[Contribution No. 43 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

Benzothiophene: Heat Capacity, Heat of Transition, Heat of Fusion and Entropy. An Order–Disorder Transition[1,2]

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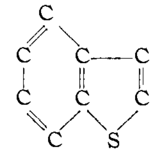
The heat capacity of benzothiophene was studied between 12 and 335°K. The solid exhibited a large λ-type transition between 250 and 261.6°K. The high temperature crystals II were readily supercooled, and heat capacity measurements were made below the transition temperature both on the stable low temperature crystals I and on the supercooled crystals II. The triple point (304.50°K.) and the heat of fusion (2826.8 cal. mole^{-1}) were determined. The entropy of the solid at 298.16°K. and that of the liquid at the triple point were found to be 42.33 and 53.31 cal. deg.$^{-1}$ mole^{-1}, respectively. Supercooled crystals II were found to have a residual entropy of approximately $R \ln 2$ cal. deg.$^{-1}$ mole^{-1}, and the transition, I → II, was found to involve an entropy change of approximately $R \ln 4$ cal. deg.$^{-1}$ mole^{-1}. It is suggested that some type of order–disorder phenomenon may cause these entropy differences between crystals I and II.

A study of the low temperature thermal properties of benzothiophene has been made as a part of the program of this Laboratory to determine the thermodynamic properties of selected sulfur compounds that occur in or are derived from petroleum.

Benzothiophene has been found in several shale oils,[3] in a Colorado shale-oil naphtha distillate,[4] in a high-sulfur virgin distillate of West Texas origin,[5] and in Middle East, Venezuela and Texas gas oils.[6]



This paper presents values of the following thermal properties of benzothiophene, as determined by the methods of low temperature calorimetry: the heat capacity of two crystalline modifications and of the liquid (12–335°K.), the heats of transition and fusion, the triple point, the cryoscopic constant, and the entropy of the solid at 298.16°K. and of the liquid at the triple point. The difference in entropy of the two crystalline modifications is discussed in terms of a possible order–disorder phenomenon.

The Material.—The benzothiophene used in this investigation was an API-USBM Standard Sample, serial no. 15, purified by API Research Project 48A, at the Laramie, Wyo., station of the Bureau of Mines, from material contributed by The Texas Co. The sample had the following physical properties: $n^{35}\text{D}$ 1.6332, $n^{40}\text{D}$ 1.6302; d^{35} 1.1988 g./ml., d^{40} 1.1937 g./ml.[7]

The Apparatus.—The measurements were made with an adiabatic vacuum-type calorimetric apparatus similar to that described by Ruehrwein and Huffman.[8] The sample of benzothiophene (*ca.* 0.4 mole), freed of air and water, was sealed in a platinum calorimeter that contained perforated horizontal gold disks to facilitate attainment of thermal equilibrium and prevent settling of the solid phase during fusion experiments. To minimize heat interchange between the calorimeter and its electrically heated adiabatic shield system, the temperature of the latter was maintained as close as possible to that of the calorimeter surface. The temperature difference between the environment and the calorimeter was determined by means of a system of interconnected thermocouples. A strain-free platinum resistance thermometer was used to measure the temperature of the calorimeter. A coil of constantan wire (AWG 40), mounted on the same mica cross as the thermometer, served as a heating element. The electrical measurements required for determining the resistance of the thermometer and the electrical energy were made with 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 saturated cadmium cells, which had been certified by the National Bureau of Standards. An electric stopclock driven by alternating current, the frequency of which was controlled within ±0.001%, was used in all the time measurements.

As benzothiophene is a solid at room temperature, the sample was melted and siphoned into the calorimeter from a volumetric bulb. Experience has shown that attainment of thermal equilibrium below 50°K. is very slow in low temperature calorimetric studies of many sulfur compounds. To increase the rate of equilibration, helium gas (*ca.* 20 mm. pressure at room temperature) was left in the calorimeter.

Triple Point and Purity Determination.—By use of the method described in a previous publication from this Laboratory,[9] the triple point and sample purity were determined from the results of a study of the equilibrium melting temperature as a function of the fraction of sample melted (F). The results of this study are summarized in Table I. The triple point (304.50 ± 0.05°K.) and the concentration of impurity (0.032 ± 0.01 mole per cent.) were determined from a straight line through the points corresponding to 46 and 88% melted on a plot of T_{obsd} *vs.* $1/F$. It is apparent from a comparison of columns 3 and 4 of Table I that the observed points do not follow the theoretical linear relationship. The departure from linearity is probably due to solid solution formation. This conjecture that some of the impurity formed solid solution is further substantiated by the fact that the concentration of liquid-soluble impurity, as calculated from the premelting heat capacity data, was only 0.004 mole %.

