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Publication Date
1978-09-01

LBL-8076
Preprint

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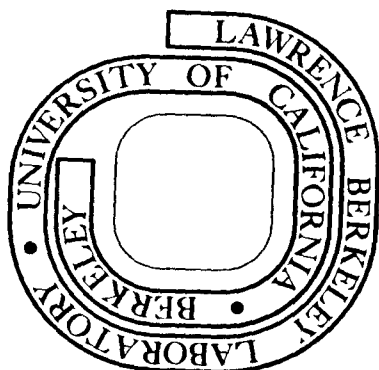
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September, 1978

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THERMODYNAMIC PROPERTIES OF SeS GAS

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ABSTRACT

Mass-spectrometric Knudsen effusion measurements show the heat of

formation of SeS to be 1.4 (±1.7) kcal per mole at 1000°K. SeS can be

an important vapor species when selenium is an impurity in metal sulfides.

In the vacuum deposition of sulfide and selenide coatings, the presence of SeS gas, if its concentration is high enough, might affect the coating compositions. Thus thermodynamic properties of SeS are of practical interest in semiconductor technology.

The SeS gas molecule was observed by Umilin et al.[1] and by Chernozubov and Selivanov.[2] Ahmed and Barrow[3] have reported spectroscopic data for it. While the present work was in progress Drowart and Smoes published a mass-spectrometric study of the stability of SeS.[4]

We used a quadrupole mass-filter to study the gas-phase reaction,

$$1/2 \ S_2 + 1/2 \ Se_2 = SeS \qquad (1)$$

These gases were generated by vaporizing a mixture of In_2S_3 and In_2Se_3 in a 99.5% alumina Knudsen cell. Orifice diameters of 1.03 and 0.52 mm were used. Measurements were made of the S_2^+, Se_2^+ and SeS^+ ion currents at 64, 160 and 112 atomic mass units, respectively, at a series of temperatures between 1117° and 1195°K (Table I).

In mass-spectrometric measurements the pressure P_m of a given vapor species in a Knudsen cell can be determined from the corresponding total ion current I_m^+ by means of the relation,

$$P_m \ \sigma_m \ g_m = I_m^+ \ T. \qquad (2)$$

In this expression σ_m is the ionization cross-section for the formation of the ion in question, g_m is the machine constant and T is the absolute temperature. For a quadrupole mass-filter, g_m depends on the ion mass. In this study the coincidences of masses 64 for $^{32}S^{32}S$ and ^{64}Zn and of mass 112 for $^{78}Se^{34}S$, $^{80}Se^{32}S$, and ^{112}Cd were exploited to obtain relative values of g_m needed for calibration.

CdS[5] and ZnSe[6] vaporize congruently in a Knudsen cell. Taking CdS as an example, this means that,

$$P_{Cd}/M_{Cd}^{1/2} = 2\ P_{S_2}/M_{S_2}^{1/2} \tag{3}$$

where P is the pressure of the species indicated in the subscript, and M the molecular weight. Combining (2) and (3) gives

$$\frac{I^+_{64}}{I^+_{112}} = \frac{a_{S_2}(64)\ g_{64}\ \sigma_{S_2}\ P_{S_2}}{a_{Cd}(112)\ g_{112}\ \sigma_{Cd}\ P_{Cd}} = \frac{1}{2}\left(\frac{64}{112}\right)^{1/2}\frac{a_{S_2}(64)\ g_{64}\ \sigma_{S_2}}{a_{Cd}(112)\ g_{112}\ \sigma_{Cd}}.$$

In this example the ion currents are those for the $^{112}Cd^+$ and $^{32}S^{32}S^+$ ions, with the corresponding abundances $a_{Cd}(112) = 0.24$ and $a_{S_2}(64) = 0.90$. For these calibrations the potential of the ionizing electrons was 40 V, whereas the listed values of σ^7 are given for V_{max}, the potential at which σ is a maximum. Values of σ at 40V. were calculated by assuming σ to be a linear function of the potential, equal to zero at the appearance potential and to the listed value at V_{max}. The calculated values were $\sigma_{Zn}=4.11$, $\sigma_{Se_2} = 6.87$, $\sigma_{Cd} = 5.13$ and $\sigma_{S_2} = 4.78$.

