complex seems not to form under the experimental conditions.

The principal vanadium species present in the exchange mixtures appear to be the pervanadyl ion,[12] generally formulated as $V(OH)_4^+$, and the vanadyl ion,[13,14] written as VO^{++}. The potential measurements of Carpenter[12] and of Coryell and Yost[10] suggest that formation of chloride complexes (as might form in the ether extraction separation method) does not take place in hydrochloric acid solutions up to 2 *f*, although such complexes could exist at higher chloride ion concentrations.

Rona[15] has found rapid, but measurable, exchange of uranium between uranium(IV) oxychloride, $UOCl_2$, and uranyl chloride, UO_2Cl_2, in aqueous solutions, which system bears a formal resemblance to that reported in this paper.

Summary

Exchange of radiovanadium between vanadyl and pervanadyl ions in 0.6 and 0.9 *f* perchloric acid and in 7 *f* hydrochloric acid has been found to be complete at room temperature in exchange times of one minute. Although identical results were obtained with three different chemical separation methods, the possibility of an induced exchange cannot be ruled out.

LOS ANGELES 24, CALIFORNIA

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[12] J. E. Carpenter, THIS JOURNAL, **56**, 1847 (1934).

[13] H. T. S. Britton, *J. Chem. Soc.*, 1842 (1934).

[14] H. T. S. Britton and G. Welford, *ibid.*, 758 (1940).

[15] E. Rona, Abstracts, 113th Meeting of the A. C. S., Chicago, Illinois, April, 1948.

[CONTRIBUTION NO. 18 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

2,3-Dithiabutane: Low Temperature Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions[1,2]

BY D. W. SCOTT, H. L. FINKE, M. E. GROSS, G. B. GUTHRIE AND H. M. HUFFMAN

The organic sulfur compounds are divided into a number of structural classes, and it is of interest to study the thermodynamic properties of members of each class to determine the effect of structure on these properties. The simplest member of the alkyl disulfide class, 2,3-dithiabutane (dimethyl disulfide), was selected for the initial study of that class. In this paper are presented: (a) the results of low temperature thermal studies and vapor pressure measurements which yield a value of the entropy of 2,3-dithiabutane in the vapor state, and (b) thermodynamic functions of 2,3-dithiabutane calculated from spectroscopic and molecular structure data.

The Material.—The 2,3-dithiabutane was an API–BM "Sample of Organic Sulfur Compounds" prepared and purified by API Project 48A at the Laramie Station of the Bureau of Mines.

In the course of the low temperature investigations, a calorimetric study was made of the melting point against the fraction melted. From these data the impurity was calculated to be 0.03 ± 0.01 mole per cent. The results of this study are given in Table I.

In the ebulliometric vapor pressure studies, the boiling and condensation temperatures of the sample were found to differ by only 0.001° at the normal boiling point. The material is therefore in group V on Swietoslawski's scale of degree of purity[3] (difference in boiling and condensation temperatures 0.000–0.005°).

TABLE I

2,3-DITHIABUTANE MELTING POINT SUMMARY, 0 °C. = 273.16 °K., $N_2/F = 0.0311\,\Delta T$

% Melted	*T*, °K. Obsd.	*T*, °K. Calcd.
10.5	188.368	188.343
26.1	.404	.401
50.7	.420	.420
70.8	.426	.426
90.9	.429	.429
100		.430
Pure		.440
Triple point	188.44 °K.	
Impurity	0.031 ± 0.010 mole%	

The Apparatus.—The low-temperature measurements were made in an apparatus similar to that described by Ruehrwein and Huffman.[4] Very briefly, the method was as follows: about 0.57 mole of the material under investigation was contained in a sealed platinum calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for the determination of the resistance of the thermometer and the elec-

[1] This investigation was performed at the Petroleum Experiment Station of the Bureau of Mines jointly by The Thermodynamics Laboratory and the American Petroleum Institute Research Project 48A on The Production, Isolation, and Purification of Sulfur Compounds and Measurement of Their Properties.

[2] Article not copyrighted.

[3] Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945.

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

trical energy were made on a White double potentiometer in conjunction with a high-sensitivity galvanometer and accurately calibrated resistances. The potential was in terms of a bank of *six* thermostated saturated cadmium cells, which had been certified by the National Bureau of Standards. Time measurements were made with an electric stop clock, which was operated by an a.c. power supply, the frequency of which was accurate to 0.001%. 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%. The energy measurements were made in terms of the international joule and were converted to calories by dividing by 4.1833.

The vapor pressure measurements were made by a static method over the temperature range 0–60° and by an ebulliometric method over the temperature range 60–130°. The apparatus and methods used for each type of vapor-pressure measurement have been described previously.[5] In the course of some preliminary studies by the static method, a slow reaction was found to occur between 2,3-dithiabutane and mercury, as shown by a film of white solid material (possibly mercury methylmercaptide) which formed on the wall of the manometer tube. In making the final measurements, this reaction with mercury was minimized by keeping the sample refrigerated with solid carbon dioxide at all times except when measurements were actually in progress. The results obtained by the static method were in satisfactory accord with those obtained by the ebulliometric method, in which the sample was not exposed to mercury. This was shown by fitting Antoine equations to the data obtained by the static method alone and to the data obtained by the ebulliometric method alone. At 60°, where the two sets of measurements join, the pressures calculated from the two equations differed by only 0.09% and the values of dp/dt from the two equations differed by only 0.05%. It therefore appears that any reaction with mercury which may have occurred during the final measurements by the static method was insufficient to introduce any significant errors into the data obtained. However, because of this complication, a somewhat larger uncertainty was assigned to the heat of vaporization calculated from the vapor pressure data than would otherwise have been done.

