[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low Temperature Heat Capacity, Entropy at 298.16°K. and High Temperature Heat Content of Titanium Disulfide

BY S. S. TODD AND J. P. COUGHLIN

The low temperature heat capacity of titanium disulfide was measured throughout the temperature range from 51 to 298°K. The entropy was evaluated as $S°_{298.16} = 18.73 \pm 0.15$ cal./deg./mole. The high temperature heat content of titanium disulfide was measured throughout the temperature range from 298 to 1010°K. A transition, involving no isothermal heat absorption but corresponding to a maximum in heat capacity, was found at 420°K.

Introduction

No thermodynamic data for the titanium sulfides are to be found in the literature, although the compounds in the titanium–sulfur system are well known.[1] This paper presents low temperature heat capacity, entropy and high temperature heat content values for the disulfide.

Material

The titanium disulfide was prepared at the Mississippi Valley Experiment Station of the Bureau of Mines and furnished through the courtesy of R. G. Knickerbocker. It was made by the reaction of titanium tetrachloride and hydrogen sulfide at 625°. X-Ray diffraction results agreed with those of Biltz, Ehrlich and Meisel.[1]

Our analysis gave 42.48% titanium, as compared with the theoretical 42.76%. The principal impurities were indicated by spectrographic analysis to be 0.2% silicon, 0.1% iron and 0.05% copper. Complete ignition to oxide confirmed to within 0.7% the theoretical TiO_2:TiS_2 weight ratio. It was concluded that the purity of the sample was somewhat better than 99%.

Measurements and Results

The low temperature heat capacity measurements of titanium disulfide were made with previously described apparatus and methods,[2] the mass of material employed being 94.244 g. The results, expressed in defined calories per degree per mole (112.03 g.), are in Table I. A regular trend with temperature is exhibited as there is no evidence of any abnormality.

TABLE I

LOW TEMPERATURE HEAT CAPACITY OF TiS_2 (MOL. WT. 112.03)

T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
53.91	3.242	114.88	9.345	216.23	14.61
57.79	3.630	124.56	10.13	226.30	14.83
62.01	4.067	136.11	10.97	236.24	15.07
66.11	4.493	146.24	11.60	245.81	15.28
70.64	4.988	156.04	12.18	256.28	15.48
75.53	5.522	166.00	12.72	266.28	15.68
79.83	5.973	176.01	13.19	276.43	15.84
83.94	6.402	186.03	13.62	288.67	16.06
94.97	7.516	196.17	13.97	296.66	16.23
104.46	8.470	206.21	14.32	298.16	(16.23)

The entropy increment for the measured temperature range was calculated by Simpson rule integration of a plot of C_p *vs.* log T, as $S°_{298.16} - S°_{51.00} = 17.35$ cal./deg./mole. The entropy increment between 51.00° K. and absolute zero was obtained by extrapolation, employing the Debye and Einstein function sum $D\left(\frac{219}{T}\right) + 2E\left(\frac{418}{T}\right)$ which represents the measured heat capacities to within 1.0% up to 250° K., and within 2.0% above 250° K. The extrapolated portion is $S°_{51.00} = 1.38$. The total for 298.16° K. is $S°_{298.16} = 18.73 \pm 0.15$ cal./deg./mole.

The high temperature heat content measurements of titanium disulfide also were conducted with previously described apparatus.[2] The sulfide (4.9533 g. mass) was contained in a platinum-rhodium alloy capsule during the measurements. After being filled with sulfide, the capsule was evacuated and the pore space filled with helium. Finally, the capsule neck was sealed gas tight by platinum welding. The heat content of the empty capsule was determined by separate measurements.

The measured results, expressed in defined calories per mole, are in Table II. A close examination of these results indicates a small anomaly near 420° K. This is best seen by plotting the difference function

$$\Delta = (H_T - H_{298.16}) - 16.23\,(T - 298.16°)$$

in which $(H_T - H_{298.16})$ is the measured heat content at T and 16.23 is the heat capacity at 298.16° K. The slope of this function increases rapidly to a maximum value near 420° K. (approximate, rounded temperature), then decreases to virtually zero in the range 470 to 520° K., and finally again increases beyond 520° K. As a maximum in $d\Delta/dT$ corresponds to a maximum in dH/dT, it appears that the heat capacity passes through a "peak" near 420° K., without any isothermal heat absorption.

Measurements above 1010.7° K. were precluded by the high sulfur pressure developed by thermal decomposition of the sulfide, which ruptured the capsule at 1053° K.

TABLE II

HIGH TEMPERATURE HEAT CONTENT OF TiS_2 (MOL. WT. 112.03)

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
360.8	1050	411.7	1985	562.9	4,645
373.2	1295	423.7	2225	610.2	5,505
373.6	1260	433.6	2415	710.5	7,405
380.9	1420	437.8	2495	806.4	9,195
387.6	1565	474.9	3135	908.1	11,120
395.3	1695	514.8	3785	1010.7	13,190
400.9	1830	518.1	3845		

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(1) W. Biltz, P. Ehrlich and K. Meisel, *Z. anorg. Chem.*, **234**, 97 (1937).

