and is in fact now mainly limited by the statistical counting error. This improvement is probably attributable to the provision of streamlined flow and to the use of solution counting procedures.

An explanation for Wang and Miller's[11] agreement with these values in very dilute regions and the divergence of their curve at about 0.2 M is not easy to obtain. Experience with the capillary method has shown that it is quite sensitive to operating conditions; for instance, as well as the effect of flow rate, there may be incomplete defibering and degassing of solutions which can lead to anomalous high results.

No discussion of the final $\mathfrak{D}_{Na^+}$ values and their concentration dependence will be made at this time. However, the almost linear dependence of $\mathfrak{D}_{Na^+}$ with c, up to concentrations of 4 M is noteworthy, as well as the extrapolation of the points on the same plot to the Nernst limiting value. The linear relation between $\mathfrak{D}\eta/\eta_0$ and $\sqrt{c}$ found by Mills and Kennedy[2] for unhydrated ions is not observed.

Acknowledgments.—I wish to acknowledge the help given me by Capt. F. D. Bethwaite in designing the capillary apparatus and by Mr. M. Vernon who performed many of the analyses.

CANBERRA, AUSTRALIA

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[11] J. H. Wang and Sara Miller, THIS JOURNAL, **74**, 1611 (1952).

[CONTRIBUTION NO. 51 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

3-Methyl-2-thiabutane: Calorimetric Studies from 12 to 500°K.; the Chemical Thermodynamic Properties from 0 to 1000°K.[1]

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The chemical thermodynamic properties of 3-methyl-2-thiabutane were investigated between 0 and 1000°K. Low temperature calorimetric studies were made from 12 to 344°K., and values were obtained of the heat capacity in the solid and liquid states [C_{satd}], the heat of fusion (2236 cal. mole^{-1} at the triple point, 171.65°K.), and the entropy of the liquid at saturation pressure at 298.16°K., 62.88 cal. deg.$^{-1}$ mole^{-1}. From flow calorimetric studies, there were obtained values of the heat of vaporization (ΔH_v), heat capacity in the ideal gaseous state [C_p°], and the second virial coefficient [$B = V(PV/RT - 1)$]. Some of the results are represented by the following empirical equations: (A) C_{satd} (liq.) $= 50.83 - 0.16245T + 5.951 \times 10^{-4} T^2 - 5.318 \times 10^{-7} T^3$, cal. deg.$^{-1}$ mole^{-1} (177–344°K.); (B) $\Delta H_v = 10{,}761 - 4.661\,T - 0.01369\,T^2$, cal. mole^{-1} (318–358°K.); (C) $C_p^\circ = 3.78 + 9.489 \times 10^{-2}\,T - 3.944 \times 10^{-5}\,T^2$, cal. deg.$^{-1}$ mole^{-1} (347–500°K.); and (D) $B = 211 - 147.0 \exp(800/T)$, cc. mole^{-1} (318–500°K.). The entropy in the ideal gaseous state at 298.16°K., 85.87 cal. deg.$^{-1}$ mole^{-1}, and the standard heat of formation from graphite, hydrogen and gaseous diatomic sulfur, −36.83 kcal. mole^{-1} at 298.16°K., were computed from these data and heat of combustion data to be reported elsewhere. Values of the functions $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S° and C_p° were computed from spectroscopic and molecular structure information. The parameters required to describe restricted internal rotation and to evaluate anharmonicity corrections were chosen to give agreement between calculated and experimental values of the entropy and vapor heat capacity. Values of the heat, free energy and equilibrium constant of formation of 3-methyl-2-thiabutane were computed from the calculated thermodynamic functions and the experimental value of heat of formation at 298.16°K.

Investigations of the thermodynamic properties of selected organic sulfur compounds are being conducted in this Laboratory. Intensive studies are made of those compounds that will yield data required in approximate calculations[2] of the properties of entire families of sulfur compounds. Attention is now being given to the seven isomeric $C_4H_{10}S$ thiols and sulfides—the most useful group of compounds for obtaining information regarding the effects of structural isomerism on thermodynamic properties. Data for this group of isomers may also find application in the construction of theories on the origin of petroleum; for it will be possible to compare calculated equilibrium concentrations of the $C_4H_{10}S$ compounds with those found in crude oil.[3]

Published reports on the thermodynamic properties of the $C_4H_{10}S$ isomers give results obtained in studies of 3-thiapentane[4] and 2-methyl-2-propanethiol.[5] A forthcoming article[6] will present the results of concurrent determinations of the heats of combustion, formation and isomerization, at 298.16° K., of all seven isomers. This paper reports thermodynamic data for 3-methyl-2-thiabutane (methyl isopropyl sulfide), another member of the group of $C_4H_{10}S$ isomers. Thermal data have previously been published for two lower alkane sulfides, 2-thiapropane[7] and 2-thiabutane.[8] The present investigation included experimental studies of 3-methyl-2-thiabutane that provided (1)

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[1] This investigation was part 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.

[2] *E.g.* (a) K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946); (b) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

[3] C. J. Thompson, H. J. Coleman, H. T. Rall and H. M. Smith, *Anal. Chem.*, **27**, 175 (1955).

[4] D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, G. D. Oliver, M. E. Gross, C. Katz, K. D. Williamson, Guy Waddington and H. M. Huffman, THIS JOURNAL, **74**, 4656 (1952).

[5] J. P. McCullough, D. W. Scott, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **75**, 1818 (1953).

[6] W. N. Hubbard, W. D. Good, F. R. Frow and Guy Waddington, to be published.

[7] (a) D. W. Osborne, R. N. Doescher and D. M. Yost, THIS JOURNAL, **64**, 169 (1942); (b) G. M. Barrow and K. S. Pitzer, *Ind. Eng. Chem.*, **41**, 2737 (1949); (c) J. L. Binder, *J. Chem. Phys.*, **18**, 77 (1950).

