nucleate in solution do not result in the production of oxygen nor are these reactions affected by oxygen.

The failure of hydrogen, in the presence of palladium black, to affect the viscosity of thymonucleate solutions has been taken to indicate, but not to prove, that the degradation is not due to reaction with hydrogen atoms. On the other hand, when thymonucleate solutions containing hydrogen peroxide are irradiated with ultraviolet light in the range of wave lengths where most of the light absorption is due to the peroxide, there has been found a sharp reduction in solution viscosity that can be attributed to the action of free hydroxyl radicals formed in the photolysis. With constant nucleate and hydrogen peroxide concentrations the logarithm of viscosity reduction is proportional to time of irradiation. The viscosity reduction is not a constant function of the amount of light absorbed under all conditions since the rate of reduction increases with hydrogen peroxide concentration only over a limited range. The constant maximum in the rate attained at higher peroxide concentrations may be ascribed to competition for hydroxyl radicals between nucleate on the one hand and hydrogen peroxide and its photolytic decomposition products on the other. The finding that a very small amount of nucleate causes a marked reduction in the amount of oxygen produced from hydrogen peroxide solutions by ultraviolet irradiation is an additional indication that the nucleate reacts with hydroxyl radicals.

Further evidence for the free radical nature of the decomposition is provided by the observations that the rate of degradation decreases at very low nucleate concentrations and also when other solutes, such as glucose, methanol and irradiated nucleate, are present.

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Thermodynamic Properties and Rotational Isomerism of 2-Thiabutane[1]

BY D. W. SCOTT, H. L. FINKE, J. P. MCCULLOUGH, M. E. GROSS, K. D. WILLIAMSON, GUY WADDINGTON AND H. M. HUFFMAN[2]

The experimental work reported in this paper consisted of calorimetric and vapor-pressure studies of 2-thiabutane (methyl ethyl sulfide) which yielded values of the entropy and the heat capacity of this substance in the ideal gas state. These data were correlated and extended to other thermodynamic functions and to higher temperatures by calculations based on spectroscopic and molecular structure information. The interpretation of the spectroscopic and thermal data led to the conclusion that the two rotational isomers of 2-thiabutane have nearly the same energy.

Experimental

Material.—The 2-thiabutane used for the experimental measurements consisted of a small sample of highly purified material and a larger sample of material of somewhat lower purity. These were prepared and purified at the Laramie Station of the Bureau of Mines as part of A.P.I. Research Project 48A. The high-purity sample was used for the low-temperature studies and vapor-pressure measurements. From observations of the melting point as a function of per cent. melted, the purity was determined to be 99.9984 ± 0.0005 mole per cent. This determination involved the usual assumptions of liquid soluble-solid insoluble impurities and ideal solutions. The melting-point data are summarized in Table I. In the ebulliometric studies, the difference between the boiling and condensation temperatures of this sample was found to be 0.008°. The second sample, of lower purity, was used for determining the heats of vaporization and the vapor heat capacities, because these measurements required a larger volume of material. The purity of this second sample, determined at the Laramie Station by the time-temperature freezing-point method, was reported to be 99.49 ± 0.18 mole per cent.

Low-Temperature Studies.—Measurements of the heat capacity of 2-thiabutane in the solid and liquid states and its melting point and heat of fusion were made in an apparatus similar to that described by Ruehrwein and Huffman.[3] The calorimeter used to contain the sample was constructed of platinum and had internal vanes of gold to promote more rapid attainment of thermal equilibrium. The results of the heat-capacity measurements are listed in Table II. The precision of the measurements was, in general, better than 0.1%, and above 30°K. it is believed that the accuracy uncertainty should not be greater than 0.2%. Values of the heat capacity at integral temperatures, as selected from a smooth curve through all the data, are given in Table III.

TABLE I

MELTING POINT OF 2-THIABUTANE; 0°C. = 273.16°K.

