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EQUILIBRIUM SUBLIMATION AND THERMODYNAMIC PROPERTIES OF SnS *

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ABSTRACT

Knudsen effusion studies of the sublimation of polycrystalline SnS, prepared by annealing and chemical vapor transport, have been performed employing vacuum microbalance techniques in the temperature range 733—944 K and at pressures ranging from about 6×10^{-3} to 11 Pa.

The third-law heats of sublimation and second-law entropy of reaction SnS(s) = SnS(g) were determined to be $\Delta H^0_{298} = 220.4 \pm 3.0$ kJ mole^{-1} and $\Delta S^0_{298} = 162.4 \pm 4.5$ J K^{-1} mole^{-1}. From these data the standard heat of formation and absolute entropy of SnS(s) were calculated to be —102.9 ± 4.0 kJ mole^{-1} and 79.9 ± 6.0 J K^{-1} mole^{-1}, respectively.

INTRODUCTION

For the consistent interpretation of chemical vapor transport studies of the SnS—SnI_4 system [1], of the sublimation mechanism of SnS single crystals [1] and of subsequent decomposition studies of the higher tin sulfides, accurate equilibrium vapor pressures of SnS in the temperature ranges of these investigations are required. Knudsen-type effusion measurements provide quantitative vapor pressure data which serve as a basis for the evaluation of the above studies.

Tin monosulfide is known to undergo a solid phase transformation at about 875 K [2,3]. However, the nature of this transformation was only recently established to be from distorted NaCl to the T2I-type orthorhombic structure [4]. Earlier vaporization studies of SnS were performed above the transformation temperature. The apparent vapor pressure of SnS was measured in the temperature range 776—977 K using an open crucible [5]. Subsequent studies employing the transpiration method [6], the entrainment technique [7] and measurements of the boiling point under reduced pressure [8] in the range 890—1373 K yielded vapor pressures considerably higher than those reported earlier [5]. Mass spectrometric studies [9] demonstrated the predominant mode of sublimation of SnS to monomeric

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molecular species. Using carrier and effusion methods, the vapor pressure of SnS was measured in the temperature ranges 1023—1154 K and 723—833 K, respectively [10]. The vapor pressure functions reported [10] for the high and low temperature modifications of SnS are nearly identical. In view of the small heat of transformation of SnS [2], this result [10] would be expected. However, the large orifice used in the above effusion studies [10] raises doubts concerning either the equilibrium pressures below the transformation [10] or the heat of transformation [2] of SnS. Further, earlier measurements [5] and ongoing studies [1] reveal that the vaporization coefficient of SnS is significantly less than unity. These uncertainties make a redetermination of the equilibrium vapor pressure of the low temperature modification of SnS necessary In addition, since single crystalline specimens prepared by chemical vapor transport and used for kinetic studies [1] contain iodine. it was also desirable to confirm that iodine inclusions do not measurably affect the equilibrium vapor pressure of SnS.

The present work is concerned with dynamic mass-loss measurements of SnS above and below the transition temperature employing Knudsen effusion techniques and two orifice sizes. In order to establish a reference basis for the kinetic studies [1]. SnS was synthesized by annealing and by chemical vapor transport reaction employing techniques discussed earlier [11]

EXPERIMENTAL PROCEDURES

Tin monosulfide (SnS) was prepared by annealing stoichiometric amounts of tin (99.999%) and sulfur (99.999%) in pretreated [11] and evacuated ($<10^{-4}$ Pa) sealed ampoules of fused silica at about 1070 K for several hours. In order to insure complete reaction, the annealing product was sublimed repeatedly and quantitatively (~970 → 820 K) in the same ampoule. SnS was also prepared by annealing and subsequent chemical vapor transport in the presence of about 5 kPa of SnI_4 in an 870 → 770 K temperature gradient. The identification of the starting materials was established by X-ray diffraction techniques. All reflections of Debye—Scherrer powder photographs (114.59 mm diameter camera, Ni-filtered Cu$K\alpha$ radiation) could be indexed on the basis of the orthorhombic unit cell of SnS and the lattice parameters ($a = 0.4331 \pm 0.0007$ nm, $b = 1.119 \pm 0.002$ nm, $c = 0.3987 \pm 0.0006$ nm) were in good agreement with literature values [4,12] in all cases.