[8] D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, K. D. Williamson, Guy Waddington and H. M. Huffman, THIS JOURNAL, **73**, 261 (1951).

values of the heat capacity in the solid, liquid and vapor states (12 to 500° K.), (2) values of the heats of fusion and vaporization, (3) an equation of state for the vapor, and (4) values of the entropy, S°, heat capacity, C_p°, and the heat of formation, ΔH_f°(gas), in the ideal gaseous state. The calorimetric data were used with spectroscopic and molecular structure data in computing values of the following thermodynamic properties at selected temperatures from 0 to 1000° K.: $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S°, C_p°, ΔH_f°, ΔF_f° and $\log_{10}K_f$.

Experimental

Physical Constants.—The 1951 International Atomic Weights[9] and, where practicable, the 1951 values of the fundamental physical constants[10] were used. The calorimetric data are based on a molecular weight of 90.186 for 3-methyl-2-thiabutane and the following relations: 0° = 273.16°K.; and 1 cal. = 4.1840 abs. joules = 4.1833 int. joules. Measurements of temperature were made in terms of the International Temperature Scale[11] from 90 to 500°K. and the provisional scale[12] of the National Bureau of Standards from 11 to 90°K. Measurements of mass, energy, and the resistance of platinum resistance thermometers were made in terms of standard devices calibrated at the National Bureau of Standards.

The Material.—The sample of 3-methyl-2-thiabutane used in the low temperature calorimetric studies was part of the Standard Sample of Sulfur Compound, API-USBM serial No. 20, prepared and purified at the Laramie, Wyoming, Station of the Bureau of Mines. In the calorimetric melting point studies described below, it was found that the Standard Sample contained 0.018 ± 0.005 mole % liquid-soluble, solid-insoluble impurity. A sample of slightly lower purity (about 99.95 mole %) was provided by the Laramie Station for use in the flow-calorimetric studies. The samples of 3-methyl-2-thiabutane were received in sealed red-glass ampoules and were stored in the dark at 40°F. The liquid samples were dried with calcium hydride, and transfers of the material were made by vacuum distillations. At no time in the handling of the material or in the experiments were the samples in contact with any gas other than dry helium.

The Low Temperature Heat Capacity Measurements.—The thermal properties of 3-methyl-2-thiabutane in the solid and liquid states were measured between 12 and 344°K. with an adiabatic calorimeter system similar to that described by Ruehrwein and Huffman.[13] A platinum calorimeter with internal heat-distributing disks of gold was used. The calorimeter contained approximately 0.50 mole of the compound. A small amount of helium (about 30 mm. pressure at room temperature) was left in the calorimeter to promote thermal equilibration of the calorimeter and contents.

Solid 3-methyl-2-thiabutane was found to exist in a single crystalline form with regular heat capacity behavior. Observed values of the heat capacity at saturation pressure, C_{satd} of solid and liquid 3-methyl-2-thiabutane are given in Table I. The temperature increments used in the measurements were small enough to obviate the need of corrections for non-linear variation of C_{satd} with T. (The temperature increments employed were approximately 10% of the absolute temperature below 50°K.; 5 to 6° from 50°K. to the melting point; and 8 to 10° in the liquid region.) The precision of the heat capacity data was usually within ±0.1%; above 30°K., the accuracy uncertainty of the data should not exceed ±0.2%. The following empirical equation represents the heat capacity in the liquid state with an average deviation of 0.01 and a maximum deviation of 0.02 cal. deg.$^{-1}$ mole^{-1}

$$C_{satd}(\text{liq.}) = 50.83 - 0.16245T + 5.951 \times 10^{-4}T^2 - 5.318 \times 10^{-7}T^3, \text{ cal. deg.}^{-1}\text{ mole}^{-1}(177\text{–}344°\text{K.}) \quad (1)$$

TABLE I

THE MOLAL HEAT CAPACITY OF 3-METHYL-2-THIABUTANE IN CAL. DEG.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.	C_{satd}	T, °K.	C_{satd}
Crystals		54.47	11.056	Liquid	
		55.23	11.193		
12.54	0.985	59.70	11.980	177.19	37.76
13.16	1.139	64.98	12.885	183.44	37.76
13.75	1.272	70.28	13.710	186.27	37.79
14.62	1.490	75.65	14.511	190.72	37.80
15.08	1.598	81.08	15.354	200.04	37.89
16.21	1.897	86.58	16.185	210.33	38.04
16.57	1.991	92.47	16.976	220.55	38.24
17.90	2.363	98.76	17.781	229.29	38.46
18.21	2.439	105.21	18.596	234.72	38.61
19.78	2.872	112.42	19.503	239.85	38.77
20.10	2.973	119.93	20.406	245.89	38.97
21.91	3.493	127.15	21.261	250.81	39.12
22.29	3.605	134.60	22.124	256.94	39.36
24.22	4.159	141.75	22.939	267.88	39.80
24.61	4.249	142.28	23.030	278.68	40.27
26.65	4.850	147.33	23.628	289.36	40.77
26.99	4.952	149.69	23.919	299.91	41.27
29.43	5.614	152.41	24.258	303.32	41.48
32.64	6.474	157.31	24.870	313.63	42.01
36.01	7.282	157.53	24.889	323.81	42.56
39.96	8.182	158.55	25.045	333.87	43.12
44.54	9.149	163.91	25.850	343.79	43.73
49.60	10.199	164.52	25.976[c]		

[a] T is the mean temperature of each heat capacity measurement. [b] C_{satd} is the heat capacity of the condensed phase under its own vapor pressure. [c] The heat capacity data immediately below the melting point have *not* been corrected for the effects of premelting caused by the presence of impurities.

