera distance of 108.2 mm., an electron wave length of 0.05923 Å. and Eastman Kodak 33 plates. Visual interpretation and measurements of the patterns were obtained out to a q-value of approximately 95 from three of the best plates.

Interpretation of the Diffraction Pattern.—The visual correlation method[5,6] and the radial distribution method[7,8] were used in the interpretation of the diffraction pattern. The measurements of the patterns are summarized in Table I. The q_0-values are based upon measurements of each feature by two independent observers. The qualitative
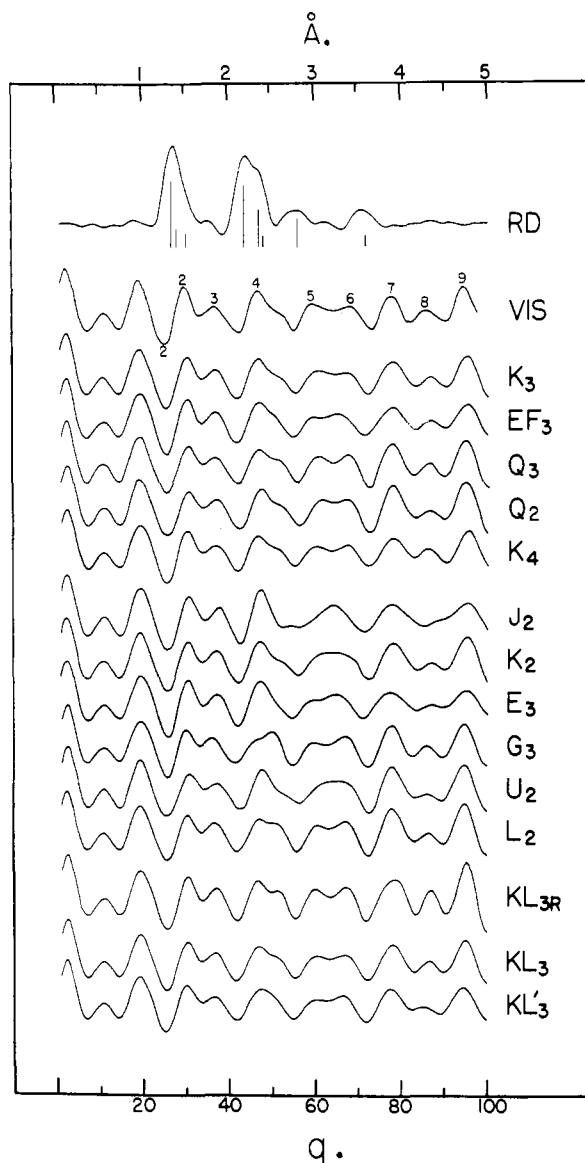

Fig. 1.—Radial distribution, visual intensity and theoretical intensity curves for trifluoroethanol.

(1) Contains material from the Ph.D. thesis of G. Vaughan, Purdue Research Foundation Fellow in Chemistry, 1951–1953.

(2) A survey of electron diffraction results through 1949 is found in the tabulation by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

(3) J. L. Brandt and R. L. Livingston, THIS JOURNAL, **76**, 2096 (1954).

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(5) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

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