Heat Capacity of Solid and Liquid.—The heat capacity of benzothiophene was measured from 12 to 335°K. The experimentally determined values of C_{satd}, the heat capacity of the condensed phase under its own vapor pressure, are listed in Table II. The values of the heat capacity of the solid at temperatures immediately below the melting point

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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] Benzothiophene is also known as benzo[b]thiophene, 1-thiaindene, benzothiofuran, thianaphthene, thionaphthene and thiocoumarone. For a discussion of the nomenclature of sulfur compounds, see J. S. Ball and W. E. Haines, *Chem. Eng. News*, **24**, 2765 (1946).

[3] F. Challenger, J. Haslam and R. J. Bramball, *J. Inst. Petroleum Tech.*, **12**, 106 (1926); W. Steinkop and W. Nitsche, *Arch. Pharm.*, **278**, 360 (1940).

[4] I. W. Kinney, Jr., J. R. Smith and J. S. Ball, "Thiophenes in Shale-Oil Naphtha," presented before a symposium on "Nonhydrocarbon Constituents of Petroleum," American Chemical Society, Milwaukee, Wis., Meeting, March, 1951.

[5] R. H. Brown and S. Meyerson, "Cyclic Sulfides in a Petroleum Distillate," *ibid.*, March, 1951.

[6] H. Hoog, *Rec. trav. chim.*, **69**, 1289 (1950); H. Hoog, G. H. Reman and W. C. B. Smithuysen, Proceedings Third World Petroleum Congress, 1951, Section IV, Subsection IV, Preprint 2.

[7] W. E. Haines, R. V. Helm and J. S. Ball, unpublished data from A.P.I. Research Project 48A, Bureau of Mines, Laramie, Wyo.

[8] R. A. Ruehrwein and H. M. Huffman, This Journal, **65**, 1620 (1943).

[9] S. S. Todd, G. D. Oliver and H. M. Huffman, *ibid.*, **69**, 1519 (1947).

TABLE I

BENZOTHIOPHENE, MELTING POINT SUMMARY

Melted, %	$1/F$	T, °K. Obsd.	Graph.[b]
7.34	13.6	304.2595	304.2147
23.32	4.288	.4156	.4112
46.48[a]	2.151	.4563	.4563
67.35	1.485	.4709	.4704
88.23[a]	1.133	.4778	.4778
100.0	1.000		.4806
Pure	0.000		.5017

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain the triple point ($T_{TP} = 304.50 \pm 0.05$°K.). [b] These are values of T on the straight line of footnote a. Impurity = 0.032 ± 0.01 mole per cent.; $N_2^*/F = 0.0153\Delta T$; N_2^* = mole fraction impurity in sample; F = fraction of sample melted; $\Delta T = T_{TP} - T_{obsd}$; 0°C. = 273.16°K.

TABLE II[a]