The Heat of Fusion, Triple Point and Sample Purity.—Three determinations were made of the heat of fusion. In each experiment, measurements were made of the total enthalpy increase over a temperature interval of approximately 20° that included the triple point. The energy absorbed non-isothermally was calculated from the heat capacity data and subtracted from the total. Corrections of from 1.5 to 2 cal. mole^{-1} were applied for the effect of premelting caused by impurity. The resulting values of the latent heat differed by less than 0.3 cal. mole^{-1}, and the average value found for the heat of fusion was 2236 cal. mole^{-1}.

TABLE II

3-METHYL-2-THIABUTANE: MELTING POINT SUMMARY

Triple point, $T_{T.P.}$ = 171.65 ± 0.05°K.; cryoscopic constant, A = 0.03819 deg.$^{-1}$; impurity = 0.018 ± 0.005 mole %.

Melted, %	$1/F$	T, °K. Obsd.	T, °K. Graph.[b]
11.17	8.953[a]	171.6074[a]	171.6074
26.89	3.719	171.6334	171.6318
51.39	1.946	171.6398	171.6400
72.39	1.381	171.6421	171.6426
91.64	1.091[a]	171.6440[a]	171.6440
100.00	1.000		171.6444
Pure	*0.0*		*171.6491*[c]

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain the triple point temperature, $T_{T.P.}$. [b] Temperatures read from the straight line of footnote *a*. [c] Triple point temperature.

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(9) E. Wichers, This Journal, **74**, 2447 (1952).

(10) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

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(13) (a) R. A. Ruehrwein and H. M. Huffman, This Journal, **65**, 1620 (1943); (b) G. D. Oliver, M. Eaton and H. M. Huffman, *ibid.*, **70**, 1502 (1948).

A study of the equilibrium melting temperature as a function of the fraction of sample melted was made by the method outlined in an earlier publication from this Laboratory.[14] The results are presented in Table II. The equilibrium temperatures, T_{obsd}, were plotted against the reciprocal of fraction melted, $1/F$. The triple point temperature, $T_{\text{T.P.}}$, was determined by linear extrapolation of these data to $1/F = 0$. The mole fraction of impurity in the sample, N_2^*, was calculated by the relationship, $N_2^*/F = A(T_{\text{T.P.}} - T_{\text{obsd}})$, where A is the cryoscopic constant, $\Delta H_{\text{fusion}}/RT_{\text{T.P.}}^2$. This procedure is based on the assumptions that the impurity forms ideal solutions in the liquid phase and is insoluble in the solid phase. The unusually close agreement between T_{obsd} and T_{graph} (Table II) shows that the impurity did not form solid solutions with 3-methyl-2-thiabutane.

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 3-METHYL-2-THIABUTANE IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{\text{satd.}} - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H_{\text{satd.}} - H_0^\circ)/T$, cal. deg.$^{-1}$	$H_{\text{satd}} - H_0^\circ$ cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
		Crystals			
10	0.05	0.13	1.3	0.18	0.53
15	.15	.43	6.4	.58	1.58
20	.33	.88	17.6	1.21	2.94
25	.58	1.44	35.9	2.02	4.38
30	.91	2.04	61.3	2.95	5.77
35	1.26	2.67	93.4	3.93	7.05
40	1.66	3.29	131.6	4.95	8.19
45	2.09	3.89	175.2	5.98	9.26
50	2.52	4.48	224.0	7.00	10.24
60	3.44	5.59	335.5	9.03	12.03
70	4.38	6.63	464.2	11.01	13.67
80	5.33	7.61	608.4	12.94	15.19
90	6.28	8.53	767.9	14.81	16.65
100	7.22	9.41	940.8	16.63	17.94
110	8.15	10.25	1127	18.40	19.20[b]
120	9.09	11.04	1325	20.13	20.41[b]
130	10.00	11.81	1535	21.81	21.58[b]
140	10.91	12.54	1756	23.45	22.74[b]
150	11.79	13.27	1990	25.06	23.93[b]
160	12.67	13.97	2235	26.64	25.15[b]
170	13.54	14.66	2493	28.20	26.40[b]
171.65	13.69	14.77	2536	28.46	26.60[b]
		Liquid			
171.65	13.69	27.80	4772	41.49	37.75
180	15.01	28.27	5088	43.28	37.77
190	16.56	28.76	5465	45.32	37.80
200	18.04	29.22	5844	47.26	37.89
210	19.49	29.63	6223	49.12	38.04
220	20.87	30.02	6605	50.89	38.24
230	22.21	30.38	6988	52.59	38.48
240	23.51	30.73	7375	54.24	38.77
250	24.77	31.06	7764	55.83	39.10
260	26.00	31.37	8157	57.37	39.48
270	27.19	31.68	8554	58.87	39.89
273.16	27.55	31.78	8680	59.33	40.03
280	28.34	31.98	8955	60.32	40.33
290	29.47	32.28	9360	61.75	40.80
298.16	30.36	32.52	9695	62.88	41.20
300	30.57	32.57	9771	63.14	41.30
310	31.64	32.86	10,190	64.50	41.82
320	32.69	33.15	10,610	65.84	42.35
330	33.71	33.43	11,030	67.15	42.90
340	34.72	33.72	11,460	68.44	43.49
350[c]	35.70	34.01	11,900	69.71	44.07
360[c]	36.67	34.29	12,350	70.96	44.66

[a] The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure. [b] Corrected for premelting. [c] Extrapolated by the use of eq. 1.

