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.

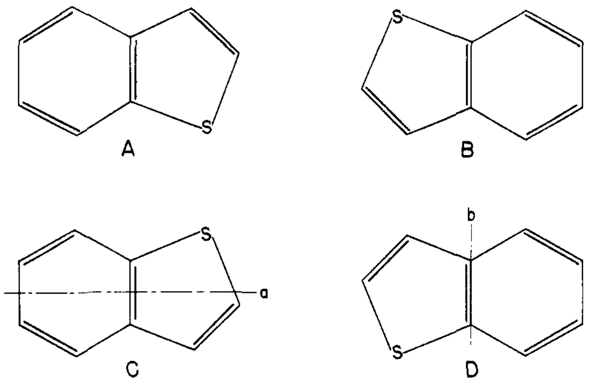

Fig. 2.—Four possible orientations of a benzothiophene molecule at a crystal lattice site.

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.

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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).

pared with the theoretical 69.59%, and 10.13% available oxygen, as compared with the theoretical 10.14%. X-Ray diffraction showed only lines agreeing completely with the pattern for bixbyite listed in the A.S.T.M. catalog.

The vanadium monoxide was a portion of the sample described by Todd and Bonnickson[5] and used by them in low temperature heat capacity measurements. According to their observations, the indicated purity is 98.2%, there being present a minor amount of sesquioxide either from incomplete reaction or from disproportionation.

Measurements and Results

The measurements were conducted with previously described apparatus.[6] The samples were enclosed in platinum–rhodium capsules which were sealed gas tight by platinum welding. Before sealing, the pore space was evacuated and filled with helium. The heat contents of the empty capsules were determined by separate experiments. During the course of the measurements, the furnace thermocouple was calibrated frequently against the melting point of pure gold.

The measured results appear in Table I, being expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole. Molecular weights accord with the 1951 International Atomic Weights,[7] and all weighings were corrected to vacuum.

TABLE I

MEASURED HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
		Mn_2O_3 (mol. wt. 157.86)			
397.3	2,480	798.0	13,970	1112.2	24,100
497.7	5,160	896.2	17,060	1197.3	27,070
596.4	7,935	1004.4	20,560	1302.1	30,720
697.5	10,920	1087.5	23,300	1350.4	32,430
		VO (mol. wt. 66.95)			
394.3	1,095	870.2	7,250	1385.2	14,880
497.6	2,355	978.0	8,790	1495.1	16,650
594.5	3,575	1071.9	10,150	1592.3	18,280
692.2	4,820	1182.2	11,830	1697.6	20,190
794.0	6,185	1286.3	13,390		

The results for manganese sesquioxide are entirely regular, there being no evidence of any isothermal heat absorption or any sharp change in slope of the heat content curve. No difficulty was encountered in the measurements below 1300°K. During heating before the 1302.1°K. measurement, the platinum–rhodium capsule swelled and leaked from decomposition pressure of the oxide. The loss of oxygen was 0.011 g. or about 0.1% of the sample mass. A second capsule leaked in similar fashion during heating before the 1350.4°K. measurement, the oxygen loss being 0.016 g. or about 0.15% of the sample mass. These two measurements were corrected accordingly, using Southard and Shomate's[1] data for Mn_3O_4.

The results for vanadium monoxide also are entirely regular. Some attack of the platinum–rhodium capsule by the oxide occurred during heating prior to the measurement at 1592.3°K. Two small pinhole leaks appeared, and there was an increase in weight (oxidation) of 0.0051 g. or 0.047% of the sample mass. This necessitated application of a minor correction to this run. During heating before the 1697.6°K. determination, further deterioration of the capsule and oxidation of the sample were noted, and the correction of this measurement amounted to 3.76%. As the exact nature of the reactions involved in capsule deterioration and increase in weight of the sample are not known, these corrections were approximated on the assumption that the heat content per gram atom of oxygen picked up through leakage of the capsule is the same as the difference in molal heat content between pure vanadium monoxide and vanadium metal. Consequently, it should be stressed that the 1697.6°K. result merits considerably less weight than the other experimental heat content values.

Table II gives smooth values of the heat content, and matching entropy increments above 298.16°K. computed by the method of Kelley.[8]

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPY INCREMENTS (CAL./DEG. MOLE) ABOVE 298.16°K.

T, °K.	Mn_2O_3		VO	
	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	2,550	7.33	1,160	3.34
500	5,220	13.28	2,380	6.06
600	8,040	18.42	3,640	8.35
700	10,990	22.97	4,940	10.36
800	14,040	27.04	6,280	12.15
900	17,190	30.75	7,660	13.77
1000	20,420	34.15	9,090	15.28
1100	23,740	37.31	10,560	16.68
1200	27,150	40.28	12,070	17.99
1300	30,650	43.08	13,610	19.22
1350	32,430	44.43	....	...
1400			15,170	20.38
1500			16,760	21.48
1600			18,370	22.52
1700			20,000	23.50

The measured heat contents are represented to within the indicated average deviations by the following equations

$Mn_2O_3(c)$:

$$H_T - H_{298.16} = 24.73T + 4.19 \times 10^{-3}T^2 + 3.23 \times 10^5 T^{-1} - 8829 \quad (0.1\%;\ 298 - 1350°K.)$$

VO(c):

$$H_T - H_{298.16} = 11.32T + 1.61 \times 10^{-3}T^2 + 1.26 \times 10^5 T^{-1} - 3941 \quad (0.2\%;\ 298 - 1700°K.)$$

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(5) S. S. Todd and K. R. Bonnickson, THIS JOURNAL, **73**, 3894 (1951).

(6) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(7) E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

(8) K. K. Kelley, U. S. Bur. Mines Bulletin 476 (1949).