and k_2 for various experimental conditions. The logarithms of the rate constants bear a linear relation to the reciprocal of the absolute temperature. The fraction deposited, F_D, was found to have the same value in a solution 3 *f* in both sodium chloride and hydrochloric acid as it had in a solution 6 *f* in hydrochloric acid under otherwise identical experimental conditions.

When solutions of irradiated stannous chloride in 3 *f* hydrochloric acid were oxidized with chlorine, F_D was 0.01 at 30 minutes at 25°. When the oxidized solution was reduced with sulfur dioxide at room temperature, F_D was 0.18 at 30 minutes, and when the reduction was continued at 95°, F_D was 0.08 at 30 minutes.

TABLE I

EMPIRICALLY DERIVED VALUES OF THE RATE CONSTANTS

Temp., °C.	Hydrochloric acid, *f*	k_1, min.$^{-1}$	k_2, min.$^{-1}$
20.25 ± 0.05	3	0.102	0.0145
	6	.102	.0040
25.15 ± 0.05	3	.135	.0169
	6	.135	.0056
30.95 ± 0.05	3	.185	.0204
	6	.185	.0074

Solutions of irradiated stannic chloride in 6 *f* hydrochloric acid were found to change in such a manner that the amount of antimony removable by copper in two-minute immersions was reduced by a factor of two for each three days of age of the solution. Because of the aging of the irradiated stannic chloride solutions reproducible deposition curves were not obtained. Aging of solutions of irradiated stannous chloride in 6 *f* hydrochloric acid did not occur until after three months.

In the separation of antimony from copper in nitric acid solution by the addition of sodium hydroxide, the amount of antimony retained in solution was found to increase with increasing *p*H from 33% at a *p*H of 10, to 74% when the supernatant liquid was 0.1 *f* in sodium hydroxide. Thus, the maximum over-all yield of Sb^{125} attainable from neutron irradiated stannous chloride under the experimental conditions investigated is 71%.

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Thermodynamic Functions of 2,2,3-Trimethylbutane

BY DONALD W. SCOTT AND GUY WADDINGTON

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The thermodynamic functions of four methyl-substituted butanes, 2-methylbutane,[1] 2,2-dimethylbutane,[2] 2,3-dimethylbutane[1] and 2,2,3,3-tetramethylbutane,[3] have previously been calculated from spectroscopic and molecular-structure data by the methods of statistical mechanics. This note reports a similar calculation of the thermodynamic functions of 2,2,3-trimethylbutane, the remaining member of the group of compounds.

Calorimetric values of the vapor heat capacity and entropy of 2,2,3-trimethylbutane were available for the evaluation of certain necessary parameters. The values of the vapor heat capacity had been reported in a previous publication from this Laboratory.[4] The values of the entropy were computed as shown in Table I from data from several different sources.

TABLE I

MOLAL ENTROPY OF 2,2,3-TRIMETHYLBUTANE, CAL. DEG.$^{-1}$

T, °K.	298.16	313.84	353.96
Entropy of liquid[a]	69.88	72.54	79.12
Vaporization, $\Delta H_{\text{vap.}}/T$[b]	25.68	23.77	19.54
Gas imperfection[c]	0.06	0.08	0.16
Compression, $R \ln (p/760)$[d]	−3.98	−2.70	0.00
Entropy (±0.30) of ideal gas at 1 atm.	91.64	93.69	98.82

[a] Unpublished results from this Laboratory. [b] Heat of vaporization at 298.16°K., N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947); at the other two temperatures, ref. 4. [c] Calculated from the equation for the second virial coefficient, $B = (PV - RT)/P = -643 - 22.98 \exp (1200/T)$ cc. mole^{-1}, based on data of ref. 4. [d] Vapor pressure equation from American Petroleum Institute Research Project 44 at Carnegie Institute of Technology, Selected Values of Properties of Hydrocarbons, Table No. 2k, dated Dec. 31, 1948.

The thermodynamic functions were calculated by means of the usual rigid rotator, harmonic oscillator, independent internal rotator approximation. The moments and reduced moments of inertia were computed by the methods of Kilpatrick and Pitzer.[5] All bond angles were assumed to be tetrahedral and the bond distances were taken to have their normal values (C–C, 1.54 Å., C–H, 1.09 Å.) with one exception. The exception is the central C–C bond distance, which is expected to be longer than normal on account of steric repulsion between the isopropyl and tertiary butyl groups. The estimated value that was used for this distance, 1.56 Å., is midway between the normal value and that in 2,2,3,3-tetramethylbutane, 1.58 Å.[6] The product of the three principal moments of inertia was calculated to be 4.638×10^{-113} g.^{3} cm.^{6} The diagonal elements of the reduced internal rotational kinetic energy matrix were 68.50×10^{-40} for the skeletal rotation, 5.239×10^{-40} for one methyl rotation, and 5.221×10^{-40} g. cm.^{2} for the other four methyl rotations. The off-diagonal elements were small enough that these diagonal elements could be used as the reduced moments of inertia. An average value of 5.225×10^{-40} g. cm.^{2} was used for all five methyl rotations.