The Thermodynamic Properties of 3-Methyl-2-thiabutane in the Solid and Liquid States.—The low temperature calorimetric data were used in calculating values of the free energy, heat content and entropy of 3-methyl-2-thiabutane at selected temperatures from 10 to 360°K. The values at 10°K. were computed from a Debye function for 5 degrees of freedom with $\theta = 113.4°$; these parameters were evaluated from the heat capacity data between 12 and 20°K. Values of the thermodynamic properties above 10°K. were computed by numerical integration of values of C_{satd} read at integral temperatures from a large scale plot of the data in Table I. The results are recorded in Table III. Corrections for the effects of premelting have been applied to the "smoothed" data given in Table III.

The Heat of Vaporization.—Measurements of the heat of vaporization and vapor heat capacity of 3-methyl-2-thiabutane were made in the flow calorimeter system described in previous publications from this Laboratory.[15] The modified apparatus and procedure described in ref. 15b were used in this investigation.

The heat of vaporization was measured at 318.06, 336.63 and 357.98°K., and the results of 3 determinations at each temperature are given in Table IV.

TABLE IV

THE MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT OF 3-METHYL-2-THIABUTANE

T, °K.	p, mm.	ΔH_v, cal.	$-B$ (obsd.), cc.	$-B$ (calcd.)[a], cc.
318.06	190.0	7894 ± 2[b]	1575	1607
336.63	380.0	7641 ± 1	1366	1372
357.98	760.0	7338 ± 2	1173	1162

[a] Calculated with the aid of eq. (4). [b] Maximum deviation of experimental results from the mean.

It is believed that the accuracy uncertainty of the tabulated data should not exceed ±0.1%. The following equation may be used for interpolation in the temperature range of the experiments, 318 to 358°K.

$$\Delta H_v = 10{,}761 - 4.661T - 0.01369T^2, \text{ cal. mole}^{-1} \quad (2)$$

Extrapolation of the heat of vaporization data by use of eq. 2 gives 8154 cal. mole^{-1} for ΔH_v at 298.16°K. Addition of the correction for gas imperfection, computed by use of equation 4 of a subsequent section, gives 8175 cal. mole^{-1} for the standard heat of vaporization, ΔH_v°, at 298.16°K.

The Vapor Heat Capacity.—The vapor heat capacity of 3-methyl-2-thiabutane was measured at two or more pressures from 1/4 to 1 atm. at each of 5 temperatures between 347 and 500°K.; the results are summarized in Table V. "Observed" values of the heat capacity in the ideal gaseous state, C_p°, listed in Table V, were determined from the data at finite pressures by the method discussed in the next section.

TABLE V

THE MOLAL VAPOR HEAT CAPACITY OF 3-METHYL-2-THIABUTANE IN CAL. DEG.$^{-1}$

T, °K.	347.20	368.20	408.20	453.20	500.20
C_p(760.0 mm.)		34.202	36.443	38.997	41.596
C_p(380.0 mm.)	32.508	33.758			
C_p(225.5 mm.)					41.439
C_p(190.0 mm.)	32.239	33.552	36.067	38.763	
C_p°(obsd.)	31.98	33.35	35.95	38.69	41.37
C_p°(calcd.)[a]	31.98	33.36	35.92	38.67	41.37
$[C_p(1\text{ atm.}) - C_p^\circ]$(obsd.)		0.85	0.49	0.31	0.23
$[C_p(1\text{ atm.}) - C_p^\circ]$(calcd.)[b]		0.84	0.51	0.32	0.21

[a] Calculated from spectroscopic and molecular structure data. [b] Calculated by use of eq. 3 and 4.

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[14] S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

[15] (a) G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947); (b) J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, *ibid.*, **76**, 4791 (1954).

Gas Imperfection and Correlation of the Heat Capacity Data.—An equation of state for 3-methyl-2-thiabutane vapor was obtained from the heat of vaporization and vapor heat capacity data of this investigation and the vapor pressure data reported by White, Barnard-Smith and Fidler.[16] Values of the second virial coefficient, B, in the equation of state, $PV = RT(1 + B/V)$, were computed by use of the Clapeyron equation. Values of d^2B/dT^2 were determined by use of the thermodynamic relationship, $(\partial^2 V/\partial T^2)_P = -(1/T)(\partial C_p/\partial P)_T$, in terms of which the variation of vapor heat capacity with pressure is represented, with slight approximations,[15b] by

$$C_p = C_p^\circ - PT(d^2B/dT^2) + 2[P^2/R][B(d^2B/dT^2)][1 - 3BP/RT] \quad (3)$$

The numerical constants of the following empirical equation for B were determined by the method recently described.[15b]

$$B = 211 - 147.0 \exp(800/T), \text{ cc. mole}^{-1} \ (318\text{–}500°\text{K}) \quad (4)$$

Values of B, computed by use of eq. 4, and values of C_p (1 atm.) $- C_p^\circ$, computed by use of eq. 3 and 4, are compared with experimental data in Tables IV and V, respectively.

To determine the "observed" values of C_p° listed in Table V, the last term in eq. 3 was evaluated by use of eq. 4, and the result was subtracted from C_p (obsd.). The adjusted values of C_p were then extrapolated linearly to zero pressure to obtain C_p° (obsd.). This *quadratic* extrapolation yielded values of C_p° that were less than 0.1% higher than values obtained by *linear* extrapolation of the unadjusted data. Linear extrapolation of observed C_p data, coupled with use of the equation of state $PV = RT + BP$, has been used previously in this Laboratory to obtain values of C_p° for gases with about the same degree of imperfection as 3-methyl-2-thiabutane. These results show that the simpler procedure gave essentially as accurate values of C_p° as the present more exact method. However, correlation of the heat capacity data with the volume implicit equation of state gives significantly different results for B and its temperature derivatives. For instance, values of the quantity $(\partial C_p/\partial P)_T = -T(d^2B/dT^2)$ at zero pressure calculated by use of the volume implicit equation of state $[PV = RT(1 + B/V)]$ differ from those computed on the basis of the volume explicit equation $(PV = RT + BP)$ by as much as 10%. Because differences of this magnitude are of significance in the use of data for B and (d^2B/dT^2) to derive intermolecular potential energy parameters,[17] the volume implicit equation was adopted for correlation of the heat capacity data.