Triple point: 167.23 ± 0.05°K. $N_2/F = 0.0420\ \Delta T$ where N_2 is the mole fraction of impurity, F the fraction of sample in liquid form, and ΔT the melting point lowering. Impurity: 0.0016 ± 0.0005 mole per cent.

Melted, %	T, °K. Obsd.	T, °K. Calcd.
6.5	167.2268	167.2247
26.9	167.2291	167.2291
50.7	167.2297	167.2298
71.0	167.2301	167.2300
91.3	167.2301	167.2301
100.0		167.2301
Pure		167.2305

Duplicate determinations each gave a value of 2,333 cal./mole for the heat of fusion.

Vapor Pressure.—The vapor pressure of 2-thiabutane was measured from 23 to 101° by an ebulliometric method, using the apparatus that has been described in a previous publication from this Laboratory.[4] The results of the measurements are given in Table IV. An Antoine equation was fitted to these data by a least-squares adjustment, and the equation which was obtained is

$$\log_{10} p = 6.93849 - 1182.562/(t + 224.784) \qquad (1)$$

The normal boiling point given by this equation is 66.65°. Values of the vapor pressure calculated by means of the

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[1] This investigation was performed as part of the work of American Petroleum Institute Research Project 48A on "The Production, Isolation, and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo. Article not copyrighted.

[2] Deceased.

[3] Ruehrwein and Huffman, THIS JOURNAL, 65, 1620 (1943).

[4] Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith, and Huffman, THIS JOURNAL, 71, 797 (1949).

TABLE II

MOLAL HEAT CAPACITY OF 2-THIABUTANE; 0°C. = 273.16°K.; MOL. WT., 76.160; MASS OF SAMPLE, 47.867 G.

T, °K.	$C_{\text{satd.}}$, cal./mole	T, °K.	$C_{\text{satd.}}$, cal./mole	T, °K.	$C_{\text{satd.}}$, cal./mole
14.15	0.832	79.40	13.823	158.10	21.142
15.18	1.041	82.12	14.184	161.48	21.430
16.98	1.419	86.28	14.671	Liquid	
17.79	1.599	86.57	14.733	147.21	32.569[a]
19.41	1.989	86.71	14.740	153.48	32.445[a]
20.76	2.347	90.62	15.179	162.30	32.318[a]
21.94	2.652	92.31	15.344	171.91	32.219
24.44	3.325	95.71	15.696	176.52	32.184
24.83	3.438	99.16	16.040	178.47	32.206
28.18	4.337	104.57	16.581	186.48	32.157
28.75	4.476	105.73	16.676	187.56	32.186
32.77	5.534	112.56	17.320	196.41	32.181
36.68	6.507	113.49	17.409	199.48	32.184
40.73	7.441	119.67	17.963	209.86	32.270
45.06	8.348	122.53	18.216	220.50	32.397
49.86	9.324	126.55	18.555	231.85	32.564
55.19	10.275	131.21	18.961	243.41	32.809
56.09	10.433	133.61	19.156	249.23	32.983
62.20	11.443	140.03	19.696	254.86	33.104
66.37	12.079	140.85	19.750	260.13	33.274
67.80	12.288	146.74	20.230	266.35	33.436
70.69	12.665	147.90	20.316	278.42	33.834
73.52	13.056	148.99	20.417	289.37	34.214
74.58	13.193	152.04	20.641	297.61	34.545
78.33	13.685	154.78	20.880		

[a] Supercooled liquid.