The vapor pressure measurements on SnS were carried out with a Cahn RH vacuum microbalance with automatic recording of the mass-loss of the sample as a function of time. The apparatus and details of the temperature control, calibration and measurements have been previously described [13]. All reported temperatures are corrected accordingly.

The Knudsen cells used in this work were fabricated from fused silica. The crucible and lid, attached by ground joints, had a height of 30 mm and an outer diameter of 18 mm. The bottom part of the crucible was slightly tapered to fit firmly into a tungsten wire basket. The effective orifice area in the center of the lid was calibrated by vaporizing high-purity (99.999 + %)

vacuum distilled zinc under pressure conditions (10^{-2}—10 Pa) corresponding to the actual Knudsen measurements. The vapor pressure function by Barrow et al. [14] for zinc was used in the evaluation. The effective orifice areas of cells No. 1 and 2 were determined to be 5.844×10^{-4} cm^2 and 6.767×10^{-3} cm^2, respectively. The uncertainty in these quantities is estimated to be <5%, the number of figures used has only calculational significance. After outgassing the crucibles for 15 h at about 1270 K at a pressure of less than 10^{-4} Pa, there was no measurable mass-loss of the Knudsen cells in the temperature range of the investigation. Any mass change of the suspension wire (tungsten) during the actual runs was found to be negligible.

Mass-loss data were recorded continuously, and only after steady state values were attained at a given temperature were the data used for evaluation. Two different orifice sizes and three independent runs yielded a total of 85 data points. The amount of starting material was about 1500 mg. The measurements were made in both increasing and decreasing temperature order in a nonsystematic way. The average mass losses for individual measurements were about 200—250 μg. The corresponding experimental times for the majority of the data ranged from about 10 min at high temperatures to 21 h at low temperatures. X-ray diffraction patterns of the vaporization residues agreed with those of the starting materials in all cases.

RESULTS AND DISCUSSION

The predominant mode of sublimation of SnS [9] is given by the reaction

$$SnS(s) = SnS(g) \qquad (1)$$

The effect of higher molecular gaseous tin sulfides [9] on the total mass-loss is negligible. The numerical results of the vapor pressure measurements on SnS based on reaction (1) are listed in Table 1. The first two columns contain the corrected temperature in K and the mass-loss rate in g sec^{-1}, respectively. The uncertainty in the temperature is estimated to be less than ±2 K and in the mass-loss ±3 μg. In the third column are listed values for the total pressure P_t which is equal to K_p for this system Standard Gibbs free energies for reaction (1) are given in column four.

In view of the solid phase transformation of SnS(s) at about 875 K [2—4], the calculation of the third-law heats of reaction (1), ΔH^0_{298}, is based on the corresponding thermochemical data for the low temperature (β) and high temperature (α) modifications of SnS(s). An independent evaluation of the vapor pressure data obtained above and below the transition temperature yielded vapor pressure functions identical within error limits with the corresponding equation based on the combined data. This demonstrated that the heat of transformation of SnS is small, as reported earlier [2]. Therefore, the following evaluation is based on all data. A discussion of this observation in connection with earlier results [10] will be given below. For consistency, literature data used for the evaluation were converted to SI units using 1 cal$_{th}$ = 4.184 J and 1 atm = 101325 Pa. The absolute entropy and heat capacity of SnS(β, s) are $S^0_{298} = 77.0$ J K^{-1} mole^{-1} [15] and $c^0_p = 35.7 + 31.3 \times 10^{-3}T + 4 \times 10^5 T^{-2}$ J K^{-1} mole^{-1} [2]. The heat capacity of SnS(α, s)

TABLE 1

Vapor pressures, free energies and third-law heats of sublimation of SnS(s) according to reaction (1) [a]