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(5) J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

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Examination of the Raman and infrared data[7–11] for 2,2,3-trimethylbutane showed that in the region below 1350 cm.$^{-1}$ there were 22 observed frequencies that could reasonably be assigned as fundamentals. The 8 skeletal bending, 6 C–C stretching, 10 CH_3 rocking and 2 C–H wagging modes, 26 in all, are expected to have frequencies in this region. Four frequencies are therefore unobserved. Regularities in the frequencies of related molecules suggest that one of these four is a skeletal bending frequency, probably the very lowest, and that the other three are in the upper half of the range, *i.e.*, between 675 and 1350 cm.$^{-1}$. The parameters that had to be evaluated from the calorimetric data included these four unobserved frequencies in addition to the heights of the potential barriers hindering internal rotation. It was practical to evaluate at most three empirical parameters from the available calorimetric data. These parameters were selected to be: (a) the average value of the heights of the barriers hindering internal rotation, (b) the value of the unobserved skeletal bending frequency and (c) the average value of the three unobserved higher frequencies. The validity of assuming the same barrier heights for all internal rotations, as has previously been done in the cases of 2,2-dimethylbutane and 2,2,3,3-tetramethylbutane, is discussed in refs. 2 and 3. A satisfactory fit to the calorimetric data was obtained with the following values of the parameters: (a) 4200 cal. mole^{-1} for the average barrier height, (b) 232 cm.$^{-1}$ for the skeletal bending frequency and (c) 1330 cm.$^{-1}$ for the average value of the three higher frequencies. Average or conventional values were used for the CH_3 bending and C–H stretching frequencies, which are not all resolved in the observed spectra. The complete set of vibrational frequencies that was used for the thermodynamic calculations is as follows (the empirical values are italicized): *232*, 261, 298, 362, 392, 442, 462, 524, 686, 832, 923,[12] 957, 1000, 1011, 1027, 1084, 1107, 1160, 1209, 1224, 1252, 1320, *1330* (*3*), 1334, 1375 (5), 1460 (10) and 2950 (16) cm.$^{-1}$.

The satisfactory fit obtained with the calorimetric data may be judged by the following comparison of observed and calculated values. The units of $S°$ and $C_p°$ are cal. deg.$^{-1}$ mole^{-1}.

T, °K.	298.16	313.84	353.96
$S°$, obsd.	91.64	93.69	98.82
$S°$, calcd.	91.60	93.68	98.91

T, °K.	328.80	348.85	369.20	400.40	434.30	461.80
$C°_p$, obsd.	42.74	45.09	47.39	50.92	54.54	57.36
$C°_p$, calcd.	42.81	45.09	47.40	50.87	54.53	57.36

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF 2,2,3-TRIMETHYLBUTANE

T, °K.	$-(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$C°_p$, cal. deg.$^{-1}$
273.16	67.21	21.05	5.751	88.26	36.52
298.16	69.12	22.48	6.703	91.60	39.33
300	69.26	22.58	6.776	91.85	39.54
400	76.56	28.25	11.30	104.8	50.83
500	83.45	33.81	16.91	117.3	61.04
600	90.07	39.10	23.46	129.2	69.61
700	96.47	43.97	30.78	140.4	76.74
800	102.7	48.44	38.76	151.1	82.73
900	108.6	52.54	47.28	161.1	87.88
1000	114.3	56.30	56.30	170.6	92.32
1100	119.9	59.75	65.72	179.6	96.16
1200	125.2	62.92	75.50	188.1	99.48
1300	130.4	65.83	85.58	196.2	102.4
1400	135.4	68.52	95.94	203.9	104.8
1500	140.2	71.03	106.5	211.2	107.0

The calculated values of the functions $(F° - H_0^\circ)/T$, $(H° - H_0^\circ)/T$, $H° - H_0^\circ$, $S°$ and C_p° for selected temperatures up to 1500°K. are listed in Table II. For reasons of internal consistency, all values are given to four digits, although in some places in the table the retention of the last digit is not justified by the accuracy of the molecular-structure parameters used in the calculations or by the reliability of the approximations employed.

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[12] Fermi resonance of this frequency with the overtone, 2 × 462 = 924, accounts for the doublet, 919–927 cm.$^{-1}$, in the observed spectra.

The Free Energies and Entropies of Hydrogen, Chlorine and Hydrogen Chloride from Spectroscopic Data[1]

BY R. H. SHERMAN AND W. F. GIAUQUE

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Recent work in this Laboratory has required the use of the free energy function for hydrogen chloride and it became apparent that no correct table of this function, in terms of recent values of the "natural" constants concerned, was available in the literature.

We have used the natural constants given by Du Mond and Cohen[2] and recently recommended by Rossini, Gucker, Johnston, Pauling and Vinal[3] to correct the $(F° - H_0^\circ)/T$ functions for hydrogen, chlorine and hydrogen chloride.

Hydrogen Chloride.—The free energy function for hydrogen cyloride was tabulated by Giauque and Overstreet.[4] It has recently been retabulated in Tables of the National Bureau of Standards[5] in terms of natural constants not much different than those of the Du Mond and Cohen (1951). We had expected to be able to use these values but it be-

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[1] This work was supported in part by the Office of Naval Research, United States Navy.

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