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Determination of the Vapor Pressure and Vaporization Coefficient of Polymeric Sulfur Nitride, $(SN)_x$

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The vapor pressure and vaporization coefficient of $(SN)_x$ were determined in the range 100–150 °C by a modification of the direct Knudsen method. Saturation pressures were derived from undersaturation information by a correlation and extrapolation of flux results from a single Knudsen cell with different orifice sizes. The vapor pressure of $(SN)_x$ is represented by $\ln P = 37.64 - 16351/T$. Enthalpy of vaporization is 32.49 ± 0.99 kcal/(mol K) and the vaporization coefficient 0.0035 ± 0.0004.

Introduction

Recent investigations[2,3] of the "nonmetallic" metal $(SN)_x$ have created considerable interest in the scientific community. The main emphasis has been on the conducting properties of the material and on the mechanism of conduction, but many physical and chemical studies have also been made. Smith et al.[4] have recently shown with mass spectrometric techniques that the vapor formed in the sublimation process is composed almost entirely of one species corresponding stoichiometrically to $(SN)_4$ but differing structurally from the "cradlelike" S_4N_4. Bright et al.[3,5] had shown that the polymeric $(SN)_x$ could be sublimed and recondensed to yield films of $(SN)_x$ similar in properties and appearance to the original bulk material. This phenomenon is of considerable interest since polymers generally do not behave in this manner.

The determination of the vapor pressure and the vaporization coefficient of $(SN)_x$ is a logical extension of these prior studies and sheds some light on the processes involved in vaporization. The vaporization coefficient is generally very small for materials when the molecular structure of the vapor species is substantially different from that of the bulk phase. This situation was found to be true for $(SN)_x$ and the unusually low vaporization coefficient generated some interesting but unique problems in the determination of saturation pressure.

Theory

The determination of vapor pressure by the Knudsen method is well-known for systems in which the pressure in the cell has reached saturation. Where this is not the case, saturation pressure (P_e) is related to the observed pressure (P_o) at varying degrees of undersaturation by the classical equation

$$P_e = P_o[1 + A_o/\alpha A_1] \qquad (1)$$

where A_o is orifice area, A_1 is evaporating area, and α is vaporization coefficient. This equation was derived for a cylindrical cell with the sample located at the base and an orifice located coaxially at the top of the cell. It was assumed in the derivation that the pressure is constant throughout the cell.

A generally more acceptable form is that derived by Motzfeldt[6]

$$P_o = P_e / \left[1 + \frac{A_o}{A_1}\left(\frac{1}{\alpha} + \frac{1}{K} - 2\right)\right] \qquad (2)$$

where K is the Clausing factor[7] of the cell. This Clausing factor is related to the theoretical value (K_T) by[8]

$$K = K_T \sum_{n=0}^{\infty} [(1 - K_T)(1 - \alpha)]^n \qquad (3)$$

It can be readily shown that when α is very small, the effective Clausing factor, K, will be ~1 and eq 2 approaches the form of eq 1. This then permits the application of the classical form of the equation when determining P_e for materials with low vaporization coefficients.

For many materials α is near unity and saturation can be achieved by the appropriate selection of cell and orifice sizes so that as the ratio $A_o/\alpha A_1$ approaches zero, P_o approaches P_e. If, however, the vaporization coefficient is very small, it becomes impractical to construct a cell which allows one to reach saturation within the cell. For this case, it is feasible at a particular temperature to obtain P_e indirectly[9] by determining values of P_o for differing degrees of undersaturation (different orifice sizes) and extrapolating these values with eq 1 to the saturation condition.

Experimental Section

Vaporization rates for $(SN)_x$ were obtained isothermally with small Knudsen cells by measuring weight loss against time with a recording Mettler thermoanalyzer[10] (Table I). All runs were carried out under apparent vacuums of 10^{-5} Torr or better.