It is believed that the accuracy uncertainty of the values of C_p°(obsd.) given in Table V does not exceed ± 0.2%. The following empirical equation represents the tabulated data within 0.03 cal. deg.$^{-1}$ mole^{-1} from 347 to 500°K.

$$C_p^\circ = 3.78 + 9.489 \times 10^{-2}T - 3.944 \times 10^{-5}T^2, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (5)$$

The Entropy in the Ideal Gaseous State.—The experimental and derived data presented in previous sections were used in computing "observed" values of the entropy in the ideal gaseous state at one atmosphere pressure. These calculations are summarized in Table VI.

The Heat of Formation.—Determinations of the heat of combustion of 3-methyl-2-thiabutane were made in the rotating-bomb combustion calorimeter described previously.[18] Details of the experiments will be presented in a subsequent paper on bomb-calorimetric studies of the $C_4H_{10}S$ thiols and sulfides, and only the pertinent results will be given here. The standard heats of formation, ΔH_f°, of 3-methyl-2-thiabutane from C (graphite), H_2(gas) and S(rhombic) were found to be −29.59 ± 0.18 kcal. mole^{-1} for the liquid and −21.41 ± 0.19 kcal. mole^{-1} for the ideal gas, both at 298.16°K. Values of the standard free energy, ΔF_f°, and logarithm of the equilibrium constant, $\log_{10}K_f$, for the formation of 3-methyl-2-thiabutane in both the liquid and gaseous states were calculated from the values for the heat of formation and entropy (Tables VI and IX) and the thermodynamic functions for graphite,[19] hydrogen[19] and rhombic sulfur.[20] The heat and free energy of formation of S_2(gas) from rhombic sulfur[21] were used in calculating ΔH_f°, ΔF_f° and $\log_{10}K_f$ for the formation of 3-methyl-2-thiabutane in the ideal gaseous state at 298.16°K. from C(graphite), H_2(gas) and S_2(gas). These data are presented in Table VII.

TABLE VI

THE MOLAL ENTROPY OF 3-METHYL-2-THIABUTANE IN CAL. DEG.$^{-1}$

0–12°K.	Debye extrapolation[a]		0.302
12–171.65°	Graphical, $\int C_{\text{satd}}\, d \ln T$		28.151
171.65°	Fusion, 2236/171.65		13.027
171.65–298.16°	Graphical, $\int C_{\text{satd}}\, d \ln T$		21.400
S_{satd}, liq., 298.16°K. (±0.12)[b]			62.88
T, °K.	318.06	336.63	357.98
S_{satd}, liq.[c]	65.58	68.00	70.71
$\Delta H_v/T$[d]	24.82	22.70	20.50
S (ideal) − S (real)[e]	0.09	0.14	0.22
$R \ln (p/760)$[f]	−2.76	−1.38	0.00
$S°$, gas (obsd.) (±0.20)[b]	87.73	89.46	91.43
$S°$, gas (calcd.)[g]	87.75	89.48	91.45

[a] A Debye function for 5 degrees of freedom with $\theta = 113.4$ was used for this extrapolation. [b] Estimated accuracy uncertainty. [c] Interpolated in Table II. [d] Entropy of vaporization; calculated from data of Table IV. [e] Entropy of gas imperfection; calculated by use of eq. 4. [f] Entropy of compression to 1 atm.; calculated from data of ref. 16. [g] Calculated from spectroscopic and molecular structure data.

TABLE VII

THE MOLAL HEAT AND FREE ENERGY AND THE LOGARITHM OF THE EQUILIBRIUM CONSTANT FOR THE FORMATION OF 3-METHYL-2-THIABUTANE AT 298.16°K.

State[a]	Reference state[b]	ΔH_f°, kcal.	ΔF_f°, kcal.	$\log_{10}K_f$
Liquid	S(rhombic)	−29.59 ± 0.18	2.09	−1.53
Gas	S(rhombic)	−21.41 ± 0.19	9.26	−6.79
	S_2(gas)	−36.83	−6.16	+4.52

[a] Standard state of 3-methyl-2-thiabutane. [b] Reference state of elemental sulfur in the reactions

(A) $4C(\text{graphite}) + 5H_2(\text{gas}) + S(\text{rhombic}) \rightarrow C_4H_{10}S$ (liq. or gas)

(B) $4C(\text{graphite}) + 5H_2(\text{gas}) + {}^1/_2S_2(\text{gas}) \rightarrow C_4H_{10}S$ (gas)

Calculation of Thermodynamic Properties

The calorimetric investigations discussed above provided values of the important chemical thermodynamic properties of 3-methyl-2-thiabutane from 0 to 500°K. Because values at higher temperatures are often required in practical applications, thermodynamic properties from 0 to 1000°K. were computed on the basis of calorimetric, spectroscopic and molecular structure information. The method of calculation is described in the following paragraphs.

The Vibrational Assignment.—The vibrational spectra of 3-methyl-2-thiabutane have been determined in laboratories coöperating with APIRP 48A. The results, summarized in Table VIII, were ob-

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(16) P. T. White, D. G. Barnard-Smith and F. A. Fidler, *Ind. Eng. Chem.*, **44**, 1430 (1952).

(17) D. R. Douslin and Guy Waddington, to be published.

(18) (a) W. N. Hubbard, C. Katz and Guy Waddington, *J. Phys. Chem.*, **58**, 142 (1954); (b) W. N. Hubbard, D. W. Scott and Guy Waddington, *ibid.*, **58**, 152 (1954).

(19) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, 34, 143 (1945).