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

TABLE III

MOLAL HEAT CONTENT AND ENTROPY INCREMENTS ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$	T, °K.	$H_T - H_{298.16}$	$-S_T$ $S_{298.21}$
350	860	2.65	700	7,210	15.22
400	1800	5.16	800	9,090	17.73
420	2180 (α)	6.09 (α)	900	11,000	19.98
420	2180 (β)	6.09 (β)	1000	12,970	22.05
500	3540	9.05	1100	15,020	24.00
600	5350	12.35			

Table III gives the smooth curve values of the heat content and entropy increments above 298.16° K., for use in thermodynamic calculations.

The heat content values are represented, to within the average deviations shown in parentheses, by the equations

$$TiS_2(\alpha): H_T - H_{298.16} = 8.08T + 13.67 \times 10^{-3}T^2 - 3624; \ (1.0\%; 298\text{–}420°K.)$$

$$TiS_2(\beta): H_T - H_{298.16} = 14.99T + 2.57 \times 10^{-3}T^2 - 4569; \ (0.3\%; 420\text{–}1010°K.)$$

BERKELEY 4, CALIFORNIA

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Use of the Hammett Equation in the Prediction of Product Ratios in the Schmidt Reaction of Unsymmetrical Diarylethylenes

BY WILLIAM E. MCEWEN AND NARIMAN B. MEHTA

The Schmidt reaction has been applied to five additional *m*- and *p*-substituted 1,1-diphenylethylenes. The ratios of acetophenone to the *m*- or *p*-substituted acetophenone produced in the various reactions have been correlated by an adaptation of the Hammett equation.

In the pinacol–pinacolone rearrangement of a symmetrical pinacol[1] or the Schmidt reaction of an unsymmetrical diarylethylene,[2] a mixture of products is obtained, the ratio of the components depending on the relative rates of migration of the groups which, in the transition state, are in a position to migrate. This competitive migration, when applied to aryl groups, has been compared with the process of aromatic substitution.[3] More detailed treatments of a similar nature, with reference to other rearrangements, have recently appeared.[4]

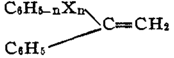
Among numerous other applications, Hammett has shown that the relative reactivities of *m*- and *p*-positions in benzene derivatives with respect to nitration, are in accord with the Hammett equation.[5] This being the case, and extending the analogy between aromatic substitution and the process of migration of aryl groups in competitive rearrangements, the Hammett equation in the latter situation might be modified to

$$\text{log intrinsic migratory aptitude} = \sigma\rho \qquad (1)$$

An examination of the previous data on the Schmidt reaction of unsymmetrical diarylethylenes[2a] indicates that a linear relationship between the logarithms of the product ratios and the sigma values of the aryl groups undergoing migration does exist. To verify this relationship, five additional reactions of *m*- or *p*-substituted diphenylethylenes with hydrazoic and sulfuric acids have been studied. The results are summarized in Table I. With reference to the mechanism of these reactions,[2a] it should be kept in mind that the aryl group which undergoes migration ends up as aniline or an aniline derivative and the remaining aryl group appears finally as acetophenone or a *m*- or *p*-substituted acetophenone. Hence a high product ratio of acetophenone to the *m*- or *p*-substituted acetophenone indicates preferential migration of the *m*- or *p*-substituted phenyl group.

TABLE I

YIELDS OF KETONES IN THE OLEFIN REACTIONS

Starting material  X	Yield of ketones, % Acetophenone	*m*- or *p*-X·Acetophenone
3,4-Di-CH_3	36.6	6.76
p-C_2H_5	44.6	9.75
m-CH_3	34.2	14.5
p-F	45.8	26.1
p-Br	16.0	29.6

An analysis by the method of least squares of the new data, together with the data previously reported,[2a] indicates that the following relationship between product ratios (migratory aptitudes) and the sigma values of the groups undergoing migration holds

$$\text{log migratory aptitude} = -2.11\sigma + 0.293 \qquad (2)$$

The experimental data fit this equation with an average accuracy of ±18%. Figure 1B summarizes the data. In Table II are listed the experimentally observed migratory aptitudes of the nine *m*- or *p*-substituted phenyl groups studied (phenyl = 1), and the modified values derived by use of equation (2). The intercept in equation

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(1) (a) W. E. Bachmann and J. W. Ferguson, THIS JOURNAL, **56**, 2081 (1934); (b) W. E. Bachmann and F. H. Moser, *ibid.*, **54**, 1124 (1932); (c) M. Tiffeneau and A. Orekhoff, *Bull. soc. chim. France*, **35**, 1639 (1924); (d) H. H. Hatt, A. Pilgrim and E. F. M. Stephenson, *J. Chem. Soc.*, 478 (1941); (e) R. Gaertner, *J. Org. Chem.*, **15**, 1006 (1950).

(2) (a) W. E. McEwen, M. Gilliland and B. I. Sparr, THIS JOURNAL, **72**, 3212 (1950); (b) L. P. Kuhn and J. DiDomenico, *ibid.*, **72**, 5777 (1950).

(3) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 517.

(4) (a) P. D. Bartlett and J. D. Cotman, Jr., THIS JOURNAL, **72**, 3095 (1950); (b) P. I. Pollak and D. Y. Curtin, *ibid.*, **72**, 961 (1950); (c) W. von E. Doering and L. Speers, *ibid.*, **72**, 5515 (1950); (d) S. L. Friess and N. Farnham, *ibid.*, **72**, 5518 (1950); (e) D. J. Cram, *ibid.*, **71**, 3863 (1949).

(5) L. P. Hammett, "Physical Organic Chemistry," 1st ed., McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 198.