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KINETICS OF VAPORIZATION OF ALUMINUM NITRIDE AND MAGNESIUM NITRIDE

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Research and Development

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Bette A. H. Blank

(Ph. D. Thesis)

April 23, 1965

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KINETICS OF VAPORIZATION OF ALUMINUM NITRIDE AND MAGNESIUM NITRIDE

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April 23, 1965

ABSTRACT

The kinetics of vaporization of aluminum nitride and magnesium nitride to metal gas atoms and nitrogen gas was studied, both in vacuum and in gaseous atmospheres of argon and nitrogen. An equation for $\log K_{eq}$ and the equilibrium total pressure of AlN sublimation as a function of temperature was found to be:

$$\log K_{eq} = \frac{3}{2}\log P_T - 0.3150 = -\left(\frac{145.516 \pm 9.429}{45.76}\right)\frac{10^4}{T} + 11.277 \pm 1.270 .$$

The third-law and second-law enthalpies for the sublimation of aluminum nitride are 153.2 and 150.4 ± 9.4 kcal/mole, respectively. The third-law and second-law enthalpies of activation (ΔH^*_{298}) are 175.9 and 150.8 ± 12.1 kcal/mole, respectively. The second-law entropy and entropy of activation are 58.44 and 44.96 cal/°K/mole AlN, respectively.

The $\log K_{eq}$ and total pressure of the decomposition of Mg_3N_2 to Mg gas atoms and N_2 gas can be expressed as a function of temperature by the following equation:

$$\log K_{eq} = 4 \log P_T - 0.9780 = -\left(\frac{245.979 \pm 16.64}{45.76}\right)\frac{10^4}{T} + 28.733 \pm 3.162.$$

The ΔH°_{298} = 242.3 by the third-law method, and 239.1 ± 16.5 kcal/mole by the second-law method. The $\Delta \overline{H}^{*}_{298}$ (third law) = 286.3 kcal/mole, and 218.7 ± 12.9 kcal/mole by the second-law method. The second-law ΔS°_{298} and ΔS^{*}_{298} are 121.56 and 66.35 eu, respectively. The heat of formation of Mg_3N_2 calculated from our approximate equilibrium data is -136.8 kcal/mole.

Evaporation of Mg_3N_2 in atmospheres of argon and nitrogen of pressures, which are of the order of magnitude of the sublimation pressure or greater, decreases the rate of evaporation. Nitrogen reduces the evaporation rate by about an order of magnitude more than does argon at the same background pressures.

I. INTRODUCTION

Metal nitrides are of commerical importance as refractory containers, reactor heat exchangers and as components of abrasives and of heat and impact resistant enamels. Thermodynamic properties of nitrides are desired in order to allow the prediction of conditions under which they are stable with respect to reaction, when used in these and other commercial applications. A convenient way to obtain thermodynamic stability as a function of temperature is to measure dissociation pressures, which are related to the free energy of the dissociation reaction by the equation $\Delta F^\circ = R\,T\,\ell n\,Keq$, where ΔF° is the standard free energy, R the gas constant, T the temperature in degrees Kelvin, and Keq the equilibrium constant for the reaction.

Certain metal nitrides are of theoretical as well as practical interest because their high temperature decomposition to nitrogen molecules and metal gas atoms is characterized by a slow reaction step. This slow step is manifested in a low evaporation coefficient, α the ratio of the measured Langmuir pressure[1] to the equilibrium pressure. The evaporation coefficients of most metal halides are nearly one, the maximum theoretical value.[2] The few oxides for which measurements are available appear to be between 0.01 and 1, while for several nitrides, values of α of 10^{-3} or less have been reported.[3, 4, 5, 6] The reason for the low rates of sublimation of the nitrides are not yet established; and, in fact, few reliable measurements on which to base theory are available.

The torsion effusion and closely related torsion Langmuir methods for vapor pressure determinations have been demonstrated to provide effective means of obtaining thermodynamic and kinetic data.[3] In the

present study, the torsion effusion and torsion Langmuir methods have been used to study the thermodynamics and kinetics of evaporation of aluminum nitride and magnesium nitride in vacuo and the effect of argon and nitrogen atmospheres on the free surface vaporization of magnesium nitride.