BENZOTHIOPHENE MOLAL HEAT CAPACITY, CAL. DEG.$^{-1}$

T, °K.	$C_{satd.}$	T, °K.	$C_{satd.}$	T, °K.	$C_{satd.}$
Crystals I		154.91	19.725	54.50	9.767
		159.98	20.462	56.00	9.956
12.28	1.046	163.40	20.935	59.09	10.309
12.41	1.068	166.55	21.308	59.87	10.405
13.73	1.387	170.71	21.865	64.26	10.903
13.83	1.403	174.33	22.332	65.86	11.063
15.17	1.741	176.37	22.602	69.86	11.460
15.80	1.917	179.96	23.129	72.37	11.701
16.59	2.118	183.12	23.559	76.02	12.062
17.93	2.469	186.55	24.032	78.60	12.322
17.96	2.467	190.18	24.567	79.17	12.368
19.51	2.881	192.83	24.945	82.72	12.714
20.27	3.087	196.27	25.446	84.03	12.859
21.42	3.382	199.96	26.020	86.02	13.043
22.83	3.735	202.76	26.442	89.22	13.360
23.94	4.017	205.60	26.859	89.90	13.406
25.61	4.427	209.32	27.480	93.33	13.693
26.61	4.665	212.83	28.027	97.55	14.066
28.60	5.124	214.54	28.273	101.11	14.390
28.90	5.195	218.74	29.036	107.51	15.006
31.95	5.853	223.04	29.721	113.12	15.755
35.67	6.567	223.56	29.789	118.99	16.732
39.24	7.193	227.80	30.580	124.77	17.490
42.95	7.779	232.09	31.220	131.58	18.236
46.82	8.351	232.64	31.333	138.59	18.901
50.79	8.906	233.32	31.507	262.00	33.399
54.26	9.352	236.49	32.135	263.13	33.566
55.28	9.473	239.23	32.629	268.10	34.450
59.27	9.956	240.96	32.869	269.20	34.489
64.31	10.538	241.17	32.935	271.37	34.877
69.36	11.060	245.26	33.775	271.75	34.783
74.47	11.558	246.22	33.924	274.06	35.294
79.73	12.086	251.81[b]	36.724	276.12	35.475
85.14	12.636	256.09[b]	41.959	278.15	35.711
85.68	12.675	259.4[b]	76.2	278.76	35.880
90.32	13.127	Crystals II		283.85	36.594
93.13	13.370	12.41	1.571	284.89	36.690
100.23	14.010	13.61	1.906	286.47	36.943
107.57	14.682	15.24	2.341	291.39	37.674
115.16	15.389	17.47	2.952	291.94	37.802
122.94	16.143	20.06	3.639	294.00	38.032
127.75	16.609	22.47	4.250	299.98	39.365
130.93	16.938	24.77	4.803		
134.52	17.296	27.57	5.455	Liquid	
138.62	17.716	30.89	6.182		
139.94	17.855	34.42	6.857	307.75	45.549
144.29	18.393	38.26	7.502	312.43	45.920
146.48	18.547	42.20	8.125	313.80	45.974
148.13	18.700	46.47	8.734	321.78	46.575
153.16	19.426	51.22	9.365	329.68	47.110
		54.28	9.750		

[a] All data in this paper are based on a molecular weight of 134.194 for benzothiophene and the following definitions: 1 cal. = 4.1833 int. joules; 0°C. = 273.16°K. [b] λ-Region. The temperature increments of these measurements are in order of increasing T,°K.: 4.503°, 4.062° and 2.46°.

were not corrected for premelting caused by liquid-soluble solid-insoluble impurities. The temperature increments employed (less than 10% of the absolute temperature below 50°, 5–6° from 50 to 100°, 6–10° above 100°K.) were small enough that no correction was necessary for non-linear variation of C_{satd} with temperature. The precision of the results was, in general, better than ±0.1%. Above 30°K., it is believed that the accuracy uncertainty, unless otherwise stated, should not exceed ±0.2%. Below 30°K., the uncertainty is greater because of the lower thermometer sensitivity and the use of smaller temperature increments.

A large λ-type transition with a maximum energy absorption immediately below 261.6°K. was observed. The crystal form stable above this temperature was designated crystals II and that stable below the transition crystals I. It was possible to supercool crystals II. Heat capacity measurements were made on crystals I between 12°K. and the transition temperature, on crystals II between 12 and 140°K. (in the metastable region) and between the transition temperature and melting point (the stable region), and on the liquid between the melting point and 335°K. The precision of the heat capacity measurements on crystals II in the stable region and on crystals I immediately below and in the λ-region was less than usual, because the calorimeter and contents approached thermal equilibrium at an abnormally low rate. In some cases thermal equilibrium may not have been realized. Fortunately, the effect of this uncertainty upon the total entropy is quite small.

Crystals II were obtained readily in a supercooled state by cooling rapidly from 10° or more above the transition to below 140°K. From 12 to 140°K. satisfactory heat capacity measurements were made on supercooled crystals II. Between 140°K. and the transition, the supercooled crystals II transformed to crystals I at a rate great enough to make heat capacity measurements on crystals II impractical in this temperature range. However, the total enthalpy change between 140 and 270°K. was measured. A heat capacity curve through this region consistent with the observed total enthalpy change was used in the entropy calculation for crystals II.

Heat of Fusion.—Duplicate determinations of the heat of fusion gave values of 2827.7 and 2825.9 cal. mole^{-1}. The mean value, 2826.8 ± 0.9 cal. mole^{-1}, was used in calculating the entropy. The uncertainty given is the precision uncertainty; the accuracy uncertainty may be greater because of the unknown nature of the impurity and its behavior in the premelting region. The cryoscopic constant ($\Delta H_{fusion}/RT^2_{TP}$) calculated from the heat of fusion and triple point is 0.0153 deg.$^{-1}$.