Results

The results of the low temperature heat capacity measurements are given in Table II, and Table III lists the values of $C_{\text{satd.}}$ at integral temperatures as selected from a smooth curve through all of the data. Two experimental values of the heat of fusion were determined and are given in Table IV.

TABLE II

THE MOLAL HEAT CAPACITY OF 2,3-DITHIABUTANE: 0 °C. = 273.16 °K., MOL. WT. = 94.200

T, °K.	ΔT	$C_{\text{satd.}}$, cal. deg.$^{-1}$	T, °K.	ΔT	$C_{\text{satd.}}$, cal. deg.$^{-1}$
13.08	0.935	1.076	131.28	7.923	19.890
14.13	1.159	1.290	132.57	7.660	20.019
15.86	2.360	1.673	139.56	8.625	20.595
16.14	2.245	1.741	140.74	8.667	20.700
18.30	2,556	2.279	148.36	8.990	21.327
18.49	2.489	2.331	149.27	8.400	21.412
20.56	1.995	2.880	157.64	9.566	22.086
20.99	2.542	3.000	158.13	9.314	22.119
22.77	2.440	3.482	166.56	8.261	22.810
23.92	3.332	3.785	167.30	9.033	22.887
25.47	2.973	4.192	174.21	7.044	23.451
27.32	3.501	4.675	181.17	6.880	24.116
28.57	3.249	5.009		Liquid	
30.86	3.590	5.594	191.99	4.916	34.331
34.28	3.241	6.463	196.27	5.097	34.235
37.78	3.778	7.262	199.10	9.326	34.221
42.14	4.928	8.211	203.91	10.195	34.176
47.38	5.560	9.296	208.94	10.344	34.127
52.64	4.947	10.333	214.10	10.173	34.115
55.95	4.659	10.953	219.27	10.323	34.091
60.86	5.156	11.805	224.26	10.151	24.091
66.23	5.576	12.677	229.57	10.297	34.080
71.63	5.229	13.455	239.84	10.248	34.141
77.06	5.644	14.228	250.07	10.212	34.204
82.56	5.344	14.980	260.25	10.162	34.294
85.80	5.654	15.396	270.38	10.109	34.432
87.98	5.507	15.677	272.08	11.937	34.449
92.22	7.177	16.135	280.46	10.051	34.583
93.39	5.303	16.276	283.97	11.851	34.656
98.60	5.129	16.821	290.47	9.983	34.780
99.30	6.979	16.878	295.77	11.751	34.899
104.07	5.793	17.373	300.41	9.917	34.973
106.68	7.794	17.627	300.64	9.730	34.958
110.22	6.520	17.978	310.83	10.662	35.189
114.85	8.538	18.414	321.44	10.550	35.468
117.15	7.336	18.640	331.96	10.489	35.762
123.22	8.205	19.187	342.40	10.393	36.065
124.78	7.925	19.333	352.27	9.356	36.366

The results of the vapor pressure measurements are given in Table V. The data obtained by both methods were fitted to an Antoine equation by a least squares adjustment, using appropriate weighting factors for each point. The equation obtained is

$$\log_{10} p = 6.97792 - 1346.342/(t + 218.863) \quad (1)$$

Values of the vapor pressure calculated by means of this equation are included in Table V for comparison with the observed values. The normal boiling point of 2,3-dithiabutane calculated from eq. (1) is 109.75°.

The heat of vaporization at 25° was calculated from the vapor pressure data by means of the Clapeyron equation. Since no equation of state or values of the critical constants were available for 2,3-dithiabutane, it was desirable to estimate the molar volume of the saturated vapor by means of an empirical correlation based on equation of state data for other substances. Values at 298.16° K.

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(5) Waddington, Knowlton, Scott, Oliver, Todd, Hubbard, Smith and Huffman, THIS JOURNAL, **71**, 797 (1949).

TABLE III

MOLAL HEAT CAPACITY OF 2,3-DITHIABUTANE AT INTEGRAL TEMPERATURES

T, °K.	$C_{\text{satd.}}$, cal. deg.$^{-1}$	T, °K.	$C_{\text{satd.}}$, cal. deg.$^{-1}$	T, °K.	$C_{\text{satd.}}$, cal. deg.$^{-1}$
13	1.060	90	15.900	210	34.130
14	1.260	95	16.440	220	34.090
15	1.480	100	16.950	230	34.090
20	2.730	110	17.950	240	34.140
25	4.070	120	18.900	250	34.200
30	5.370	130	19.780	260	34.290
35	6.630	140	20.635	270	34.420
40	7.750	150	21.470	280	34.580
45	8.810	160	22.280	290	34.760
50	9.820	170	23.090[a]	298.16	34.925
55	10.780	180	23.900[a]	300	34.960
60	11.660	188.44	24.585[a]	310	35.175
65	12.470	Liquid		320	35.430
70	13.225	188.44	34.370	330	35.710
75	13.945	190	34.340	340	35.990
80	14.640	200	34.210	350	36.290
85	15.295			360	36.590

[a] Extrapolated values.