The sublimation of aluminum nitride was first investigated by Hock and White[4] in graphite Knudsen cells by weight loss methods. They found an evaporation coefficient of approximately 10^{-4} by measuring the change in apparent pressure as a function of the ratio of the area of the effusion hole to the area of the sample. Dreger, Dadape and Margrave[5] studied the Langmuir free surface evaporation rate for aluminum nitride in the temperature range 1450° - 1870°K by weight loss techniques. Their Langmuir third law heat of sublimation was 369.4 ± 2.8 kcal/mole N_2 or 184.7 ± 1.4 kcal/mole AlN. By taking the ratio of their Langmuir pressures to the equilibrium vapor pressure, they calculated an evaporation coefficient of 2.32×10^{-3}. (Tacitly assumed to be independent of temperature).

Hildenbrand and Theard[6] made some preliminary studies on aluminum nitride by the torsion effusion method. From the dependence of apparent pressure on orifice area, they calculated an evaporation coefficient of 2×10^{-3}, derived equilibrium pressures, and calculated the heat of formation of the solid at 298°K to be -73 ± 2 kcal/mole AlN. Of these studies of the vaporization of aluminum nitride, only the work of Derger et al. has appeared in the general literature. None of these studies incorporated both Knudsen and Langmuir experiments.

The evaporation studies for aluminum nitride are supplemented by related thermochemical studies. Margrave and Neugebauer[7] have measured

the standard heat of formation of aluminum nitride by direct nitridation of aluminum in a bomb and obtained a standard heat of formation of -76.5 kcal/mole. A. D. Mah et al.[8] reported the heat of formation to be -75.6 kcal/mole AlN, in good agreement. These recent, closely agreeing values for $\Delta H^{\circ}_{f\,AlN\,298^{\circ}K}$ contrast with earlier results of Neumann et al.,[9] who reported -57.4 kcal/mole, of Fichter and Jenney[10] (71.5 kcal/mole), and of Schissel and Williams[11] (-63 kcal/mole). The true value for $\Delta H^{\circ}_{f\,AlN\,298^{\circ}K}$ appears to be -76 ± 1 kcal/mole.

The equilibrium products of magnesium nitride evaporation under most conditions are Mg(g) and N_2(g), although Soulen, Sthapitanonda, and Margrave,[12] in examining the absorption spectra of the vapor from 1200-1400° C, found some bands which have been attributed[13] to Mg_2(g). In a recent study by Ditchburn and Marr[14] of Mg vapor, Mg_2 spectra were not obtained because they studied the vapor at pressures lower than 1.3 mm Hg, where Mg_2 would be dissociated. In our study of the dissociation of Mg_3N_2, the pressures were believed to be below the range of stability of Mg_2(g).

Soulen et al.[12] studied the vaporization of magnesium nitride in MgO cells by both effusion weight loss methods and by the transport method, using N_2 as the carrier gas.

Hildenbrand and Theard[6] studied the vaporization of magnesium nitride by the torsion-effusion method between 1100° and 1260°K, using three different orifice areas. Use of the equation

$$P_e = P_t \left(1 + \frac{ca}{\alpha A}\right) \qquad (1)$$

where c is the Clausing factor, a is the orifice area, α is the condensation

coefficient, and A is the effective evaporating surface area, gave them a condensation coefficient of 5×10^{-3}. The equilibrium pressures measured in their study is lower by more than a factor of 10 than pressures calculated for the dissociation of $Mg_3N_2(s) \rightarrow 3Mg(g) + N_2(g)$ from data accepted in the compilation of the JANAF Tables.[5] By the third-law method, Hildenbrand and Theard found $\Delta H^\circ_{298°K}$ to be 243.5 ± 0.5 kcal /mole Mg_3N_2 and 309 kcal/mole by the second-law method. They calculated the heat of formation of magnesium nitride(s) to be -136 kcal/mole as compared with -110.2 ± 1 kcal/mole given in the JANAF Tables,[5] which accepted the results of Mitchell's[6] work. Other values that have been reported[7] for the $\Delta H_{f_{298}}$ of magnesium nitride, -116.00 ± 0.02 kcal/mole, -115.18 kcal/mole, and -119.70 kcal/mole are only in little better agreement with the vaporization study results.