Transition Temperature and Heat of Transition.—The λ-type transition between 250 and 261.6°K. was markedly slow in occurring; a period of about 2 weeks was required to transform crystals II completely to crystals I. To study the thermal behavior of benzothiophene in the temperature region of maximum energy absorption, successive fractions of the sample were transposed and the corresponding "equilibrium" temperatures were observed. In no instance was true equilibrium established; approximately 12 hours after a heating period the rate of change of temperature was still about 0.0005° min.$^{-1}$. It was, therefore, necessary to extrapolate the time–temperature observations for each fraction transposed to infinite time to obtain an equilibrium temperature. These exponential extrapolations ranged from 0.149 to 0.167°. The equilibrium temperatures that corresponded to various fractions transposed follow: 59.8%, 260.6°K.; 73.7%, 260.9°K.; 94.0%, 261.5°K. A value of 261.6°K. was chosen as the temperature at which 100% of the sample was transposed.

Two measurements of the total enthalpy change between 250 and 261.6°K. yielded values of 1137.8 and 1133.0 cal.

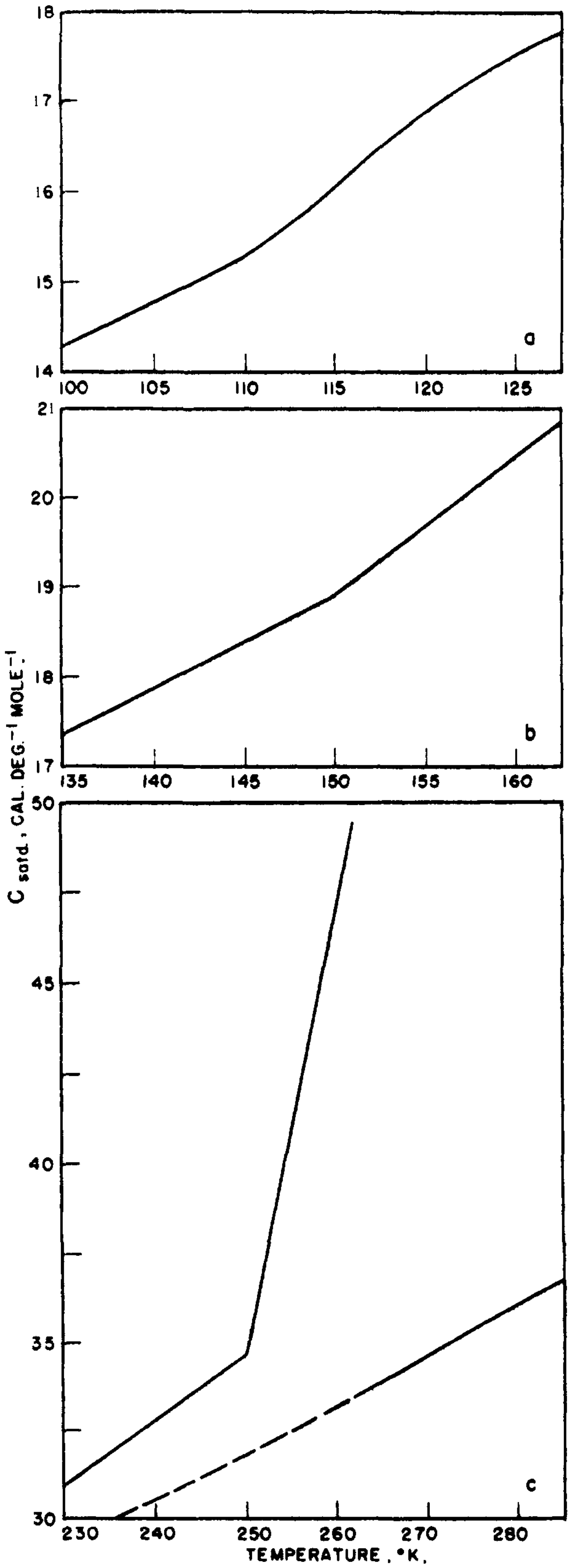

Fig. 1.—Heat capacity curves: a, crystals II supercooled; b, crystals I; c, transition I → II.

mole^{-1} (mean 1135.4 ± 2.4 cal. mole^{-1}). The enthalpy associated with the "normal" heat capacity curve through this region was subtracted from the total change to compute the enthalpy of transition, 719.6 ± 2.4 cal. mole^{-1}. The uncertainty assigned is the precision uncertainty; the accuracy uncertainty may be considerably greater.