Within the Mettler system, the Knudsen cell was positioned on top of a two-hole ceramic tube containing the thermocouple in such a way that the base of the cell was in direct contact with the hot junction of the thermocouple. Equilibrium temperature readings from this couple were observed with a precision potentiometer independently of the Mettler system. The calibration of the platinum—platinum–10% rhodium thermocouples was taken to be the same as that obtained by direct calibration at NBS for couples from the same rolls of wire. The isothermality of the furnace area was ensured by extensive testing in previous work with the thermoanalyzer.[11] The balance was frequently calibrated with standard weights and the chart speed was periodically checked; no calibration or adjustment of either was necessary.

The material used for this study was prepared at NRL using the method described by Mikulski et al.[12] A mass spectral analysis of the $(SN)_x$ used in this study was found to be the same as that for University of Pennsylvania material which was prepared by the same method and shown by commercial analysis[12] to be analytically pure. The material from the two sources is believed to be identical.

The $(SN)_x$ was loaded into the Knudsen cell under an inert atmosphere. The cell was generally filled to within $^1/_{16}$ in. of the top

Table I. Experimental Data

Orifice diameter, cm	Rate, mg/min	Temp, °C	Obsd pressure, P_0, Torr
0.023	0.00727	114.1	0.00726
	0.02083	123.5	0.02104
	0.0600	136.1	0.06155
	0.2133	146.4	0.22158
0.036	0.0500	125.5	0.02066
	0.10167	134.1	0.04247
	0.1400	135.7	0.05859
	0.3040	144.3	0.12856
	0.3775	146.9	0.16014
0.055	0.00669	105.9	0.00115
	0.01636	114.1	0.00286
	0.02000	115.4	0.00350
	0.04667	124.4	0.00825
	0.05714	125.1	0.01011
	0.05500	125.4	0.00974
	0.11882	134.8	0.02128
	0.14833	136.0	0.02661
	0.38500	146.4	0.06993
0.0630	0.00769	105.1	0.00101
	0.02286	115.4	0.00305
	0.07200	125.3	0.00971
	0.07200	125.4	0.00971
	0.08000	125.8	0.01080
	0.19714	136.6	0.02697
	0.51667	147.0	0.07157
Free evaporation	0.06235	115.5	3^a
	0.05500	117.0	3^a
	0.20600	125.2	11^a
	0.16167	126.6	9^a
	0.34800	135.1	19^a
	0.34800	135.4	19^a
	0.68500	146.0	38^a

[a] Pressure $\times 10^5$.

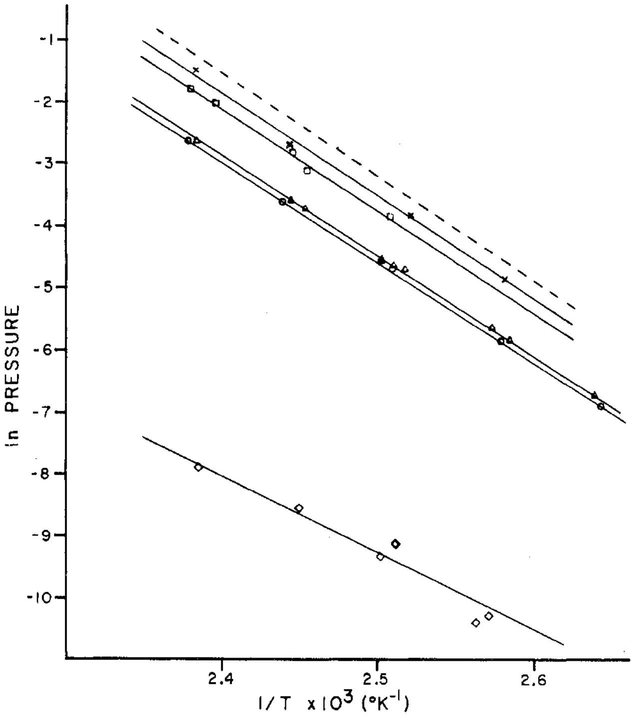

Figure 1. Experimental pressures of $(SN)_x$ vs. reciprocal of absolute temperatures: saturation values, P_e (- - -); undersaturation values, P_0, at (×) 0.23 mm, (□) 0.36 mm, (△) 0.55 mm, and (○) 0.63 mm; Langmuir free-evaporation pressures (◇).