TABLE III

MOLAL HEAT CAPACITY OF 2-THIABUTANE AT INTEGRAL TEMPERATURES

T, °K.	$C_{\text{satd.}}$, cal./mole	T, °K.	$C_{\text{satd.}}$, cal./mole	T, °K.	$C_{\text{satd.}}$, cal./mole
14	0.80	80	13.91	170	32.23
15	1.00	85	14.53	180	32.18
20	2.15	90	15.10	190	32.17
25	3.48	95	15.63	200	32.19
30	4.82	100	16.13	210	32.27
35	6.10	110	17.09	220	32.39
40	7.28	120	17.99	230	32.54
45	8.34	130	18.85	240	32.75
50	9.35	140	19.68	250	33.00
55	10.25	150	20.49	260	33.26
60	11.10	160	21.30	270	33.56
65	11.88	167.23	21.90	280	33.89
70	12.59	Liquid		290	34.25
75	13.26	167.23	32.26	298.16	34.57

TABLE IV

VAPOR PRESSURE OF 2-THIABUTANE

Boiling point, °C.		Pressure, mm.	
Water	2-Thiabutane	Obsd.	Calcd.
60	23.435	149.41	149.38
65	28.695	187.57	187.57
70	33.997	233.72	233.75
75	39.339	289.13	289.18
80	44.717	355.22	355.24
85	50.136	433.56	433.52
90	55.600	525.86	525.82
96	61.104	633.99	633.93
100	66.655	760.00	760.01
105	72.241	906.06	906.00
110	77.870	1074.6	1074.4
115	83.551	1268.0	1268.1
120	89.265	1489.1	1489.2
125	95.020	1740.8	1740.7
130	100.825	2026.0	2026.0

above equations are listed in the fourth column of Table IV for comparison with the observed values.

Heat of Vaporization and Vapor Heat Capacity.—Measurements of the heat of vaporization and vapor heat capacity of 2-thiabutane were made with a cycling vaporizer and flow calorimeter as described in previous publications from this laboratory.[5] A metal cycling vaporizer, a description of which will be included in a pending publication, replaced the glass vaporizer formerly used.

The heats of vaporization at 301.66, 319.76 and 339.81 °K. were found to be 7563, 7329 and 7055 cal./mole. The values given are averages of at least three separate determinations whose maximum deviations from the mean were ±4, ±2 and ±4 cal./mole, respectively. The accuracy of these values is believed to be about ±0.1%. For interpolation within the temperature range covered by the experimental measurements, the following equation may be used

$$\Delta H_{\text{vap.}} = 9528 - 0.481T - 0.02000T^2 \qquad (2)$$

The heat capacity of the vapor was determined at two or more pressures at each of five temperatures ranging from 327 to 487 °K. The results of these measurements are listed in Table V. Values of $C_p{}^0$, the heat capacity in the ideal gas state, were obtained at each temperature by linear extrapolation to zero pressure of plots of heat capacity *vs.* pressure. An accuracy uncertainty of ±0.2% is assigned to these calorimetric values of $C_p{}^0$. They may be represented without significant loss of accuracy by the following equation, which of course is valid only over the temperature range of the experimental measurements

$$C_p{}^0 = 5.11 + 6.545 \times 10^{-2}T - 2.1735 \times 10^{-5}T^2 \qquad (3)$$

TABLE V

VAPOR HEAT CAPACITY OF 2-THIABUTANE, CAL./DEG./MOLE

T, °K.	327.00	366.20	402.20	449.15	487.20
C_p (758 mm.)		26.710	28.287	30.346	32.000
C_p (381 mm.)	24.696	26.448			
C_p (186 mm.)	24.429	26.301	28.003	30.168	31.883
$C_p{}^0$ (obsd.)	24.18	26.17	27.91	30.11	31.85
$C_p{}^0$ (calcd.)[a]	24.18	26.11	27.84	30.02	31.68
$(\partial C_p/\partial P)_T$, obsd.	1.04	0.54	0.38	0.24	0.16
$(\partial C_p/\partial P)_T$, calcd.	1.04	0.58	0.36	0.22	0.15

[a] From spectroscopic and molecular structure data.