TABLE IV

MOLAL HEAT OF FUSION, ΔH, CALORIES

Expt. 1	Expt. 2	Av.
2197.0	2197.2	2197.1 ± 0.1[a]

[a] Precision uncertainty.

TABLE V

VAPOR PRESSURE OF 2,3-DITHIABUTANE

	Vapor pressure, mm.		
t, °C.	80% of sample	20% of sample	Calcd. (eq. 1)
	Static Method		
0.00	6.77	6.79	6.70
15	16.75	16.70	16.63
20	22.06	21.98	21.95
25	28.73	28.64	28.64
30	37.03	36.93	36.98
35	47.31	47.20	47.26
40	59.85	59.78	59.83
45	75.11	75.00	75.07
50	93.40	93.33	93.41
55	115.21	115.18	115.29
60	141.19	141.03	141.24

Ebulliometric Method

Boiling point, °C.		Vapor pressure, mm.	
Water	2,3-Dithiabutane	Obs.	Calcd. (eq. 1)
60.000	61.411	149.41	149.37
65	67.301	187.57	187.56
70	73.234	233.72	233.72
75	79.201	289.13	289.04
80	85.218	355.22	355.09
85	91.283	433.56	433.44
90	97.393	525.86	525.76
95	103.540	633.99	633.81
100	109.739	760.00	759.87
105	115.984	906.06	906.04
110	122.273	1074.6	1074.7
115	128.611	1268.0	1268.4

of the second virial coefficient, B, in the equation of state $PV = RT + BP$, for twenty-three non-associated compounds boiling above 0° were available either from the literature or from unpublished results of this Laboratory. When the ratio of $-B$ to the molar volume of the liquid, $(-B/V_L)_{298.16}$, was plotted *vs.* the vapor pressure at 298.16° K., using logarithmic scales as in Fig. 1, the twenty-three values of $(-B/V_L)_{289.16}$ fell within about 20% of the least squares straight line through all of the points. The equation of the line in Fig. 1 is

$$\log_{10} (-B/V_L)_{298.18} = 1.679 - 0.246 \log_{10} p_{298.16} \text{ (mm.)} \quad (2)$$

Equation (2) allows the second virial coefficient at 298.16° K. to be estimated to about 20% for substances for which only vapor pressure and liquid density data are available. Thus for 2,3-dithiabutane at 298.16° K., p = 28.64 mm., d = 1.052 g. ml.,[6] and V_L = 89.5 ml., then from eq. (2), $(-B/V_L) = 21 \pm 4$, $B = -1.9 \pm 0.4$ liters, and $V_g = (RT/P) - 1.9 = 647.2 \pm 0.4$ liters.

Using this value of the vapor volume, the heat of vaporization is computed to be 9,181 cal./mole with an estimated uncertainty of ±75 cal./mole. The latter value includes the uncertainty in the estimation of the vapor volume as well as that resulting from experimental uncertainty in the vapor pressure data.

The experimental results have been utilized to compute the entropy of 2,3-dithiabutane at 298.16° K. for both the liquid and the vapor states. These entropy calculations are summarized in Table VI.

TABLE VI

ENTROPY OF 2,3-DITHIABUTANE, CAL./DEG./MOLE

$S_{13°\text{K.}}$ Debye, 3.5° freedom, $\theta = 99.9$	0.382
$\Delta S_{13-188.44}$ solid, graphical	28.484
$\Delta S_{188.44}$ fusion, 2197.1/188.44	11.659
$\Delta S_{188.44-298.16}$ liquid, graphical	15.735
Entropy of liquid at 298.16°K.	56.26 ± 0.10
$\Delta S_{298.16}$ vaporization, 9181/298.16	30.79
$\Delta S_{298.16}$ compression	−6.51
Entropy of ideal gas at 1 atm. and 298.16°K.	80.54 ± 0.30

Vibrational Assignment and Normal Coordinate Calculations.—In order to obtain information about the barriers to internal rotation in the 2,3-dithiabutane molecule, and in order to extend the calorimetric data to other thermodynamic functions and to higher temperatures, a complete vibrational assignment was necessary. The spectroscopic data used in making the vibrational assignment were the Raman measurements of Gerding and Westrik[7] and the infrared measurements of Trotter and Thompson[8], as given in Ta-

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(6) Haines, Wenger, Helm and Ball, Bureau of Mines Report of Investigations 4060, December, 1946.

(7) Gerding and Westrik, *Rec. trav. chim.*, **61**, 412 (1942).