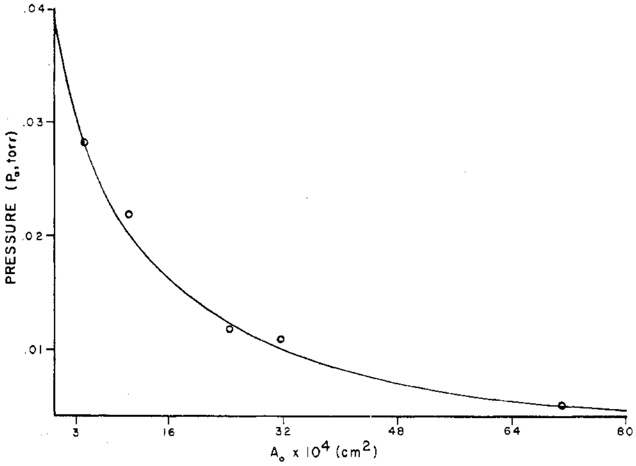

Figure 2. Observed undersaturation pressures vs. orifice areas at 400 K.

to further reduce the possibility of pressure differentials within the cell. The Mettler apparatus itself afforded a means of cleaning exposed surfaces. Prior to the actual rate measurements, the sample and cell were always heated to 80 °C overnight and to 175 °C for a short period of time. Experimental vaporization rates for $(SN)_x$ were not stable and reproducible without this preheat, indicating that the procedure was required to remove surface-adsorbed volatile impurities.

Knudsen Cell. The typical cell was of high-purity Poco graphite which, along with its cover, was prefired in the Mettler system to a constant weight at a temperature above 900 °C. The cell was designed for a positive gasket seal of 1 mil thick palladium sheet in which the small orifice was formed. Nominal orifice diameters were 0.25, 0.38, 0.50, 0.64, and 0.79 mm. The forming of satisfactory holes in the thin sheet was initially a problem, and machining techniques had to be developed for rigidly supporting the sheet and forming clean, round holes. The size of each orifice was measured with a traveling microscope before and after each experiment and dimensions were generally reproducible to better than 0.002 mm. The inside diameter of the cylindrical graphite cell used to contain the $(SN)_x$ was always 0.635 cm.

Results

The experimental results for the sublimation of $(SN)_x$ using four different orifice sizes and corresponding degrees of undersaturation are shown in Figure 1. Each observed pressure was calculated directly from the Knudsen equation using the molecular weight of $(SN)_4$ species which has been shown by Smith et al.[4] to be the principal species in the vapor state.

Interpolated pressures at each of several different temperatures for the different orifice sizes were fitted with eq 1 using a nonlinear least-squares method to yield the equilibrium pressure and the αA_l term. Figure 2 presents a plot of the dependence of observed pressure on the orifice area at a temperature of 400 K. Saturation pressures obtained in this manner at several temperatures are plotted on Figure 1, and the equation representing the results over the experimental temperature range is

$$\ln P = 37.64 - 16351/T \qquad (4)$$

For the experimental range, this gives an enthalpy of vaporization of 32.49 ± 0.99 kcal/(mol K) and an entropy of vaporization of 80.98 ± 2.48 cal/mol.

The composite value of αA_l was obtained at several temperatures in the course of the vapor pressure determinations. In order to evaluate α, it was necessary to know the absolute surface for evaporation. This was obtained from several free-evaporation experiments using the same-size crucible and varying the total exposed surface area of the crystals. The observed flux was found to be independent of the absolute surface area for at least a doubling of the apparent area, indicating that the vaporization surface of $(SN)_x$ can be taken to be the internal cross-sectional area of the cell. The vaporization coefficient obtained by using the geometric area for A_1 was 0.0035 ± 0.0004 and was independent of temperature for the experimental range. The vaporization coefficient, α, is by definition the ratio of the free-evaporation and saturation fluxes, or

$$\alpha = J_{\text{free}}/J_{\text{satn}} \tag{5}$$

The coefficient at any particular temperature can, therefore, be directly obtained experimentally.