Thus, the study of Hildenbrand and Theard suggests magnesium nitride to have a higher thermodynamic stability than indicated from various calorimetric studies and to have a low evaporation coefficient. The reliability of the extrapolation technique used by Hildenbrand and Theard to calculate the evaporation coefficient has not been clearly established and has been subject to some question.[8] Free surface evaporation studies to establish the evaporation coefficient as a function of temperature are therefore highly desirable, and redetermination of equilibrium pressures to verify Hildenbrand and Theard's thermodynamic results is of considerable interest.

II. EXPERIMENTAL

The torsion effusion method has been described in several publications.[9-21] Schulz[22] used an apparatus similar to the one used in this work to make a critical study of this method. No extensive experimental details will be presented here.

Figure 1 shows a schematic diagram of the torsion apparatus, while Fig. 2 shows a photograph of the apparatus. The main vacuum chamber is a steel cylinder about 14 in. in diameter and 18 in. high. Situated in the center of this chamber is a 3 in. diam cylindrical heating element made of 20 mil tantalum sheet. Several layers of dimpled radiation shields are wrapped around the heating element. A glass tube of approximately 4 in. diameter and 3 ft length rises vertically from the main vacuum chamber. At the top of this tube is a specially designed goniometer. A 1/4 in. aluminum rod that is attached to the goniometer enters the top of the glass tube through an O-ring joint, and a 2 mil diam tungsten torsion wire 14 in. long is fastened to the lower end of the rod. From the tungsten wire a second 1/4 in. aluminum rod is suspended. To this rod is glued a 1/2 in. diam circular mirror which hangs directly behind an optically flat window in the vertical glass tube. The lower part of the suspension system is a 3/16 in. tantalum rod which is joined to the aluminum rod below the mirror. The torsion cell is fastened to the lower end of this rod. During a run, the cell hangs free in the center of the heating elements.

A cell of new design was used in this work (Fig. 3). Advantages of this cell are: simplicity of machining, flat walls where the effusion holes are drilled, and large sample capacity. The cover of the cell is carefully machined to the body of the cell which is held in place by friction. Each