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

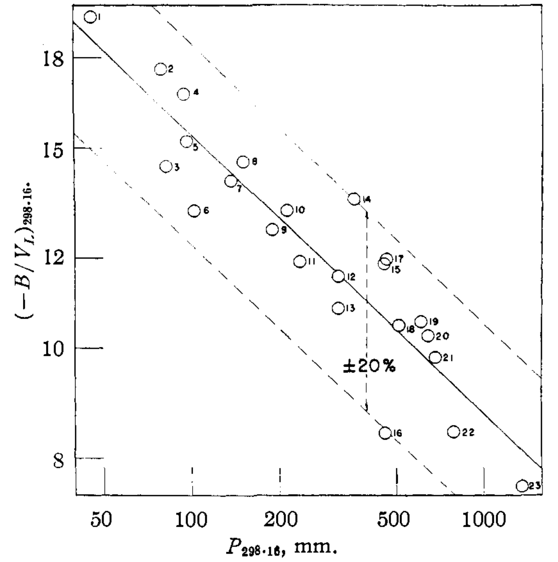

Fig. 1.—$(-B/V_L)_{298.16}$ *vs.* vapor pressure at 298.16°K. for: 1, *n*-heptane; 2, thiophene; 3, 3,3-dimethylpentane; 4, benzene; 5, cyclohexane; 6, 2,2,3-trimethylbutane; 7, methylcyclopentane; 8, *n*-hexane; 9, 3-methylpentane; 10, 2-methylpentane; 11, 2,3-dimethylbutane; 12, cyclopentane; 13, 2,2-dimethylbutane; 14, carbon disulfide; 15, spiropentane; 16, 1,1,2-trichloro-1,2,2-trifluoroethane; 17, 2-methyl-2-butene; 18, *n*-pentane; 19, 2-methyl-1-butene; 20, 1-pentene; 21, 2-methylbutane; 22, trichlorofluoromethane; 23, dichlorofluoromethane.

ble VII; the Raman data of earlier investigators[9] were also considered.

TABLE VII

SPECTRA OF 2,3-DITHIABUTANE

Raman (liq.)	ρ	Infrared (liq.)	Assignment	
±116 (d)			Int. rot. about S–S	
240 (7)	0.70		S–S–C bend	A
272 (4)	1.0		S–S–C bend	B
467 (0)			2 × 240 = 480	
510 (9)	.26	517 (m)	S–S str.	A
		533 (vw)	2 × 272 = 544	
694 (10)	.44	690 (s)	C–S str.	A & B
744 (0)		741 (?)	240 + 517 = 757	
952 (1)		950 (s)	CH_3 rock.	A & B
1117 (0)			?	
		1192 (vw)	517 + 690 = 1207	
1307 (1)		1298 (s)	CH_3 bend. sym.	A & B
1387 (2 br. d.)	.89		CH_3 bend. unsym.	A & B
		1410 (s)	Fermi resonance with	
		1432 (s)	2 × 690 = 1380	
2914 (9)	.17		CH_3 str. sym.	A & B
2985 (5)	.95		CH_3 str. unsym.	A & B

In the preliminary interpretation of these spectroscopic data, it was recognized that there were fewer strong Raman lines and infrared bands than the number of allowed fundamental frequencies in the region of the C–S stretching and methyl rocking vibrations (600–1100 cm.$^{-1}$). Thus it appeared likely that certain of these modes had frequencies which differed so little from one another that they were unresolved in the observed spectra. This supposition was confirmed by normal coördinate calculations which will now be discussed.

The FG matrix method of Wilson[10] was used. The structure taken for the 2,3-dithiabutane molecule (Fig. 2) was based primarily on the electron diffraction results of Stevenson and Beach,[11] who, however, were unable to determine the dihedral angle between the two S–S–C planes. This angle was estimated by analogy with the corresponding dihedral angles in S_2Cl_2 (92 ± 12°)[12] and $(CH_3)_2S_3$ (about 106°)[13] to be approximately a right angle, and a value of 90° was used in all of the computations. An accurate value of this angle is not essential for the normal coördinate treatment, since the only calculated frequencies that are sensitive to the value taken for the dihedral angle are the two S–S–C bending frequencies, and these are readily assignable from the observed spectra.

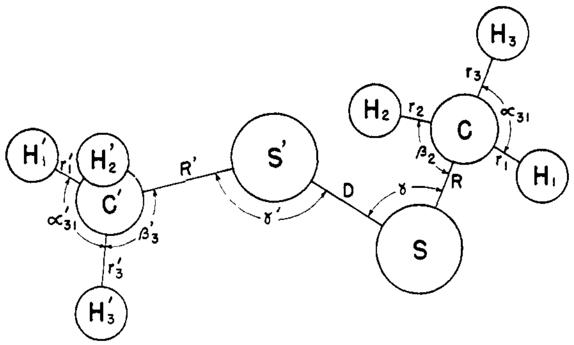

Fig. 2.—Typical internal coördinates of the 2,3-dithiabutane molecule.

The internal coördinates chosen to describe the motions of the 2,3-dithiabutane molecule were the increases in the lengths of the six C–H bonds (r's), the two S–C bonds (R's), and the S–S bond (D), and the increases in the six H–C–H angles (α's), the six S–C–H angles (β's), and the two S–S–C angles (γ's). Typical coördinates are shown in Fig. 2. Omission of the three internal rotations is justified, since these will not interact significantly with the C–S stretching and methyl rocking modes about which the normal coördinate calculations are primarily concerned. The molecule has C_2 symmetry and the vibrations fall into two symmetry classes, A and B, depending on whether they are symmetric or anti-symmetric with respect to rotation about the two-fold axis. The twenty-three internal coordinates were combined into twenty-one true symmetry coördinates and two redundant coördinates: For the A vibrations

1. $(1\sqrt{6})(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_1' + \Delta r_2' + \Delta r_3')$
2. $(1/\sqrt{12})(2\Delta r_1 - \Delta r_2 - \Delta r_3 + 2\Delta r_1' - \Delta r_2' - \Delta r_3')$

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[9] (a) Venkateswaren, *Indian J. Physics*, **6**, 51 (1931); (b) Bonino and Manzoni-Ansidei, *Mem. accad. sci. inst. Bologna, classe sci. fis.*, **9**, 1 (1934).