T (K)	Mass-loss rate ($g\ sec^{-1} \times 10^{-8}$)	$P_t(K_p)$ (Pa)	ΔG°_T (kJ mole^{-1})	ΔH°_{298} (kJ mole^{-1})
Run No. 1: SnS prepared by annealing; effective orifice area = 5.844 × 10^{-4} cm^2				
766	0.3257	0.0287	96.0	218.4
780	0.4815	0.0428	95.1	219.6
792	0.8146	0.0730	93.1	219.4
799	0.9551	0.0860	92.8	220.1
807	1.278	0.1156	91.8	220.3
813	2.062	0.1873	89.3	218.7
826	2.789	0.2553	88.5	219.8
831	2.991	0.2747	88.6	220.7
836	3.501	0.3224	87.9	220.6
845	5.258	0.4868	86.0	220.0
851	6.603	0.6137	85.0	220.0
859	8.292	0.7739	84.1	220.2
863	9.769	0.9142	83.4	220.1
869	11.74	1.102	82.6	220.2
874	14.01	1.319	81.8	220.1
877	15.02	1.417	81.5	220.4
881	17.22	1.628	80.9	220.4
884	19.43	1.841	80.3	220.2
890	22.58	2.146	79.6	220.4
900	30.80	2.943	78.2	220.4
906	36.87	3.536	77.3	220.5
912	45.05	4.334	76.3	220.4
916	48.90	4.714	76.0	220.6
917	49.84	4.806	75.9	220.5
921	57.00	5.510	75.2	220.5
923	60.39	5.844	74.9	220.5
931	73.75	7.168	74.1	220.7
935	88.45	8.617	72.9	220.3
937	89.41	8.718	72.9	220.6
937	90.98	8.871	72.8	220.4
944	109.4	10.71	71.8	220.5
944	109.4	10.71	71.8	220.5
				Ave 220.2 ±0.5
Run No. 2: SnS grown in the presence of 5 kPa SnI_4 in an 870 → 770 K temperature gradient; effective orifice area = 5.844 × 10^{-4} cm^2				
789	0.7205	0.0644	93.5	219.3
804	1.303	0.1177	91.3	219.3
816	1.663	0.1513	91.0	220.8
823	2.107	0.1926	90.2	221.0
825	2.387	0.2184	89.5	220.7
838	3.851	0.3550	87.5	220.5
848	5.731	0.5315	85.7	220.2
857	7.695	0.7174	84.4	220.2
870	11.48	1.079	82.8	220.5
877	15.21	1.435	81.4	220.3
882	17.04	1.612	81.0	220.7

TABLE 1 (continued)

T (K)	Mass-loss rate (g sec^{-1} × 10^{-8})	$P_t(K_p)$ (Pa)	ΔG°_T (kJ mole^{-1})	ΔH°_{298} (kJ mole^{-1})
894	26.21	2.496	78.9	220.3
897	29.34	2.800	78.3	220.2
898	29.78	2.843	78.2	220.2
911	44.47	4.275	76.3	220.2
911	44.80	4.308	76.3	220.2
917	54.61	5.268	75.2	220.0
929	76.45	7.420	73.5	219.9
929	78.62	7.633	73.3	219.8
936	93.21	9.084	72.5	220.0
936	94.91	9.251	72.4	220.0
				Ave.: 220.2 ± 0.4
Run No 3 SnS prepared by annealing; effective orifice area = 6.767 × 10^{-3} cm^2				
733	0.7817	0.0058	101.6	219.2
753	1.634	0.0123	99.7	220.2
774	3.788	0.0290	97.0	220.7
782	4.990	0.0384	96.1	220.9
795	8.781	0.0681	93.9	220.6
802	11.23	0.0875	93.1	220.8
811	14.99	0.1175	92.2	221.3
822	23.47	0.1851	90.3	221.0
823	23.54	0.1858	90.4	221.2
828	29.76	0.2356	89.3	220.9
830	31.93	0.2530	89.0	220.8
830	32.05	0.2540	89.0	220.9
837	34.29	0.2728	89.2	222.0
845	54.68	0.4372	86.7	220.8
846	59.52	0.4764	86.3	220.6
853	71.84	0.5771	85.6	220.8
859	88.65	0.7147	84.7	220.8
859	90.58	0.7303	84.6	220.6
864	105.5	0.8530	83.9	220.7
864	105.8	0.8554	83.9	220.7
868	122.5	0.9927	83.2	220.6
868	122.4	0.9919	83.2	220.6
868	125.5	1.017	83.1	220.5
878	170.4	1.389	81.7	220.7
885	206.3	1.688	81.0	221.0
896	283.4	2.334	79.6	221.3
905	378.8	3.135	78.1	221.1
910	452.9	3.758	77.2	220.9
917	537.6	4.478	76.4	221.1
923	646.0	5.398	75.5	221.0
929	801.3	6.718	74.3	220.8
929	801.3	6.720	74.3	220.9
				Ave.: 220.8 ±0.4