Gas Imperfection and Second Virial Coefficient.—Values of the second virial coefficient, B, in the equation of state $PV = RT + BP$, were obtained at three temperatures from the heat of vaporization and vapor pressure data with the aid of the exact form of the Clapeyron equation. The relationship used was

$$B = [\Delta H_{\text{vap.}}/T(\mathrm{d}P/\mathrm{d}T)] - RT/P + V_{\text{L}}$$

where V_{L} is the molar volume of the liquid. In addition, the values of C_p as a function of pressure at five temperatures yielded values of the second derivative of B with respect to temperature since $(\partial C_p/\partial P)_T = -T(\partial^2 B/\partial T^2)_P$. These data were correlated by means of the empirical equation

$$B = -257 - 68.13e^{900/T} \text{ cc./mole} \qquad (4)$$

The method of evaluating the constants in this equation has been described elsewhere.[6] The values of the second virial coefficient obtained from the experimental data for 301.66, 319.76 and 339.81 °K., −1568, −1366 and −1246

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[5] (a) Waddington, Todd and Huffman, THIS JOURNAL, **69**, 22 (1947); (b) Waddington and Douslin, *ibid.*, **69**, 2275 (1947).

[6] Scott, Waddington, Smith and Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

cc./mole, may be compared with the values calculated by means of eq. (4), −1600, −1393 and −1230 cc./mole, respectively. The last two lines in Table V compare the observed values of $(\partial C_p/\partial P)_T$ with those calculated by use of eq. (4).

Entropy.—The calorimetric data were utilized to calculate the entropy of 2-thiabutane in both the liquid and vapor states. The entropy calculations are summarized in Table VI. For computing the correction for gas imperfection, which is given by $P(\partial B/\partial T)_P$ in terms of the second virial coefficient, eq. (4) was used.

TABLE VI

ENTROPY OF 2-THIABUTANE, CAL./DEG./MOLE

0–14°K.	Extrapolation, 2.333 $D(153/T)$	0.275
14° = 167.23°	Solid, graphical	23.964
167.23°	Fusion, 2333/167.23	13.951
167.23–298.16°	Liquid, graphical	18.945
Entropy of liquid at 298.16°K.		57.14 ± 0.10

T, °K.	301.66	319.76	339.81
Entropy of liquid	57.54	59.58	61.76
Vaporization, $\Delta H_{\text{vap.}}/T$	25.07	22.92	20.76
Compression, $R \ln (P/760)$	−2.80	−1.37	0.00
Gas imperfection	0.08	0.12	0.18
Entropy (±0.15) of ideal gas at 1 atm.	79.89	81.25	82.70

Discussion

Vibrational Assignment.—Before using the thermal data to obtain information about the barriers hindering internal rotation in the 2-thiabutane molecule, it was necessary to make an adequate vibrational assignment. The spectroscopic data used for this purpose were the Raman measurements of Rank, Shull and Axford[7] and of Matossi and Aderhold,[8] the infrared measurements in the rock-salt region obtained at this Station,[9] and one additional infrared band in the KBr region reported by Trotter and Thompson.[10]

In making the assignment, it was necessary to consider the two rotational isomers of the 2-thiabutane molecule—the *trans* or extended configuration of C_s symmetry and the skew or gauche configuration of C_1 symmetry. Both forms must be present in appreciable concentrations at ordinary temperatures, since more spectroscopic frequencies are observed than can be attributed to a single species. Furthermore, there must be very little difference in energy between the two configurations, since the relative intensities of the Raman lines of 2-thiabutane are constant over a wide range of temperature.[7] In anticipation of the results of a subsequent section, it may be stated here that the spectroscopic evidence for the two configurations having nearly the same energy is confirmed by the thermal data.