[10] Wilson, (a) *J. Chem. Phys.*, **7**, 1047 (1939); (b) **9**, 76 (1941).

[11] Stevenson and Beach, THIS JOURNAL, **60**, 2872 (1938).

[12] Guthrie, Thesis, California Institute of Technology, 1949.

[13] Donohue and Schomaker, *J. Chem. Phys.*, **16**, 92 (1948).

3. $(1/2)(\Delta r_2 - \Delta r_3 + \Delta r_2' - \Delta r_3')$
4. $(1/\sqrt{12})(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\alpha_{12}' + \Delta\alpha_{23}' + \Delta\alpha_{31}' - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 - \Delta\beta_1' - \Delta\beta_2' - \Delta\beta_1')$
5. $(1/\sqrt{12})(2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{31} + 2\Delta\alpha_{23}' - \Delta\alpha_{12}' - \Delta\alpha_3')$
6. $(1/2)(\Delta\alpha_{31} - \Delta\alpha_{12} + \Delta\alpha_{31}' - \Delta\alpha_{12}')$
7. $(1/\sqrt{12})(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + 2\Delta\beta_1' - \Delta\beta_2' - \Delta\beta_3')$
8. $(1/2)(\Delta\beta_2 - \Delta\beta_3 + \Delta\beta' - \Delta\beta_3')$
9. $(1/\sqrt{2})(\Delta R + \Delta R')$
10. ΔD
11. $(1/\sqrt{2})(\Delta\gamma + \Delta\gamma')$
12. $(1/\sqrt{12})(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\alpha_{12}' + \Delta\alpha_{23}' + \Delta\alpha_{31}' + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_1' + \Delta\beta_2' + \Delta\beta_3')$
    $\equiv 0$ (Redundant coördinate)

and for the B vibrations

1. $(1/\sqrt{6})(\Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_1' - \Delta r_2' - \Delta r_3')$
2. $(1/\sqrt{12})(2\Delta r_1 - \Delta r_2 - \Delta r_3 - 2\Delta r_1' + \Delta r_2' + \Delta r_3')$
3. $(1/2)(\Delta r_2 - \Delta r_3 - \Delta r_2' + \Delta r_3')$
4. $(1/\sqrt{12})(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} - \Delta\alpha_{12}' - \Delta\alpha_{23}' - \Delta\alpha_{31}' - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_1' + \Delta\beta_2' + \Delta\beta_3')$
5. $(1/\sqrt{12})(2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{31} - 2\Delta\alpha_{23}' + \Delta\alpha_{12}' + \Delta\alpha_{31}')$
6. $(1/2)(\Delta\alpha_{31} - \Delta\alpha_{12} - \Delta\alpha_{31}' + \Delta\alpha_{12}')$
7. $(1/\sqrt{12})(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 - 2\Delta\beta_1' + \Delta\beta_2' + \Delta\beta_3')$
8. $(1/2)(\Delta\beta_2 - \Delta\beta_3 - \Delta\beta_2' + \Delta\beta_3')$
9. $(1/\sqrt{2})(\Delta R - \Delta R')$
10. $(1/\sqrt{2})(\Delta\gamma - \Delta\gamma')$
11. $(1/\sqrt{12})(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} - \Delta\alpha_{12}' - \Delta\alpha_{23}' - \Delta\alpha_{31}' + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_1' - \Delta\beta_2' - \Delta\beta_3')$
    $\equiv O$ (Redundant coördinate)