Entropy of Solid and Liquid.—The calorimetric data were utilized to calculate the entropy of benzothiophene in the solid state at 298.16°K. and in the liquid state at the triple point. Also, the entropy of crystals II at 261.6°K. was calculated over two paths: (1), the equilibrium crystals I from 0°K. to the transition temperature and their transformation to crystals II, and (2), the supercooled crystals II from 0 to 261.6°K. Crystals II were found to have a residual entropy of 1.459 ± 0.14 cal. deg.$^{-1}$ mole^{-1}. The results of these calculations are summarized in Table III.

Table III

Molal Entropy of Benzothiophene, Cal. Deg.$^{-1}$

	(A) Equilibrium crystals and liquid	
0–12°K.	Debye extrapolation, 4.5 degrees of freedom, $\theta = 105.2$°K.	0.338
12–261.6°	Solid, graphical $\int C_{satd}\, d \ln T$, + λ	38.153
Entropy (±0.10) of crystals II at 261.6°K.		38.491
216.6–298.16°	Solid, graphical $\int C_{satd}\, d \ln T$	3.838
Entropy (±0.12) of crystals II at 298.16°K.		42.329
298.16–304.50°	Solid, graphical $\int C_{satd}\, d \ln T$	1.693
304.50°	Fusion 2826.8/304.50	9.283
Entropy (±0.15) of liquid at 304.50°K.		53.305
	(B) Supercooled crystals II	
0–12°K.	Debye extrapolation, 4 degrees of freedom, $\theta = 86.1$°K.	0.528
12–261.6°	Solid, graphical $\int C_{satd}\, d \ln T$	36.504
Entropy (±0.10) of crystals II at 261.6°K. less residual entropy at 0°K.		37.032

The total entropy change associated with the λ-type transition was calculated to be 2.750 ± 0.03 cal. deg.$^{-1}$ mole^{-1}, approximately $R \ln 4$ (2.754 cal. deg.$^{-1}$ mole^{-1}). The uncertainty in the entropy of transition arises mainly from the difficulty in determining the true shape of the "lambda" in the region of high energy absorption and of the "normal" heat capacity curve.

Discussion.—Several interesting phenomena were noted in this study of benzothiophene. An abrupt change in curvature in the C_{satd} *vs.* T curve for the supercooled crystals II was observed between 110 and 120°K. Figure 1a shows the heat capacity curve, which is similar to the "glassy bump" observed with supercooled liquids. A "glassy bump" in the heat capacity curve has been observed previously in supercooled crystalline modifications of 1, *cis*-2-dimethylcyclohexane[10] and cyclohexanol.[11] The shape of the heat capacity curve of supercooled crystals II in the anomalous region depended upon the rate of cooling.

The C_{satd} *vs.* T curve for crystals I has a small but definite abrupt change in slope near 150°K. as shown in Fig. 1b. No anomalous behavior was noted during two separate series of heat capacity measurements in this temperature region. The data were reproducible and the precision of the measurements was normal.

The results of the study of the λ-type transition are illustrated graphically in Fig. 1c. Three heat capacity measurements were made in the rising por-

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(10) H. M. Huffman, S. S. Todd and G. D. Oliver, This Journal **71**, 584 (1949).

(11) K. K. Kelley, *ibid.*, **51**, 1400 (1929).

tion of the "lambda." Thermal equilibration was extremely slow and, consequently, the precision of the results was much less than normal.

