Torsion-Effusion Study of Sublimation of Barium Nitride

ROY C. BLAIR and ZUHAIR A. MUNIR[1]
Department of Materials Science, School of Engineering, San Jose State College, San Jose, Calif. 95114

By employing the torsion-effusion method, the sublimation pressure of barium nitride was determined over the temperature range 914–1051° K. The least-square expression for the total pressure in atmospheres is $\log P = (6.38 \pm 0.63) - (1.07 \pm 0.06)10^4/T$ where T is the temperature in ° K and the stated errors are standard deviations. In accordance with the sublimation reaction $Ba_3N_2(s) = 3\ Ba(g) + N_2(g)$, the second-law heat and entropy of sublimation at 298° K were calculated to be 204 ± 19 kcal/mol and 124 ± 15 eu, respectively. Third-law ΔH^0_{298} was calculated to be 221.7 ± 9.0 kcal/mol.

The existence of group IIA metal nitrides as minor impurities in liquid alkali metals has been associated with accelerated corrosion of the structural components of reactor systems (*3, 5*). Knowledge of the thermodynamic properties of these impurities is, of course, an essential part of all attempts to understand their role in the corrosion process. Although several of these compounds have been investigated, no recent information on the thermal stability of barium and strontium nitrides appears to have been published. This note reports the results of a determination of the sublimation pressure and heat of sublimation of barium nitride.

EXPERIMENTAL PROCEDURE

The pressures reported here were determined by the torsion-effusion method. This method is based on the principle that when gases effuse through two eccentrically situated orifices they will exert force on the cell containing the subliming solid. If the cell is suspended by a fine wire (usually 2-mil tungsten) then the force of effusion causes the wire to twist by a certain angle. Measurement of the angle of twist and knowledge (through calibration) of the torsion constant of the wire enable one to calculate the force of effusion. By relating this force to the geometry of the cell, the pressure of the effusing vapors can then be determined. Details of this method can be found elsewhere (*4*), and description of the apparatus used in this study has been given in earlier publications (*1, 2, 10*).

Torsion cells used in this work were made of Type 316 stainless steel with geometric characteristics similar to those described previously (*2*). Barium nitride samples, having a purity of $97^+\%$, were purchased in powder form from Alfa Inorganics. The level of impurity in these samples, the lowest available at this time, is believed due to the presence of the oxide and hydroxide of barium. In agreement with X-ray studies on another alkaline earth nitride (*2*), the sublimation of barium nitride was observed to be congruent. In view of the tendency of this nitride to hydrolyze, all preparatory steps were made inside a vacuum dry box which had been flushed at least three times with high purity argon. Work was performed inside the vacuum dry box under a slight positive pressure.

RESULTS

The total sublimation pressures in equilibrium with solid barium nitride, as measured by the torsion-effusion method, are plotted in Figure 1 as log P vs. $1/T$, where P is the pressure in atmospheres and T is the temperature in °K. To establish limits of departure from conditions of molecular streaming inside the torsion cells, ratios of the mean free path, λ, to orifice diameter, d, were calculated for all the experimental points. Least-square analysis of those results whose λ/d ratios were greater or equal to one, gave the following expression for the total pressure in the temperature range 914–1051° K:

$$\log P = (6.38 \pm 0.63) - (1.07 \pm 0.06)10^4/T \qquad (1)$$

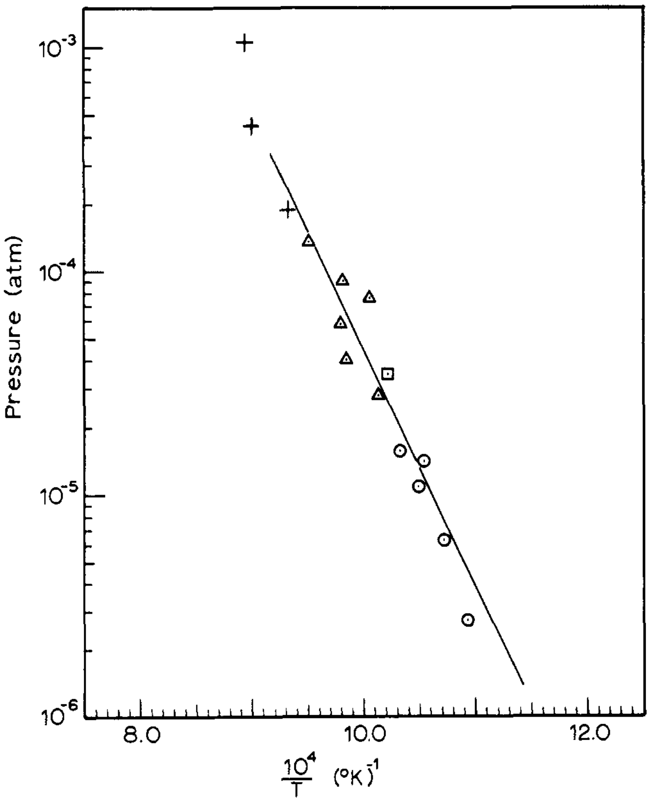

Figure 1. Sublimation pressure of $Ba_3N_2(s)$
○ cell *A*, △ cell *B*, □ cell *C*, + $\lambda/d < 1.0$, —least-squares fit