Assuming tetrahedral bond angles and omitting the redundant coördinate, the non-vanishing elements of the G matrix for the A symmetry class are found to be: $G_{11} = \mu_H + \mu_C/3$, $G_{14} = (-4\epsilon/3)\mu_C$, $G_{19} = -\mu_C/\sqrt{3}$, $G_{22} = \mu_H + (4/3)\mu_C$, $G_{25} = (4\epsilon\sqrt{2}/3)\mu_C$, $G_{27} = -\sqrt{2}(\tau + \epsilon/3)\mu_C$, $G_{2,11} = (-2\tau/\sqrt{3})\mu_C$, $G_{33} = \mu_H + (4/3)\mu_C$, $G_{36} = (4\epsilon\sqrt{2}/3)\mu_C$, $G_{38} = -\sqrt{2}(\tau + \epsilon/3)\mu_C$, $G_{44} = 2\epsilon^2\mu_H + (16/3)\epsilon^2\mu_C$, $G_{49} = (4\epsilon/\sqrt{3})\mu_C$, $G_{55} = (5\epsilon^2/2)\mu_H + (8\epsilon^2/3)\mu_C$, $G_{57} = (\epsilon^2/2)\mu_H - 2\epsilon(\tau + \epsilon/3)\mu_C$, $G_{5,11} = (-4\epsilon\tau/\sqrt{6})\mu_C$, $G_{66} = (5\epsilon^2/2)\mu_H + (8\epsilon^2/3)\mu_C$, $G_{68} = (\epsilon^2/2)\mu_H - 2\epsilon(\tau + \epsilon/3)\mu_C$, $G_{77} = \epsilon^2\mu_H + (3\tau^2/2)\mu_S + (3/2)(\tau + \epsilon/3)^2\mu_C$, $G_{7,10} = -\sqrt{8/3}\tau\mu_S$, $G_{7,11} = (\epsilon\tau/\sqrt{6} + \sqrt{3/2}\tau^2)\mu_C + (\sqrt{3/2}\tau^2 + \sigma\tau/\sqrt{6})\mu_S$, $G_{88} = \epsilon^2\mu_H + (3\tau^2/2)\mu_S + (3/2)(\tau + \epsilon/3)^2\mu_C$, $G_{8,11} = \sqrt{3/2}\,\sigma\tau\mu_S$, $G_{99} = \mu_C + \mu_S$, $G_{9,10} = (-\sqrt{2}/3)\mu_S$, $G_{9,11} = (-\sqrt{8}\sigma/3)\mu_S$, $G_{10,10} = 2\mu_S$, $G_{10,11} = (-4\tau/3)\mu_S$, $G_{11,11} = \tau^2\mu_C + (\tau^2 + 2\sigma^2 + 2\sigma\tau/3)\mu S$, together, of course, with the elements related to these by the symmetry $G_{ij} = G_{ji}$ of the matrix. Here μ_H, μ_C, and μ_S are the reciprocals of the masses of hydrogen, carbon and sulfur atoms, and ϵ, τ and σ are the reciprocals of the equilibrium lengths of the C–H bonds (1.09 Å.), S–C bonds (1.78 Å.), and the S–S bond (2.04 Å.), respectively. The G matrix for the B symmetry class is obtained from the one for the A symmetry class by deleting the tenth row and column and changing the sign of $G_{8,11}$.

Since the matrix equations were of an inconveniently high order, they were reduced by "splitting out" of each equation six of the higher frequency internal vibrations of the methyl groups, namely, the three C–H stretching vibrations and the three CH_3 bending vibrations. The equations were reduced by Wilson's method[10b] which in the present case is equivalent to setting the force constants for C–H stretching and H–C–H angle bending equal to infinity. Thus in each of the G matrices given, the first six rows and columns were eliminated, with slight modifications in the rest. The secular equations of eleventh and tenth degree were thus reduced to more tractable equations of fifth and fourth degree.

A simple potential energy function having no interaction terms was used. It was

$$2V = k_\beta[(\Delta\beta_1)^2 + (\Delta\beta_2)^2 + (\Delta\beta_3)^2 + (\Delta\beta_1')^2 + (\Delta\beta_2')^2 + (\Delta\beta_3')^2] + k_R[(\Delta R)^2 + (\Delta R')^2] + k_D(\Delta D)^2 + k_\gamma[(\Delta\gamma)^2 + (\Delta\gamma')^2]$$

Values of the four force constants were selected so that the calculated frequencies for the A symmetry class agreed satisfactorily with the observed frequencies, which were taken to be 240, 517, and 690 cm.$^{-1}$ plus two unresolved frequencies at about 950 cm.$^{-1}$. The force constants so obtained are

$k_\beta = 0.588 \times 10^{-11}$ ergs/radian^2
$k_\gamma = 1.06 \times 10^{-11}$ ergs/radian^2
$k_R = 2.73 \times 10^5$ dyne/cm.
$k_D = 2.55 \times 10^5$ dyne/cm.

TABLE VIII

CALCULATED AND OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENT FOR 2,3-DITHIABUTANE

Type of vibration	Sym. class	Calcd.	Obs.	Assigned
S-S-C bend.	A	240	240 R (p)	240
S-S-C bend.	B	281	272 R (d)	272
S-S str.	A	516	510 R (p); 517 IR	517
S-C str.	A	690	694 R (p); 690 IR	690 (2)
S-C str.	B	676		
CH_3 rock.	A	941	952 R; 950 IR	950 (4)
CH_3 rock.	A	958		
CH_3 rock.	B	944		
CH_3 rock.	B	952		
CH_3 bend. sym.	A & B	...	1307 R; 1298 IR	1300 (2)
CH_3 bend. unsym.	A(2) & B(2)	...	1410 & 1432 IR	1425 (4)
C-H str. sym.	A & B	...	2914 R (p)	2915 (2)
C-H str. unsym.	A(2) & B(2)	...	2985 R (d)	2985 (4)

These constants were then used to compute the frequencies for the B symmetry class. The calculated and observed frequencies are listed in Table VIII, which also includes the vibrational assignment used for thermodynamic calculations. The normal coördinate calculations support the idea that the two C–S stretching modes and likewise the four methyl rocking modes have frequencies too close together to have been resolved spectroscopically. The calculated values for the two C–S stretching modes differ by only 14 cm.$^{-1}$ and it seems justifiable to use the observed frequency of 690 cm.$^{-1}$ for both vibrations. An analogous situation is found in the Raman spectrum of S_2Cl_2,[14] in which the two S–Cl stretching frequencies are unresolved and appear as the broad line at 443 cm.$^{-1}$ The calculated values of the four methyl rocking frequencies cover a range of only 17 cm.$^{-1}$ and the observed value of 950 cm.$^{-1}$ may be used for all of them. The infrared band of liquid 2,3-dithiabutane at 950 cm.$^{-1}$ is unusually broad and appears to be the sum of a number of unresolved bands arising from the different methyl rocking modes.