(20) "Selected Values of Chemical Thermodynamic Properties," Circular of the National Bureau of Standards, 500, Washington, D. C. 1952, Series I, Table 14-1.

(21) W. H. Evans and D. D. Wagman, *J. Research Natl. Bur. Standards*, **49** 141 (1952).

tained by measurements on portions of the Standard Sample of 3-methyl-2-thiabutane, API-USBM serial No. 20.[22]

Interpretation of the spectrum of 3-methyl-2-thiabutane was complicated by the fact that, at room temperature, the compound consists of a mixture of three rotational tautomers, two of which are optical isomers. As will be discussed subsequently, a zero energy difference between the rotational tautomers was found to be consistent with the calorimetric data. Thus the concentration of tautomers with C_1 symmetry (the optical isomers) should be approximately twice that of the spectroscopically distinct tautomer with C_s symmetry. Evidence of both spectroscopically different species should be found in the spectra—but probably in the region of skeletal frequencies only.

TABLE VIII

THE VIBRATIONAL SPECTRA AND ASSIGNMENT FOR 3-METHYL-2-THIABUTANE[a]

Raman,[b] liq. cm.$^{-1}$	Infrared,[c] liq. cm.$^{-1}$	Assignment (C_1 tautomer)
215 (40)		C–S–C bending
Unobserved frequency at about 270 cm.$^{-1}$		C–C–S bending
336 (65)		C–C–S bending
427 (40)	*ca.* 425 vw	C–C–C bending
	457 w	882 − 427 = 455[d]
537 (5)		2 × [270] = 540[d]
553 (5)		215 + 336 = 551
610 (40)	612 m	C_s tautomer[d]
636 (80)	639 s	C–S stretching
659 (20)		C_s tautomer[d]
723 (80)	724 s	C–S stretching
775 (10)		336 + 427 = 763
823 (10)		1154 − 336 = 818
881 (50)	883 m	C–C stretching
923 (10)	926 w	CH_3 rocking
951 (20)	956 s	CH_3 rocking
1056 (40)	1060 s	CH_3 rocking (2)
1110 (40)	1111 m	CH_3 rocking
1151 (40)	1157 s	CH_3 rocking
1200 (20)		C–C stretching
1242 (40)	1245 s	CH wagging
1256 (5)	1267 sh	2 × 638 = 1276
1312 (40)	1318 m	CH wagging and CH_3 bending
1339 (5)		215 + 1110 = 1325
	1364 s	CH_3 bending, sym.
1389 (10)	1383 s	CH_3 bending, sym.
	1429 sh	2 × 724 = 1448
1449 (65)	1447 vs	CH_3 bending, unsym. (6)

[a] The region above 1500 cm.$^{-1}$ has been omitted. [b] Ref. 22a; numbers in parentheses indicate relative intensities. [c] Ref. 22b; relative intensities are indicated by vw = very weak, w weak, m = medium, s = strong, vs = very strong, and sh = shoulder. [d] See text.

To aid in identification of the skeletal bending frequencies, an approximate normal coördinate analysis for the C_1 tautomer was made in the manner described for the structurally similar molecule, 2-methylbutane[23] (interaction force constants were neglected in making the present calculations). The calculated values of the four skeletal bending frequencies are 201, 327, 350 and 417 cm.$^{-1}$. These results show that the weak infrared absorption at 457 cm.$^{-1}$ is not a fundamental of the C_1 tautomer; however, it may arise from the C–C–C bending mode of the C_s tautomer. The 457 cm.$^{-1}$ band may also be discarded as a fundamental of the C_1 tautomer because it is inconsistent with the calorimetric data. From the results of the normal coördinate analysis and the data of Table VIII, it is evident that not all of the fundamental skeletal bending frequencies were observed. The requirements of consistency with the experimental entropy data and at least a rough correspondence with the calculated frequency led to the selection of 270 cm.$^{-1}$ for the lowest C–C–S bending frequency by interpreting the weak Raman displacement at 537 cm.$^{-1}$ as the overtone, 2 × 270 = 540 cm.$^{-1}$.

It is surprising that more spectroscopic evidence for 2 rotational tautomers was not found in the region of skeletal bending frequencies. However, evidence of both tautomers was apparent in the spectral region where C–S stretching frequencies are expected to appear. Four relatively strong lines were found from 610 to 724 cm.$^{-1}$, and only 2 should appear if a single tautomer were present. The stronger pair, at 638 and 724 cm.$^{-1}$, was assigned to the C_1 tautomer, and the weaker pair, at 610 and 659 cm.$^{-1}$, was attributed to the C_s tautomer.

The remaining fundamental frequencies were assigned on the basis of spectral regularities found in studies of structurally related sulfur compounds and hydrocarbons. With one exception, the correct numbers of observed frequencies were found in expected regions of the spectra. Only 5 frequencies were observed in the region where 6 CH_3 rocking modes should appear. However, it has been found that frequencies at about 1060 cm.$^{-1}$ are characteristic of both the $-SCH_3$ group and the $-SCH(CH_3)_2$ group and may be attributed in each case to a CH_3 rocking mode (or mixed C–C stretching and CH_3 rocking mode). It has also been observed that, because of the large mass of the S atom, the carbon–hydrogen vibrational modes of one group attached to an S atom are nearly independent of the nature of a second attached group. Consequently, the strong Raman line and infrared band near 1060 cm.$^{-1}$ were assigned to two unresolved CH_3 rocking frequencies.

The vibrational assignment used for calculating thermodynamic functions was, for the rotational tautomer with C_1 symmetry: skeletal bending, 215, [270], 336 and 427; skeletal stretching, 638, 724, 882 and 1200; CH_3 rocking, 925, 954, 1058 (2), 1110 and 1154; CH wagging, 1244 and 1315; CH_3 bending, 1315, 1364, 1386 and 1450 (6); and CH stretching, 2950 (10) cm.$^{-1}$. Not all of the CH_3 bending and C–H stretching frequencies were resolved, and average or conventional values were used for these thermodynamically unimportant frequencies.