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[a] The number of figures reported in columns two and three has only calculational significance The errors reported for the average of the third-law heats of sublimation represent one standard deviation

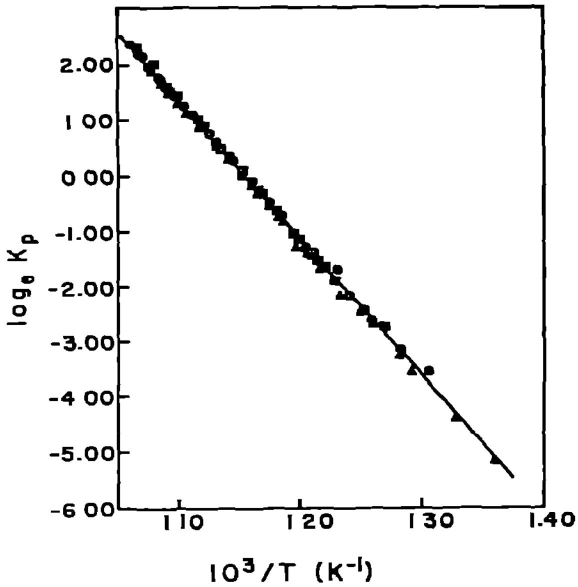

Fig. 1 Graphical representation of $\log_e K_p$ of reaction (1) vs. $1/T$. (●) Run No. 1, (■) run No. 2, (▲) run No. 3

is $c_p^0 = 40.9 + 15.6 \times 10^{-3}T$ J K^{-1} $mole^{-1}$ [2]. The enthalpy and calculated entropy of the reaction SnS(β, s) = SnS(α, s) at the temperature of transformation (875 K) are $\Delta H^0_{875} = 669$ J $mole^{-1}$ [2] and $\Delta S^0_{875} = 0.765$ J K^{-1} $mole^{-1}$. The corresponding data for SnS(g) are $S^0_{298} = 242.3$ J K^{-1} $mole^{-1}$ [16] and $c_p^0 = 36.9 + 0.3 \times 10^{-3}T - 2.3 \times 10^5 T^{-2}$ J K^{-1} $mole^{-1}$ [17]. The third-law heats of reaction (1), ΔH^0_{298}, computed with the above thermochemical data, are listed in column 5 of Table 1. The average value of the third-law enthalpy of reaction (1), based on all three runs, is $\Delta H^0_{298} = 220.4 \pm 0.1$ kJ $mole^{-1}$, where the uncertainty represents a 95% confidence level. The error in this quantity is estimated to be ± 3 kJ $mole^{-1}$. The random deviation of the individual heats of reaction (Table 1, column 5) from the mean value confirms that any differences between the heats of sublimation of the low and high temperature modifications of SnS(s) are not measurable under these conditions.

The second-law enthalpy and entropy of reaction (1) are obtained from the slope and intercept of a linear least-squares treatment of all data represented in Fig. 1. For the mean temperature of all runs, these values are $\Delta H^0_{839} = 208.0 \pm 3.8$ kJ $mole^{-1}$ and $\Delta S^0_{839} = 144.0 \pm 4.5$ J K^{-1} $mole^{-1}$, where the confidence limits are at the 95% level. Upon conversion to 298 K, these data become $\Delta H^0_{298} = 218.1 \pm 3.8$ kJ $mole^{-1}$ and $\Delta S^0_{298} = 162.4 \pm 4.5$ J K^{-1} $mole^{-1}$. The second-law enthalpy of reaction (1) agrees within error limits with the above third-law value based on an independent entropy of reaction. Using the entropy change of reaction (1) obtained from the second-law treatment of all data (162.4 J K^{-1} $mole^{-1}$) in the third-law calculations yields results within error limits of the above discussed enthalpy of reaction. These data are summarized in Table 2. The data in Fig. 1 confirm that the equilib-

TABLE 2

Summary of the heats of sublimation of SnS according to reaction (1) and the heats of formation of SnS from Knudsen effusion measurements

Run No. (orifice No.)	Temp range (K)	Second-law		Third-law	
		ΔH°_{298} (kJ mole^{-1})	ΔS°_{298} (J K^{-1} mole^{-1})	ΔH°_{298} [a] (kJ mole^{-1})	ΔH°_{298} (f) (kJ mole^{-1})
1	766—944	214.9	159.2	220.2	—102.7
(1)				(217.6)	
2	789—936	221.9	167.2	(220.2	—102.7
(1)				(217.6)	
3	733—929	218.3	162.1	220.8	—103.3
(2)				(218.3)	
Combined	733—944	218.1	162.4	220.4	—102.9
(1 and 2)				(217.9)	