No detailed assignment was attempted for the thermodynamically unimportant methyl bending and C–H stretching frequencies, which are obviously not all resolved in the observed spectra. The average values listed for these higher frequencies in Table VIII are adequate for the calculation of thermodynamic properties.

The Raman line at 116 cm.$^{-1}$ must arise from one of the internal rotational motions of the molecule, since it cannot be explained as a difference-combination. It is attributed to torsion about the S–S bond, because methyl torsional modes are seldom observed spectroscopically, and because S_2Cl_2 likewise has a low Raman frequency at 106 cm.$^{-1}$ which is most reasonably explained as arising from torsion about the S–S bond.

As shown in Table VII, the observed frequencies not assigned as fundamentals are readily assigned as allowed overtones or sum-combinations with the exception of the very weak Raman line at 1117 cm.$^{-1}$

Internal Rotation

Internal rotation in the 2,3-dithiabutane molecule is a case of compound rotation and it was treated by the methods of Kilpatrick and Pitzer.[15] The same molecular structure parameters were used here as in the normal coördinate calculations, except that the electron-diffraction value of 107° was taken for the S–S–C angle. The 1948 atomic weights and the values of the fundamental constants given by Wagman,[16] *et al.*, were used in all computations of this paper. For over-all rotation, the product of the three principal moments of inertia was found to be 1.001 × 10^{-113} g.^{3} cm.^{6} The reduced internal rotational matrix, in atomic weight-Ångström units, is

$$(D) = \begin{bmatrix} 3.101 & 0.794 & 0.044 \\ 0.794 & 16.425 & 0.794 \\ 0.044 & 0.794 & 3.101 \end{bmatrix}$$

The off-diagonal elements are relatively small; dropping these off-diagonal elements affects the value of the determinant of D by about 2.5% or its square root by about 1.3%. Therefore it is permissible to treat the internal rotations independently, using the diagonal elements as reduced moments of inertia. In c. g. s. units these are 5.15 × 10^{-40} g. cm.^{2} for methyl rotation and 27.27 × 10^{-40} g. cm.^{2} for rotation about the S–S bond.

The detailed shape of the potential barrier hindering rotation about the S–S bond is unknown. The calculated thermodynamic properties will be given with sufficient accuracy by assuming a simple two-fold cosine-type barrier, $v/2(1 + \cos 2\phi)$, where v is the barrier height and ϕ is the angle of rotation measured from the *cis* configuration. From the observed torsional frequency of 116 cm.$^{-1}$, the barrier height is calculated to be 9,500 cal./mole. Qualitatively, it is evident that the rotation is quite highly restricted. No serious error in the calculated thermodynamic functions would have resulted from treating this degree of freedom as a harmonic oscillation with a frequency of 116 cm.$^{-1}$; however the treatment as a restricted rotation includes an appropriate correction for anharmonicity.

The value calculated here for the barrier height has little quantitative significance from the standpoint of molecular structure for several reasons. First, the assumed barrier shape is certainly an oversimplification; the potential energy is probably greater in the *cis* than in the *trans* position. Second, the uncertainties in the molecular structure parameters used with the assumed potential function could lead to an error in the calculated barrier height greater than five per cent. Third, the effect of coupling between internal rotation about the S–S bond and the vibrational degrees of freedom of the molecule has been neglected. A normal coördinate treatment of just the torsion about the S–S bond and the symmetrical S–S–C bending mode showed that the calculated barrier height would be about four per cent. greater if coupling with this low frequency skeletal bending mode were taken into account. The effect of coupling with the other higher-frequency vibrations is much smaller.

For the methyl rotations, three-fold cosine-type potential barriers were assumed. The calorimetric value of the entropy was used to evaluate the barrier height, and the value 1140 cal./mole was obtained. This may be compared with the barriers to rotation of a methyl group bonded to sulfur in methanethiol, 1460 cal./mole,[17] and 2-thiapropane, 2000 cal./mole.[18]

Statistically Calculated Thermodynamic Functions.—The free energy function, heat constant, entropy, and heat capacity of 2,3-dithiabutane vapor were computed for selected temperatures up to 1000° K., using the moments of inertia, vibrational frequencies, and barriers to internal rotation given in previous sections. The symmetry number of the 2,3-dithiabutane molecule is 2, and the two equilibrium positions with regard to skele-

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[14] Gerding and Westrik, *Rec. trav. chim.*, **60**, 701 (1941).

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

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

[17] Russell, Osborne and Yost, THIS JOURNAL, **64**, 165 (1942).

[18] Osborne, Doescher and Yost, *ibid.*, **64**, 169 (1942).

tal rotation result in *d* and *l* forms of the molecule. The thermodynamic functions are tabulated in Table IX. Some entries in the table are given to more significant figures than is justified by their absolute accuracy, in order to retain internal consistency among the different functions.