Preliminary free-evaporation fluxes were observed on the Mettler system using pressed pellets of $(SN)_x$ in thermal contact with graphite crucibles. The results in the form of Langmuir pressures are shown graphically in Figure 1, and the average value of α is 0.0024 ± 0.001, which is in reasonable agreement with that observed in the treatment above.

Discussion

The inherent accuracy of the direct Knudsen method for the determination of vapor pressure under saturation conditions in the molecular-flow regime is well recognized. However, there are numerous materials with very low vaporization coefficients where it is either impractical or impossible to construct cells for the attainment of saturation conditions. For materials of this type, the authors believe that the experimental techniques described in this paper for the treatment of Knudsen results at undersaturation can be used to obtain saturation pressures with accuracies approaching those inherent in the direct method. Vapor pressures for these materials are generally obtained using mass spectrographic techniques and accuracy is often limited by the lack of knowledge of fragmentation parameters and ionization cross sections.

The enthalpy of vaporization (32.49 kcal/mol) obtained in this study is in reasonable agreement with the value (29 kcal/mol) obtained by mass spectral techniques.[4] The value of the vaporization coefficient (0.0024) obtained directly with eq 5 from the free-evaporation measurement and that obtained from the analysis of the undersaturation data (0.0035) are not independent since the same saturation pressure is used in both cases. However, the authors believe that the agreement obtained does tend to validate the extrapolation technique and the simplifying assumption made in correlating the undersaturation data with the classical form of eq 1.

The heat of vaporization is, of course, a measure of the energy needed to break the bond between atoms in the bulk phase to give the species in the gas phase. The heat of vaporization, then, is often closely approximated by the bond strength between the atoms involved in the bond breakage. In the case of $(SN)_x$, there is a large discrepancy between the value of the heat of vaporization (30 kcal) and the S–N bond strength (~50–60 kcal).[13] Since the low vaporization coefficient suggests that the vapor species is in fact quite different from the bulk species, this seemingly large discrepancy can be understood. It is highly probable that some molecular rearrangement takes place which is exothermic to the extent of ~30 kcal. One possible example of such a process would be the formation of a cyclic equilibrium species with the formation of an S–N bond. The mass spectral data[4] appear to rule out the formation of an eight-membered ring, but other ring systems can be postulated. Although this study does not conclusively prove the formation of such a species, it does give evidence for the formation of a "nonlinear" structure in the gas phase at equilibrium.

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Preparation and Properties of Li_xVS_2 ($0 \leq x \leq 1$)

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We report the preparation of Li_xVS_2 for $0 \leq x \leq 1.0$, this being the first report of the existence of VS_2. We present a partial phase diagram for this system based on x-ray diffraction measurements and differential scanning calorimetry. These measurements, as well as magnetic susceptibility measurements, show the existence of a number of phase transitions which are related to both the large crystallographic hexagonal c/a ratio and probable electronic instabilities in the V d band.

There is considerable current interest in van der Waals bonded metal chalcogenides and their compounds with lithium as potential cathodic electrodes in nonaqueous lithium batteries.[1,2] The group 4B and 5B MX_2 and $LiMX_2$ (X = S, Se) have been reported with the exception of VS_2.[3-5] It is surprising that VS_2 alone of these MX_2 compounds has not been prepared by direct combination of the elements especially since VSe_2 is readily prepared. In addition, only Li_xTiS_2 has been studied in any detail over the range of compositions $0 \leq x \leq 1$.[6] The compounds Na_xVS_2 ($0.3 \leq x \leq 1$) have been reported.[7] We report here a new method of delithiation of $LiVS_2$[8] and some simple physical properties of Li_xVS_2 ($0 \leq x \leq 1$).

Experimental Section

The $LiVS_2$ used was prepared as previously described[8] except that V_2O_5 was used instead of V_2O_3. Iodine solutions of ~0.2 N were prepared from freshly sublimed I_2 and acetonitrile freshly distilled from P_2O_5 and were standardized with thiosulfate. In the presence of acetonitrile, starch complexes with iodine did not form, but the color of the iodine itself was adequate and accurate as checked by