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(22) (a) Raman Data: F. A. Miller, Gulf Research Fellowship, Mellon Institute, to be published by American Petroleum Institute Research Project 44 in the Catalog of Raman Spectral Data. (b) Infrared data: American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data Serial Nos. 1197, 1198, 1546 and 1624. The spectra numbered 1197 and 1198 were not determined with the Standard Sample of 3-methyl-2-thiabutane, and these data are not included in Table VIII.

(23) D. W. Scott, J. P. McCullough, K. D. Williamson and Guy Waddington, THIS JOURNAL, **73**, 1707 (1951)

Table IX

The Molal Thermodynamic Properties of 3-Methyl-2-thiabutane[a]

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.$^{-1}$	$\Delta H_f°$,[b] kcal.	$\Delta F_f°$,[b] kcal.	$\log_{10}Kf$[b]
0	0	0	0	0	0	−30.06	−30.06	Infinite
273.16	−66.10	17.33	4.734	83.43	27.04	−36.38	− 8.70	6.96
298.16	−67.66	18.21	5.429	85.87	28.70	−36.83	− 6.16	4.52
300.00	−67.76	18.28	5.484	86.04	28.82	−36.86	− 5.96	4.34
400	−73.49	21.74	8.696	95.23	35.41	−38.51	+ 4.60	− 2.51
500	−78.71	25.08	12.54	103.79	41.36	−39.84	15.54	− 6.79
600	−83.58	28.22	16.93	111.80	46.50	−40.88	26.70	− 9.73
700	−88.15	31.16	21.81	119.31	50.97	−41.64	38.03	−11.87
800	−92.49	33.88	27.10	126.37	54.89	−42.15	49.44	−13.51
900	−96.63	36.41	32.77	133.04	58.32	−42.43	60.92	−14.79
1000	−100.58	38.76	38.76	139.34	61.35	−42.48	72.42	−15.83

[a] To form an internally consistent set of values of the thermodynamic properties and to retain the higher accuracy of increments with temperature of a given property, the values in this table are given to more significant figures than are justified by their absolute accuracy. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of 3-methyl-2-thiabutane by the reaction: 4 C(graphite) + $5H_2$(gas) + $^1/_2S_2$(gas) → $C_4H_{10}S$(gas).

The Moments and Reduced Moments of Inertia.—Since the vibrational assignment was made for the C_1 tautomer, moments of inertia were computed for the same structural configuration.[24] The general method of Kilpatrick and Pitzer[25] was used to obtain the product of principal moments of inertia and the reduced moments of inertia. By analogy with structurally similar compounds, the molecular dimensions of 3-methyl-2-thiabutane were estimated to be as follows: C–C distance, 1.54 Å.; C–S distance, 1.82 Å.; C–H distance, 1.09 Å.; C–S–C angle 105°; and all other angles 109° 28′. The value obtained for the product of principal moments of inertia was 1.394×10^{-113} g.^{3} cm.^{6}. The diagonal elements of the internal rotational kinetic energy matrix were taken as the reduced moments of inertia, namely: 5.138×10^{-40} and 5.205×10^{-40} g. cm.^{2} for the methyl groups in the isopropyl group; 5.147×10^{-40} g. cm.^{2} for the methyl group in the $-SCH_3$ group; and 30.58×10^{-40} g. cm.^{2} for rotation about the central C–S bond. Neglect of the off-diagonal elements of the kinetic energy matrix was justified by the fact that the square root of the determinant of the matrix differed by only 4% from the square root of the product of the diagonal elements.[25]

The Potential Barriers to Internal Rotation and the Effect of Anharmonicity.—Because the C–S bond distance is relatively large, the heights of potential barriers to internal rotation in sulfur compounds are remarkably constant in a series of related compounds. Accordingly, 3950 cal. mole^{-1} was used for the two barrier heights for rotation about C–C bonds, as in 2-propanethiol[26]; and 2000 cal. mole^{-1} was used for the barrier height for rotation about the terminal C–S bond, as in 2-thiapropane[7] and 2-thiabutane.[8]

Although an unsymmetrical potential barrier to internal rotation about the central C–S bond might be expected for 3-methyl-2-thiabutane because the analogous barrier in 2-methylbutane is highly unsymmetrical, best agreement between calculated and observed values of $S°$ and $C_p°$ was obtained by use of a simple 3-fold barrier. This result implies a zero energy difference between rotational tautomers, but the approximations that were made in the calculations make it impossible to exclude energy differences no greater than about 500 cal. mole^{-1}. The height of the skeletal barrier, 2600 cal. mole^{-1}, was chosen to give agreement between calculated and observed values of $S°$ at 318.20°K., where neglect of anharmonicity produces negligible error. The differences between calculated and observed values of $C_p°$ were then considered to be due to the neglect of anharmonicity. From these results, the effect of anharmonicity was calculated by the method outlined in an earlier paper.[27] The following values of the empirical anharmonicity parameters defined in ref. 27 were required: $\nu = 1100$ cm.$^{-1}$; $Z = 1.49$ cal. deg.$^{-1}$ mole^{-1}.

Comparisons of calculated and observed values $C°$ and $S°$ are made in Tables V and VI, respectively. Agreement within 0.03 cal. deg.$^{-1}$ mole^{-1}, within 0.1%, was obtained over the 180° range of temperature for which experimental data were available. Thus, the calculational procedure employed should be reliable for use in computing thermodynamic functions above 500°K.