TABLE IX

THERMODYNAMIC FUNCTIONS OF 2,3-DITHIABUTANE

T, °K.	$(H_0^0-F_T^0)$ cal./deg./mole	$H_T^0-H_0^0$ kcal./mole	S cal./deg./mole	C_p^0 cal./deg./mole
298.16	64.64	4.732	80.51	21.97
300	64.72	4.769	80.62	22.04
400	69.58	7.164	87.49	25.81
500	73.81	9.915	93.64	29.23
600	77.56	13.00	99.22	32.20
700	81.02	16.35	104.37	34.75
800	84.25	19.93	109.16	36.96
900	87.27	23.73	113.63	38.86
1000	90.13	27.71	117.84	40.53

Summary

The heat capacity of 2,3-dithiabutane has been measured over the temperature range 13 to 350°K. The triple point (188.44°K.) and heat of fusion (2197.1 ± 0.1 cal./mole) were determined. The vapor pressure has been measured over the temperature range 0 to 130° and the following equation was found to fit the vapor pressure data: $\log_{10} p$ (mm.) = 6.97792 − 1346.342/(t + 218.863). The normal boiling point is 109.75°; the heat of vaporization calculated from the vapor pressure data is 9,181 ± 75 cal./mole at 298.16°K. The entropy of the liquid is 56.26 ± 0.10 cal./deg./mole and the entropy of the ideal gas at one atmosphere pressure is 80.54 ± 0.30 cal./deg./mole, both at 298.16°K.

A vibrational assignment has been made for 2,3-dithiabutane with the aid of normal coördinate calculations. Internal rotation about the S–S bond is highly restricted; a 9500 cal./mole two-fold potential barrier was used for thermodynamic calculations. The barrier height for methyl rotation was found to be 1140 cal./mole. Values of the free energy function, heat content, entropy, and heat capacity were calculated by the methods of statistical mechanics for selected temperatures up to 1000°K.

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[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF THE TULANE UNIVERSITY OF LOUISIANA]

Dissociation Constants of Polyethyleneamines[1,2]

BY HANS B. JONASSEN, R. BRUCE LEBLANC, A. W. MEIBOHM AND RUTH M. ROGAN

The acid–base dissociation constants of ethylenediamine (abbreviated to en) and the complexity constants of some of its complexes with metal ions have been measured.[3,4]

The three next higher, straight chain members of this polyethyleneamine series are now available in a technical grade,[5] and this paper reports the determination of their acid–base dissociation constants by the method of Bjerrum.[3]

Calculation of Constants

The dissociation constants or "hydrolysis" constants for diethylenetriamine (abbreviated di en) are determined by the following equilibria present in aqueous solution:

$$\text{di enH}_3^{+3} \rightleftarrows \text{di enH}_2^{+2} + \text{H}^+$$

$$K_1 = [\text{di enH}_2^{+2}][\text{H}^+]/[\text{di enH}_3^{+3}] \quad (1)$$

$$\text{di enH}_2^{+2} \rightleftarrows \text{di enH}^+ + \text{H}^+$$

$$K_2 = [\text{di enH}^+][\text{H}^+]/[\text{di enH}_2^{+2}] \quad (2)$$

$$\text{di enH}^+ \rightleftarrows \text{di en} + \text{H}^+$$

$$K_3 = [\text{di en}][\text{H}^+]/[\text{di enH}^+] \quad (3)$$

These constants can be calculated from *p*H measurements of solutions containing known amounts of di en and a mineral acid.

Throughout this discussion, activity and concentration are used interchangeably. Since the ionic strength of all solutions is very high and is maintained constant, the activity coefficients will be assumed to be constant.

Equations can be derived relating the concentration of the amine, the concentration of HNO_3, and the *p*H to the dissociation constants of the amines. The following symbols are used in the derivation of these equations:

C_{HNO_3} = total concentration of nitric acid in the solution

C_{dien} = total concentration of di en in the solution

$$C_{\text{dien}} = [\text{di en}] + [\text{di enH}^+] + [\text{di enH}_2^{+2}] + [\text{di enH}_3^{+3}] \quad (4)$$

$$C_s = C_{\text{HNO}_3} - [\text{H}^+] + [\text{OH}^-] \quad (5)$$

$$C_s = [\text{di enH}^+] + 2[\text{di enH}_2^{+2}] + 3[\text{di enH}_3^{+3}] \quad (6)$$

$$n = C_s/C_{\text{dien}} \quad (7)$$

Substituting the values of C_s and C_{dien} into (7), the following equation is obtained

$$\bar{n} = \frac{[\text{di enH}^+] + 2[\text{di enH}_2^{+2}] + 3[\text{di enH}_3^{+3}]}{[\text{di en}] + [\text{di enH}^+] + [\text{di enH}_2^{+2}] + [\text{di enH}_3^{+3}]} \quad (8)$$

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(1) In part from the thesis submitted by R. Bruce LeBlanc to the Graduate School of the Tulane University of Louisiana in February, 1949, in partial fulfillment of the requirements for the degree of Master of Science.

(2) Presented, in part, before the General Technical Session of the Fourth Annual Southwest Regional meeting of the American Chemical Society in December, 1948, at Shreveport, Louisiana.

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(4) G. A. Carlson, *et al.*, THIS JOURNAL, **67**, 1334 (1945).

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