As a guide in assigning the observed skeletal frequencies to one or the other of the two rotational isomers, approximate normal coördinate treatments were carried out. The problems were simplified to those of a four-atom chain by substituting masses of 15.034 and 14.026 atomic weight units for the methyl and methylene groups, respectively. A simple potential function with no interaction terms was used. The force constants were 3.5 × 10^5 and 3.1 × 10^5 dynes/cm. for C–C and S–C stretching and 1.3 × 10^{-11} and 0.8 × 10^{-11} erg/radian^2 for C–C–S and C–S–C bending, respectively. Such a crude model and oversimplified potential function would not be expected to yield accurate values of the skeletal frequencies but would be expected to show the correct relative order of these frequencies. That is, if a particular mode of vibration is calculated to have a higher frequency in the C_1 form than in the C_s form of the four-atom chain, it is reasonable to expect it likewise to have a higher frequency in the C_1 form than in the C_s form of the actual molecule. The calculated frequencies and the assignment of the observed skeletal frequencies made by analogy with them are given in the first part of Table VII. The C–C–S bending and C–C stretching frequencies of the two forms are apparently not resolved in the observed spectra.

TABLE VII

SKELETAL FREQUENCIES OF 2-THIABUTANE

	Calcd. for four-atom chain		Observed	
	C_s, cm.$^{-1}$	C_{11}, cm.$^{-1}$	C_s, cm.$^{-1}$	C_1, cm.$^{-1}$
C–S–C bend.	234	246	216	273
C–C–S bend.	345	385	355	
S–C stretch.	726	696	679	654
S–C stretch.	776	786	757	784
C–C stretch.	946	941	973	

HYDROGEN FREQUENCIES BELOW 1400 CM.$^{-1}$ FOR ETHANETHIOL, METHANETHIOL AND 2-THIABUTANE

	C_2H_5SH	CH_3SH	$C_2H_5SCH_3$
CH_3 bend. sym.	1385		1378
CH_3 bend. sym.		1335	1323
CH_2 twist	1309		1311
CH_2 wag	1269		1264
CH_3 rock	1097		1098?
CH_3 rock		1074	1062
CH_3 rock	1049		1042
CH_3 rock		976	956
CH_2 rock	745		727

The vibrational modes of 2-thiabutane that are essentially motions of the hydrogen atoms would be expected to have frequencies that are characteristic of a methyl group or an ethyl group bonded to a sulfur atom. These frequencies should therefore be nearly the same in the two rotational isomers and should also be nearly the same as the internal frequencies of the methyl group in methanethiol and the ethyl group in ethanethiol. In fact, as shown in the second part of Table VII, there is a marked correspondence between the hydrogen frequencies of methanethiol and ethanethiol and those of 2-thiabutane, and most of the hydrogen frequencies of the latter can be assigned by analogy with the other two compounds.[11] The

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(7) Rank, Shull and Axford, *J. Chem. Phys.*, **18**, 392 (1950).

(8) Matossi and Aderhold, *Z. Physik*, **68**, 683 (1931).

(9) Catalog of Infrared Spectral Data, American Petroleum Institute Research Project 44 at the National Bureau of Standards. Serial No. 813, 2-thiabutane (liquid), contributed by the Bureau of Mines, Bartlesville, Oklahoma.

(10) Trotter and Thompson, *J. Chem. Soc.*, 481 (1946).

(11) The frequencies given in Table VII for methanethiol follow the assignment of Thompson and Skerrett [*Trans. Faraday Soc.*, **36**, 812 (1940)] but have been revised to accord with the more recent infrared data of reference 10. Those given for ethanethiol differ from the assignment of Sheppard [*J. Chem. Phys.*, **17**, 79 (1949)] in the case of the CH_2 twisting mode and one methyl rocking mode. This reassignment for ethanethiol requires some discussion, since it directly concerns the assignment for 2-thiabutane. The frequency of 1049 cm.$^{-1}$ was assigned to methyl rocking in ethanethiol instead of 870 cm.$^{-1}$ because the latter is outside the usual range of methyl rocking fre

frequency of 1098 cm.$^{-1}$ is questionable because it has been reported only by Matossi and Aderhold[8] and may have arisen from an impurity, since Rank, Shull and Axford[7] did not observe it with a sample known to be of high purity. However, 1098 cm.$^{-1}$ cannot be far wrong for the frequency in question, and this value was adopted for thermodynamic calculations. No detailed assignment was attempted for the thermodynamically unimportant C–H stretching, CH_2 bending, and unsymmetrical methyl bending frequencies, which are obviously not all resolved in the observed spectra. Average values of 2950 and 1435 cm.$^{-1}$ were used for these.