In this manner it was possible to determine the ratios, $g_{64}/g_{160} = 1.05$ and $g_{64}/g_{112} = 0.76$ which were then used to calculate the equilibrium constants for reaction (1) from the ion currents listed in Table 1:

$$K = \frac{P_{SeS}}{\left(P_{S_2}P_{Se_2}\right)^{1/2}} = \alpha\ \frac{I^+_{112}}{\left(I^+_{64}I^+_{160}\right)^{1/2}},$$

where $\alpha = \dfrac{g_{64}}{g_{112}}\left(\dfrac{g_{160}}{g_{64}}\right)^{1/2}\dfrac{\left(\sigma_{S_2}\ \sigma_{Se_2}\right)^{1/2}}{\sigma_{SeS}}\dfrac{\left[a_{S_2}(64)\ a_{Se_2}(160)\right]^{1/2}}{a_{SeS}(112)} = 0.774$

These measurements were made using an ionizing potential of 36 V, and the ionization cross-sections were calculated from the listed values[7] by the method discussed above. The calculated values were, $\sigma_{S_2} = 4.12$, $\sigma_{Se_2} = 5.98$, $\sigma_{SeS} = 5.05.$

Plots of log K vs. I/T yielded from the slopes $\Delta H° = -2100$ (±2600) cal. for reaction (1) from measurements with the 1.03 mm orifice and $\Delta H° = 2500$ (±3600) cal. with the 0.52 mm orifice.

From the measurements of Ahmed and Barrow,[3] we calculated the entropy of SeS, and found $\Delta S°$ for reaction (1) to be 1.42 cal deg.$^{-1}$ at 1100°K and 1.41 cal deg.$^{-1}$ at 1200°K. Values of $\Delta H°$ for reaction (1) can thus be calculated from $\Delta S°$ and each measured K. For the 1.03 mm orifice, the mean $\Delta H°$ was 2080 cal per mole of SeS, and for the 0.52 mm orifice, 380 cal per mole. The average of all twenty values for both orifices is 1400 (±1700) cal. We prefer this value to those obtained from the slope because the latter are unduly sensitive to measurements at the temperature extremes. For reaction (1) ΔC_p is essentially zero between room temperature and 1200°K, so $\Delta H_{298}°$ is also 1400 (±1700) cal. Drowart and Smoes[4] report a $\Delta H_o°$ value of 1900 (±1600) cal corresponding to the above, and a value of 1300 (±700) cal derived from the slope.

The importance of SeS as a vapor species can be illustrated for a solution (assumed ideal) of 1% CdSe dissolved in CdS at 1000°K. From known data for CdS[5] and CdSe[6] and K = 1.01 for reaction (1) we find $P_{S_2} = 1.9 \times 10^{-5}$ atm, $P_{SeS} = 1.0 \times 10^{-5}$ atm, and $P_{Se_2} = 5.6 \times 10^{-6}$ atm. Thus, SeS is predicted to be a major Se impurity carrier in vacuum deposition processes.

ACKNOWLEDGMENT

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Table I. Ion Intensities and Calculated Equilibrium Constants for Reaction (1).

$T(°K)$	$I_{64}^+(S_2^+)$	$I_{112}^+(SeS^+)$	$I_{160}^+(Se_2^+)$	$K = \alpha \dfrac{I_{112}^+}{(I_{64}^+ I_{160}^+)^{1/2}}$
d= 1.03mm				
1117	4.91	1.38	0.283	0.91
1137	9.30	2.47	0.435	0.95
1166	12.00	3.87	0.977	0.88
1138	24.3	12.27	5.55	0.82
1154	28.2	14.52	8.48	0.73
1165	27.6	18.15	10.08	0.84
1188	37.2	23.40	12.51	0.84
1130	9.68	4.80	2.25	0.80
1156	11.4	6.87	3.36	0.86
1195	21.6	9.09	3.56	0.80
1182	15.7	7.01	3.66	0.72
1119	4.48	2.34	1.23	0.77
d= 0.52mm				
1125	1.05	0.71	0.087	1.82
1125	1.25	0.63	0.090	1.45
1125	1.25	0.82	0.093	1.86
1146	1.39	0.81	0.108	1.62
1146	1.41	0.87	0.114	1.68
1164	1.8	1.41	0.186	1.89
1188	2.75	1.56	0.192	1.66
1188	2.50	1.70	0.195	1.88

d is the orifice diameter.