Since the residual entropy of crystals II and the entropy of transition are nearly equivalent to *R* ln 2 and *R* ln 4, respectively, it is possible that simple order–disorder phenomena are responsible for some of the anomalous thermal behavior of benzothiophene. Unfortunately, the crystal structure of benzothiophene has not been studied. Interpretations that are based on thermal data must be speculative. Nevertheless, on the basis of the calorimetric data for benzothiophene and structural data for naphthalene,[12] which may be isomorphous with the sulfur compound, a reasonable qualitative explanation of the observed thermal behavior may be proposed. Since the two parts of a benzothiophene molecule are dimensionally similar,[13] it may be possible for the molecule to occupy a crystal lattice site in any one of four different orientations, *e.g.* such as those shown in Fig. 2. The four possible orientations are mutually interconvertible by appropriate rotations of 180° about an axis perpendicular to the plane of the molecule or one of the two in-plane axes *a* and *b*. If it is assumed that such random orientation is possible at the lattice sites in a benzothiophene crystal, then the observed thermal behavior is consistent with the postulates: 1. In crystals I no randomness of orientation exists. 2. In crystals II, above the transition, all the molecules are randomly distributed among the four possible orientations. 3. In supercooled crystals II at 0°K. there is a random distribution between two of the four forms.

Postulates 1 and 2 are consistent with the observed entropy of transition, and postulate 3 is consistent with the residual entropy found for crystals II.

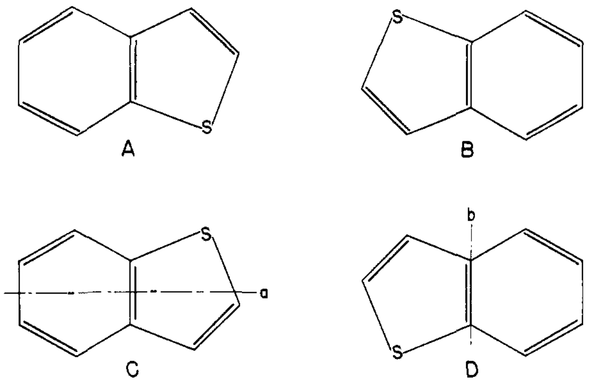

Fig. 2.—Four possible orientations of a benzothiophene molecule at a crystal lattice site.

The possibility of random orientation between two positions in crystals II at 0°K. suggests that the intermolecular potential barriers hindering rotation about two of the molecular axes are considerably larger than that about the third. Thus, by rotation about the axis with lowest potential barrier, unstable crystals II could attain partial order, presumably in the region near 115°K., but the higher barrier about the other two axes could prevent attainment of complete order. Relatively high barriers to rotation of the molecule would also account for the sluggish nature of the transition from crystals II to crystals I and for the exponential approach to thermal equilibrium noted in the I → II transition.

A more complete and reliable explanation of the thermal behavior of benzothiophene must await the results of X-ray crystallographic studies of the two crystalline forms in the appropriate temperature regions.

BARTLESVILLE, OKLA.

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[12] S. C. Abrahams, J. M. Robertson and J. G. White, *Acta Cryst.*, **2**, 233 (1949).

[13] The dimensional similarity is indicated by the fact that benzene and thiophene form a continuous series of solid solutions.

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES]

High Temperature Heat Contents of Manganese Sesquioxide and Vanadium Monoxide

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High temperature heat content measurements of crystalline manganese sesquioxide (Mn_2O_3) and vanadium monoxide (VO) were conducted throughout the temperature intervals 298–1350°K. and 298–1698°K., respectively. A table of smooth values of heat content and entropy increments above 298.16°K. is included, and the heat contents also are represented algebraically.

Introduction

Previous high temperature heat content measurements of the oxides of manganese include work on MnO by Southard and Shomate,[1] Mn_3O_4 by Southard and Moore,[2] and MnO_2 by Moore,[3] but data have been lacking for Mn_2O_3. Likewise, in the case of vanadium oxides the work of Cook[4] includes V_2O_3, V_2O_4 and V_2O_5, but no previous high temperature heat content data exist for VO.

Materials

The manganese sesquioxide was prepared by R. E. Lorenson of this Laboratory. Reagent grade manganous sulfate was dissolved in hot water and the hydroxide precipitated with ammonium hydroxide. The precipitate was washed by decantation, filtered, baked on a hot-plate, crushed to −60 mesh, and again washed thoroughly with hot water. After drying, the product was ground to −100 mesh and heated in air for 45 hours at 910–925° and 20 hours at 940–980°, followed by heating in a stream of pure oxygen for 6 hours at 550°. Analysis gave 69.64% manganese, as com-

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[1] J. C. Southard and C. H. Shomate, THIS JOURNAL, **64**, 1770 (1942).

[2] J. C. Southard and G. E. Moore, *ibid.*, **64**, 1769 (1942).

[3] G. E. Moore, *ibid.*, **65**, 1398 (1943).

[4] O. A. Cook, *ibid.*, **69**, 331 (1947).