For thermodynamic calculations it is sufficient to use the vibrational assignment for one rotational isomer if the moments of inertia for over-all and internal rotation are computed for the same configuration. Since the calculation of the moments of inertia of 2-thiabutane was somewhat simpler for the C_s or extended configuration, the vibrational assignment for this form was used. The complete set of frequencies employed for thermodynamic calculations was: 216, 355, 679, 727, 757, 956, 973, 1042, 1062, 1098, 1264, 1311, 1323, 1378, 1435 (5), and 2950 (8) cm.$^{-1}$.

Barriers to Internal Rotation.—Internal rotation in the 2-thiabutane molecule is a case of compound rotation and it was treated by the methods of Kilpatrick and Pitzer.[12] As no electron diffraction or X-ray study of the structure of 2-thiabutane has been made, the bond distances and angles were estimated by analogy with closely related molecules. The values used were: S–C distance, 1.82 Å.; C–C distance, 1.54 Å.; C–H distance, 1.09 Å.; C–S–C angle, 105°; S–C–C angle, and all methyl and methylene group bond angles, 109° 28′. The 1948 atomic weights and the values of the fundamental constants given by Wagman, *et al.*,[13] were used in all computations of this paper. The product of the three principal moments of inertia for over-all rotation was calculated to be 4.192×10^{-114} g.^{3} cm.^{6} The off-diagonal elements in the reduced internal rotational matrix (D) were found to be small; dropping them affected the square root of the determinant of D by about 1.2%. Therefore, it was permissible to treat the internal rotations independently, using the diagonal elements as reduced moments of inertia. These were 4.835×10^{-40}, 4.867×10^{-40} and 23.39×10^{-40} g. cm.^{2} for CH_3–C, CH_3–S and skeletal rotation, respectively. All the inertial quantities given above are for the extended configuration of C_s symmetry.

Taking the energy difference between the two rotational isomers to be zero permits a simple threefold cosine-type barrier to be used for the skeletal rotation as well as for the methyl rotations. The barriers for internal rotation about the two C–S bonds are not equivalent. However, the difference between them is probably small and for purposes of thermodynamic calculations not significant. Therefore, the same barrier height was used for both rotations about C–S bonds. This barrier height and that for rotation about the C–C bond were selected to fit the calorimetric values of the entropy and of the heat capacity at the lower temperatures where the effects of anharmonicity are small. The barrier heights so obtained were 1970 cal./mole for internal rotation about the C–S bonds and 3930 cal./mole for internal rotation about the C–C bond. The former value is nearly identical with the barrier height for rotation about the C–S bonds in 2-thiapropane, 2000 cal./mole.[14]

The internal rotation about the C–C bond in 2-thiabutane has no close analogy for which the barrier height is known. However, since sulfur and chlorine atoms have similar van der Waals radii, the barrier height would be expected to approximate that in ethyl chloride. The barrier height in ethyl chloride, 3700 cal./mole,[15] is in fact close to that found in 2-thiabutane.