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[1] To whom correspondence should be addressed.

where the given errors are the standard deviations. Based on the reaction

$$Ba_3N_2(s) = 3\ Ba(g) + N_2(g) \qquad (2)$$

Equation 1 can be rewritten in terms of the equilibrium constant, K, as follows:

$$\log K = (24.46 \pm 2.52) - (4.28 \pm 0.24)10^4/T \qquad (3)$$

Again, T is the temperature in °K, and the errors are standard deviations.

When we use Equation 3 and the method outlined by Kelley (*8*), the second-law heat and entropy of sublimation were calculated using reported cP values. Values of cP for $N_2(g)$ and Ba(g) are available (*7*); however, no corresponding value exists for $Ba_3N_2(s)$. Consequently, the cP equation for $Ca_2N_2(s)$ (*7*), was assumed to apply for $Ba_3N_2(s)$ as an approximation. Results of the second-law calculations gave ΔH^0_{298} and ΔS^0_{298} values of 204 ± 19 kcal/mol and 124 ± 15 eu, respectively. Third-law calculations, which employed reported free-energy functions for Ba(g) (*6*), $N_2(g)$ (*12*), and calculated *fef* values for $Ba_3N_2(s)$ (based on the cP value of calcium nitride), gave a value of 221.7 ± 9.0 kcal/mol for ΔH^0_{298}. The individual results of these calculations along with measured sublimation pressures and calculated λ/d ratios are listed in Table I. Points for which $\lambda/d < 1.0$ were not included in the calculation of the average value of ΔH^0_{298}.

Table I. Sublimation Pressures and Third-Law Heats of Sublimation of Ba_3N_2

T, °K	P, atm	λ/d	ΔH^0_{298}, kcal/mol
914	3.24×10^{-6}	18.1	225.0
933	6.38×10^{-6}	9.4	223.9
949	1.76×10^{-5}	3.5	219.4
951	1.32×10^{-5}	4.6	222.0
969	1.89×10^{-5}	3.3	222.7
978	3.59×10^{-5}	4.3	219.4
987	2.83×10^{-5}	5.5	222.9
993	7.71×10^{-5}	2.0	216.1
1016	4.10×10^{-5}	3.9	225.1
1018	9.35×10^{-5}	1.7	218.9
1025	5.88×10^{-5}	2.7	223.8
1051	1.39×10^{-4}	1.2	221.1
1072	1.88×10^{-4}	0.9	221.9[a]
1114	4.66×10^{-4}	0.4	220.5[a]
1116	1.10×10^{-3}	0.2	213.2[a]

[a] ΔH^0_{298} values not included in calculation of the average.

DISCUSSION

The scatter in the reported pressure values, and thus the relatively large uncertainties in the thermodynamic values calculated from them, is postulated to be the result of chemical effects of which the highly reactive nature of barium nitride is probably the most significant. In spite of the care exercised during all preparatory steps to minimize the interaction of moisture with the nitride samples, it was virtually impossible to eliminate entirely such an interaction under the experimental conditions described above. The final product of this possible interaction is BaO, which, by virtue of its higher stability, has a significantly lower sublimation pressure than Ba_3N_2. Examinations of the torsion cells at the end of each run showed, in some cases, the presence of a small amount of residue which proved to be barium oxide. This residue was usually about 5% of the initial sample.

In spite of the above-mentioned scatter, validity of the reported pressure values is justified on the basis of the results of the third-law calculations of the individual heats of sublimation (Table I). The maximum difference between these calculated ΔH^0_{298} values is about 4%, or about 2.5% deviation from the reported average value. In view of the reliable nature of this (third-law) method of analysis (*13*), it is believed that the results in this paper are those pertaining to the equilibrium sublimation of barium nitride. Further evidence for this comes from the fair agreement between the heat of formation of Ba_3N_2, calculated by combining the results of this study, and reported thermodynamic functions (*9*) and that reported in the literature (*11*), 83.7 and 86.9 kcal/mol, respectively.

The appreciable difference between the values of the heat of sublimation, calculated by the second- and third-law methods, ~9% is probably due, in part, to the chemical effects mentioned above. Because of its nature, the second-law method of analysis is highly susceptible to scatter in the data (*13*). Though less significant, another possible reason for this difference may stem from the assumption that the free-energy functions of barium nitride can be approximated by those of Ca_3N_2.

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