[a] Values without parentheses are based on literature entropies, those with parentheses are based on second-law entropy change of combined results (162.4 J K^{-1} mole^{-1})

rium vapor pressure of SnS(s) can be expressed by the equation

$$\log_e P_t(\text{Pa}) = -\frac{(25020 \pm 460)}{T} + (28.85 \pm 0.54) \qquad (2)$$

for both the low and high temperature modifications of SnS with a confidence level of 95%. In addition, a comparison of runs No. 1 and 2 (Table 1 and Fig. 1) reveals, that any differences in thermodynamic results for the annealed and transported starting materials are insignificant under present experimental conditions.

The heat of formation of SnS(s) has been calculated from individual values of ΔH°_{298} of reaction (1) listed in Table 1. For this calculation, the dissociation energy of SnS(g) [9] (464.0 kJ mole^{-1}), the heat of formation of Sn(g) [18] (301.3 kJ mole^{-1}) and the heat of formation of S(g) (280.3 kJ mole^{-1}), based on the heat of formation of S_2(g) [19] (130.5 kJ mole^{-1}) and on the heat of dissociation of S_2(g) [20] (429.7 kJ mole^{-1}), were used. The mean value of the heat of formation of SnS(s) is $\Delta H^\circ_{298} = -102.9 \pm 0.1$ kJ mole^{-1}. The error in this quantity is estimated to be about ±4 kJ mole^{-1} With the above second-law entropy of reaction (1), $\Delta S^\circ_{298} = 162.4$ J K^{-1} mole^{-1} and the absolute entropy of SnS(g) [16] (242.3 J K^{-1} mole^{-1}), a value for the absolute entropy of SnS(s) of $S^\circ_{298} = 79.9 \pm 4.5$ J K^{-1} mole^{-1} is obtained. The error is estimated to be ±6 J K^{-1} mole^{-1} These results are in close agreement with literature data [6—9].

The thermochemical values for the sublimation of SnS(s) determined in this work are summarized in Table 2. The agreement between individual runs and combined data indicates that errors due to sample preparation, temperature and mass-loss measurements were small.

SUMMARY AND CONCLUSIONS

Accurate equilibrium vapor pressures of the sublimation of SnS as a function of temperature both above and below the solid phase transformation have been determined. The absolute entropy and the heat of formation of SnS(s) have been obtained by second- and third-law evaluation of the experimental data.

It is apparent from the data in Table 1 and Fig. 1 that the Knudsen measurements based on the crucible with the smaller effusion orifice consistently yielded total pressures which are approximately 15% greater than those obtained with the larger orifice. This observation indicates that the vaporization coefficient of SnS is less than unity. However, both orifice sizes employed in this work are well within the practical range commonly used in measurements of this type. In addition, the data in Table 2 show that the third-law heats of reaction of the individual runs based on the same entropy of reaction agree within ±0.3 kJ mole^{-1}. Since the orifice sizes used differ by a factor of about 11, a further reduction in size would not change the results significantly.

The vapor pressures determined in this work are considerably higher than those of earlier measurements [5] using an open crucible and assuming a vaporization coefficient of unity. The results of on-going studies [1] and of those of analogous compounds [21,22] suggest that the vaporization coefficient of SnS is less than unity. Vapor pressures of SnS based on transpiration [6], entrainment [7] and boiling point [8] measurements are in good agreement with our data. In view of the large orifice area employed in previous Knudsen studies [10] and the small heat of transformation of SnS [2] supported by the present work, the higher vapor pressures of the earlier studies [10] relative to our data are not consistent with the expected effect of orifice size on pressure.

The heat of sublimation (220.4 ± 3.0 kJ mole^{-1}), of formation (—102.9 ± 4.0 kJ mole^{-1}) and the absolute entropy (79.9 ± 6.0 J K^{-1} mole^{-1}) of SnS(s), based on the present effusion studies, are in close agreement with some of the earlier results [6—9]. The equilibrium vapor pressures of the low and high temperature modification of SnS can be expressed by one function. The inclusion of transport agent, if any, during the synthesis of SnS has no measurable effect on the equilibrium pressure.

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