Thermodynamic Functions.—Thermodynamic functions were computed for 2-thiabutane using the vibrational frequencies, moments and reduced moments of inertia and barriers to internal rotation given in the two previous sections. The calculated values of the entropy at 301.66, 319.76 and 339.81°K., 79.88, 81.24 and 82.71 cal./deg./mole, may be compared with the calorimetric values of 79.89, 81.25 and 82.70 cal./deg./mole, respectively. The calculated and observed values of the heat capacity, C_p^0, are compared in Table V; the differences are about those to be expected from the neglect of anharmonicity in the calculated values. The satisfactory agreement of the calculated and observed values of the entropy and heat capacity may be regarded as confirming the spectroscopic evidence that the rotational isomers have nearly the same energy.

Values of the functions, $(H_0^0 - F_T^0)/T$, $H_T^0 - H_0^0$, S^0 and C_p^0, were computed for selected temperatures up to 1000°K. and are listed in Table VIII. Some entries in the table are given to more decimal places than is justified by their absolute accuracy, in order to retain internal consistency among the different functions.

TABLE VIII

THERMODYNAMIC FUNCTIONS OF 2-THIABUTANE

T, °K.	$(H^0 - F^0_T)/T$, cal./deg./mole	$H^0_T - H^0_0$, kcal./mole	S^0, cal./deg./mole	C_p^0, cal./deg./mole
298.16	64.25	4.583	79.62	22.72
300	64.34	4.625	79.76	22.81
400	69.11	7.152	86.99	27.74
500	73.36	10.16	93.67	32.21
600	77.28	13.57	99.89	36.06
700	80.93	17.34	105.71	39.38
800	84.37	21.42	111.14	42.25
900	87.64	25.77	116.27	44.75
1000	90.74	30.37	121.11	46.93

Steric Considerations.—In *n*-butane itself it is well-established that the skew (C_2) form has about

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quencies, and because 870 cm.$^{-1}$ can scarcely be considered a characteristic frequency of an ethyl group bonded to sulfur since no frequency near this value is found in the spectra of 2-thiabutane, 3-thiapentane or 3,4-dithiahexane. The 870 cm.$^{-1}$ frequency of ethanethiol is more likely the S–H deformation frequency and the weak Raman line at 838 cm.$^{-1}$ is probably not a fundamental. The weak band observed at 1309 cm.$^{-1}$ in the infrared spectrum of the liquid [unpublished measurements of A.P.I. Research Project 48A at the Laramie Station of the Bureau of Mines] was assigned to CH_2 twisting.

[12] Kilpatrick and Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

[13] Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[14] Osborne, Doescher and Yost, THIS JOURNAL, **64**, 169 (1942).

[15] Gordon and Giauque, *ibid.*, **70**, 1509, 4277 (1948).

800 cal./mole higher energy than the *trans* (C_{2h}) form. This difference in energy probably arises largely from steric repulsion between the terminal methyl groups in the skew configuration. In the skew configuration of 2-thiabutane, by virtue of the C–S bond distance being longer than the C–C bond distance, the terminal methyl groups are farther apart than in the skew configuration of *n*-butane. This greater separation of the methyl groups must reduce the steric repulsion between them to the point where it does not result in any energy difference between the rotational isomers large enough to detect by current spectroscopic or thermodynamic methods.

Summary

The heat capacity of 2-thiabutane in the solid and liquid states was measured over the temperature range 14–298°K. The melting point (167.23 ± 0.05°K.) and heat of fusion (2,333 cal./mole) were determined. The vapor pressure was measured over the temperature range 23–101° and the following equation was selected to represent the data: $\log_{10}p = 6.93849 - 1182.562/(t + 224.784)$. The heat of vaporization was measured at 301.66, 319.76 and 339.81°K., and the values found were 7563, 7329 and 7055 cal./mole, respectively. The heat capacity of the vapor was measured at five different temperatures in the range 327 to 487°K. The experimental values of $C_p{}^0$, the heat capacity of the ideal gas state, may be represented by the equation: $C_p{}^0 = 5.11 + 6.5448 \times 10^{-2}\,T - 2.1735 \times 10^{-5}\,T^2$. An equation for the second virial coefficient, B, in the equation of state $PV = RT + BP$ was obtained from thermal data. This equation is B (cc.) $= -257 - 68.13 \exp(900/T)$. The entropy of liquid 2-thiabutane at 298.16°K. is 57.14 ± 0.10 cal./deg./mole, and the entropy of the vapor in the ideal gas state at the normal boiling point, 339.81°K., is 82.70 ± 0.15 cal./deg./mole.