The Chemical Thermodynamic Properties.—By use of the vibrational assignment, moments of inertia, barrier heights and anharmonicity parameters given above, values of the following thermodynamic functions were computed at selected temperatures to 1000°K.: $(F° - H_0°)/T$, $(H° - H_0°)/T$, $H° - H_0°$, $S°$ and $C_p°$.[28]

These thermodynamic functions of 3-methyl-2-thiabutane, the value of $\Delta H_f°$ at 298.16°K. (Table VII), and the thermodynamic functions of C(graphite),[19]

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[24] K. S. Pitzer, *J. Chem. Phys.*, **14**, 239 (1946).

[25] J. E. Kilpatrick and K. S. Pitzer, *ibid.*, **17**, 1064 (1949).

[26] J. P. McCullough, H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, R. E. Pennington and Guy Waddington, This Journal, **76**, 4796 (1954).

[27] J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **76**, 2661 (1954).

[28] (a) The vibrational contributions to the thermodynamic functions were taken from H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D. C., July 1949; (b) restricted internal rotation contributions were computed from the tables published by K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942); (c) anharmonicity contributions were evaluated from the tables of R. E. Pennington and K. A. Kobe, *ibid.*, **22**, 1442 (1954).

H_2(gas)[19] and S_2(gas)[21] were used in computing values of ΔH_f°, ΔF_f° and $\log_{10}K_f$ at selected temperatures from 0 to 1000°K. The calculated values of the eight thermodynamic properties are given in Table IX.

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[CONTRIBUTION NO. 409 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

A Laboratory Method for Separating Nitrogen Isotopes by Ion Exchange[1]

BY F. H. SPEDDING, J. E. POWELL AND H. J. SVEC

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Various aspects of the separation of N^{15} and N^{14} isotopes from each other by an ion-exchange process have been discussed. A number of experiments have been performed to establish the feasibility of using the process and to check the countercurrent theory of separation which has been developed. The separation factor for the exchange of N^{15} and N^{14} between a solution of dilute ammonium hydroxide and the ammonium form of Dowex 50-X12 was measured and found to be 1.0257 ± 0.0002. It was shown that an adsorbed band of ammonium ion must be eluted about 39 times its length in order to achieve separation of the isotopes. A method of continuous operation using a series of ion-exchange beds has been described and factors which influence the HETP at a steady state have been investigated.

I. Theoretical Considerations

A. Introduction.—The remarkable success achieved in separating adjacent rare earths in high purity and good yields by ion-exchange methods suggested that isotopes might also be separated by a similar procedure. It was found[2,3] that, if a solution of mixed rare earth ions was adsorbed on the top of a column of sulfonated styrene–divinylbenzene copolymer in the hydrogen state, little separation occurred in the adsorption step. However, if the band was eluted with an eluent of citric acid, buffered with ammonia in an appropriate *p*H range, the individual rare earth ions separated to form sharp bands which traveled head to tail down the column. The individual rare earths could then be successively eluted off the resin bed in a pure state, with only a small amount of overlap between bands.

In order to obtain this type of elution,[4] the eluent had to contain one or more anions which complexed the rare earth ions strongly enough to compete with the resin in removing the triply charged rare earth cations from solution. It was found necessary that distinct chemical reactions occur at the front and rear edges of the adsorbed band so that the rare earths would be sharply confined between two boundaries. Under these conditions, the original rare earth band would spread out to a fixed equilibrium length which was determined solely by the composition of the eluent. Once this equilibrium was attained, the length of the band remained constant regardless of how far the band was eluted down a resin bed. As a consequence, all the boundaries of the individual rare earth bands moved at the same rate. It was also ascertained that, if the concentration of any ion in the eluate was plotted *versus* the volume of effluent solution while an individual rare earth band was passing off the column, a flat elution curve was obtained showing that the concentrations of all ions remained constant. When subsequent individual rare earth bands passed off the column the concentrations of all ionic species shifted slightly but remained at characteristic fixed values while each individual rare earth moved from the bed. The automatic adjustment, which arises primarily from the stability constants of the various complexed rare earth species, results in a self-sharpening of the bands.

It was hoped that the slight differences in the exchange constants of various isotopes of an element might also cause banding of the isotopes within a chemically constrained band, if the band was eluted under proper conditions.[5] While the chemical constraints at the ends of a band cause the over-all band to attain equilibrium in a short distance of travel, the much smaller exchange constants of the isotopes would require that the band travel a much greater distance before complete isotopic equilibrium would be approached.

Since the isotopic exchange constants for light elements are considerably larger than for heavier elements, the first experiments were carried out using nitrogen in the form of ammonium hydroxide in an attempt to separate N^{15} from N^{14}.

B. Chemical Conditions Required to Obtain a Sharp Adsorbed Ammonium Band.—In order to develop and maintain a sharp adsorbed ammonium band it is necessary to have a uniformly packed resin bed. Under these conditions, as the solution percolates down the column, a horizontal boundary between two solutions can be maintained. In practice, if sufficient care is taken in preparing the resin beds, tilting and channeling can be kept less than a few millimeters for columns 2 to 6 inches in diameter. When one ion replaces another on the resin bed there is always some change in the volume of the resin. In small diameter tubes, bridging frequently occurs during expansion and contraction of the bed and results in uneven packing of the resin particles. This leads frequently to serious tilting of the band.

To separate nitrogen isotopes the resin beds are

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] (a) F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, THIS JOURNAL, **72**, 2354 (1950); (b) F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffe, *ibid.*, **73**, 4840 (1951).

[3] F. H. Spedding and J. E. Powell, *Chem. Engr. Progr., Symposium Series*, **50**, No. 14, 7 (1954).

[4] F. H. Spedding and J. E. Powell, THIS JOURNAL, **76**, 2545, 2550 (1954).

[5] F. H. Spedding, J. E. Powell and H. J. Svec, *ibid.*, **77**, 1393 (1955).