A vibrational assignment was made for 2-thiabutane. Interpretation of the spectroscopic data led to the conclusion, which was confirmed by the thermal data, that the two rotational isomers have nearly the same energy. The heights of the potential barriers hindering internal rotation which were selected to fit the calorimetric data are 1970 cal./mole for rotation about either C–S bond and 3820 cal./mole for rotation about the C–C bond. The thermodynamic functions $(H_0^0 - F_T^0)/T$, $H_T^0 - H_0^0$, S^0 and $C_p{}^0$ were computed for selected temperatures up to 1000°K.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Empirical Analysis of Viscosity Data[1]

BY H. TRACY HALL AND RAYMOND M. FUOSS[2]

Introduction

The capillary viscometer is essentially a device in which a volume V of liquid flows through a capillary of length l and radius R in t seconds under a pressure of p g./cm.^{2}. Using Poiseuille's equation, we may calculate the viscosity η (in poises) by the relationship

$$\eta = \pi g p R^4 t / 8 V l \qquad (1)$$

For a given viscometer, the product pt should be constant if (1) is satisfied; actually, as is well known, the product usually increases as the driving pressure decreases. Three effects, inherent in the design of the viscometer, contribute to this variation: (1) all of the work done by the driving pressure is not dissipated as heat in overcoming viscous friction; (2) flow near the ends of the capillary is not laminar; (3) the volume of liquid which flows from the bulb is not the volume of the dry bulb. Of these, the first is usually the largest correction term for ordinary liquids ($\eta \approx 10^{-2}$) in conventional viscometers. If correction is made for these instrument effects, and the pt product still varies with driving pressure, then we may conclude that the liquid is non-Newtonian, *i.e.*, that $\eta = \eta(p)$. For the usual range of driving pressures (giving average velocity gradients of the order of 10^3 seconds^{-1}), $1/pt$ is linear in p over a much wider range of variables than that corresponding to linearity of pt in $1/t$. We present in this paper an empirical analysis of viscosity data, which permits isolation of the shear-dependent term of the viscosity.

Kinetic Energy and End Effect Corrections.—The liquid leaving the viscometer capillary is travelling with finite velocity; therefore, only part of the work done by the driving pressure overcomes viscous friction within the capillary. The corresponding correction has been accordingly called the kinetic energy correction. Wilberforce[3] made an important correction to Hagenbach's[4] first estimate of this quantity and also made an estimate of the end effects on Reynolds'[5] analysis of the transition from laminar to turbulent flow. Wilberforce's result may be written

$$\eta = \pi g p R^4 t / 8 V l - m \rho V / 8 \pi l t \qquad (2)$$

$$= \alpha p t - \beta / t \qquad (2')$$

If the constant m were unity, the second term on the right then would be the kinetic energy correction, calculated on the assumption that the flow throughout the length of the capillary were laminar; *i.e.*, $m = 1$ corresponds to the case of negligible end effects. Ample experimental evidence shows that, while m is near unity, its actual value is somewhat greater. In other words, practical viscometers have end effects which may not be neglected. A

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(1) Presented at the Schenectady Meeting of the National Academy of Sciences, October, 1950.

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(3) L. R. Wilberforce, *Phil. Mag.*, **31**, 407 (1891); *cf.* also G. Barr "Monograph on Viscometry," Oxford University Press, London, 1931, p. 16.

(4) E. Hagenbach, *Pogg. Ann.*, **109**, 385 (1860).

(5) O. Reynolds, *Phil. Trans.*, **174**, 935 (1883).