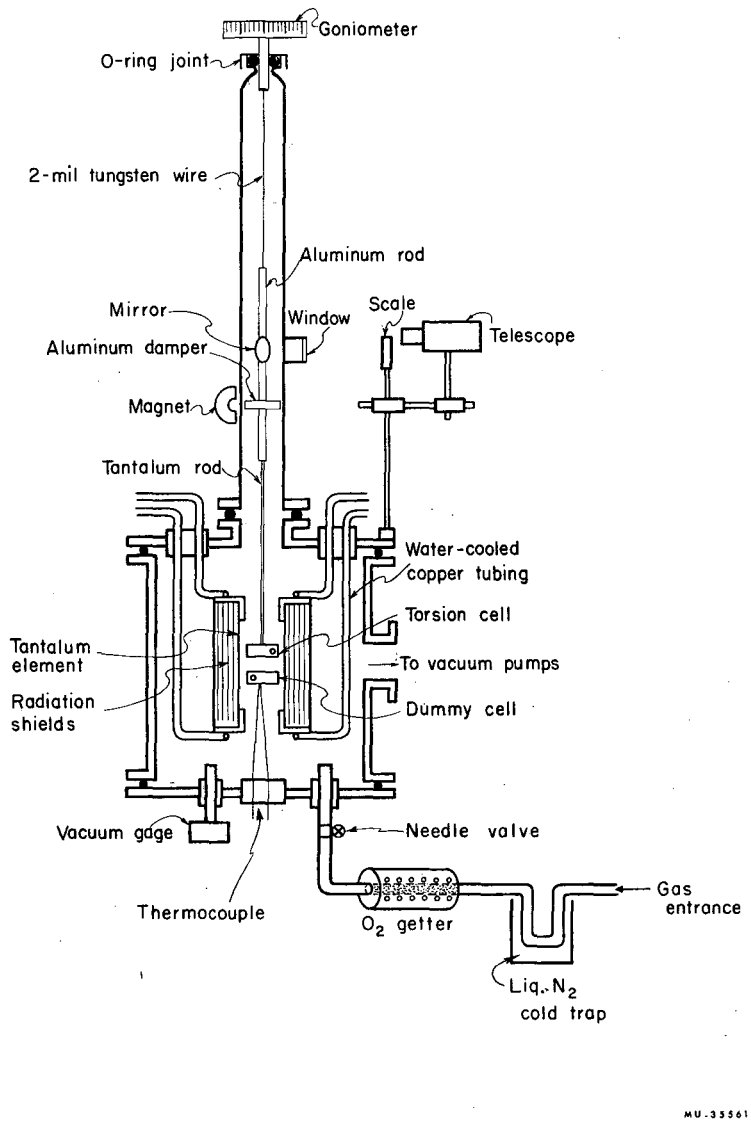

Fig. 1. Schematic diagram of torsion apparatus.

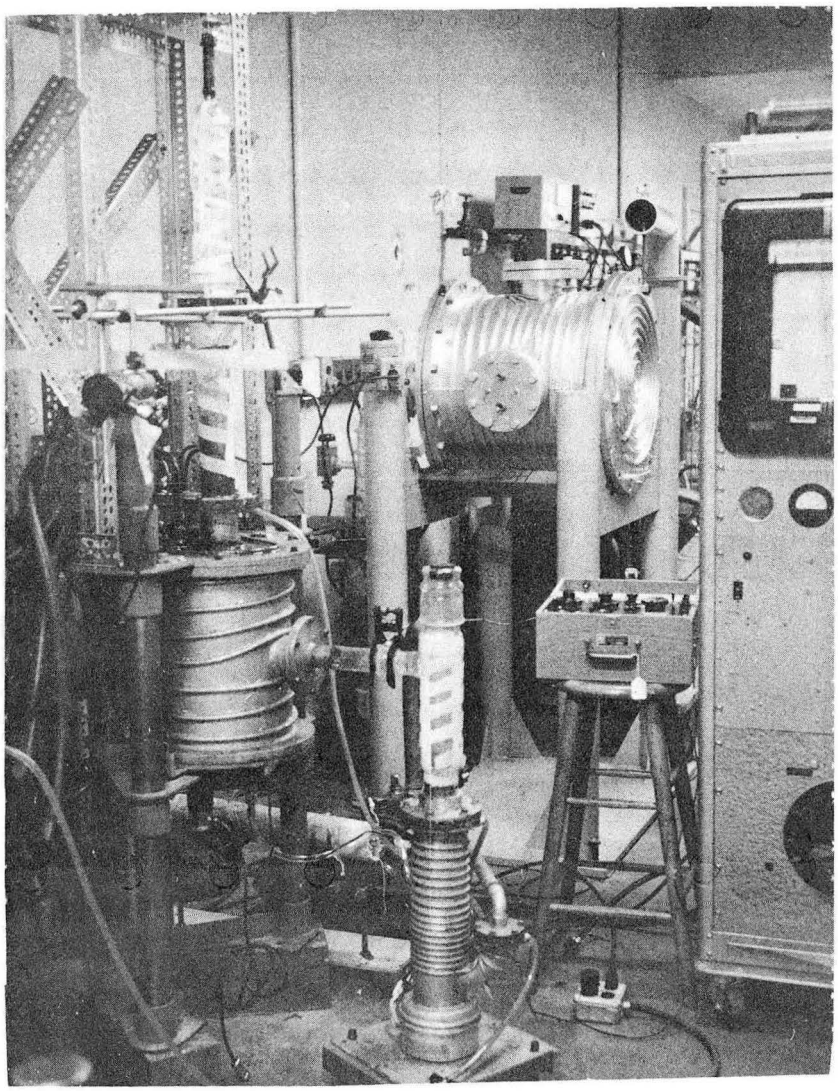

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Fig. 2. Photograph of torsion apparatus.

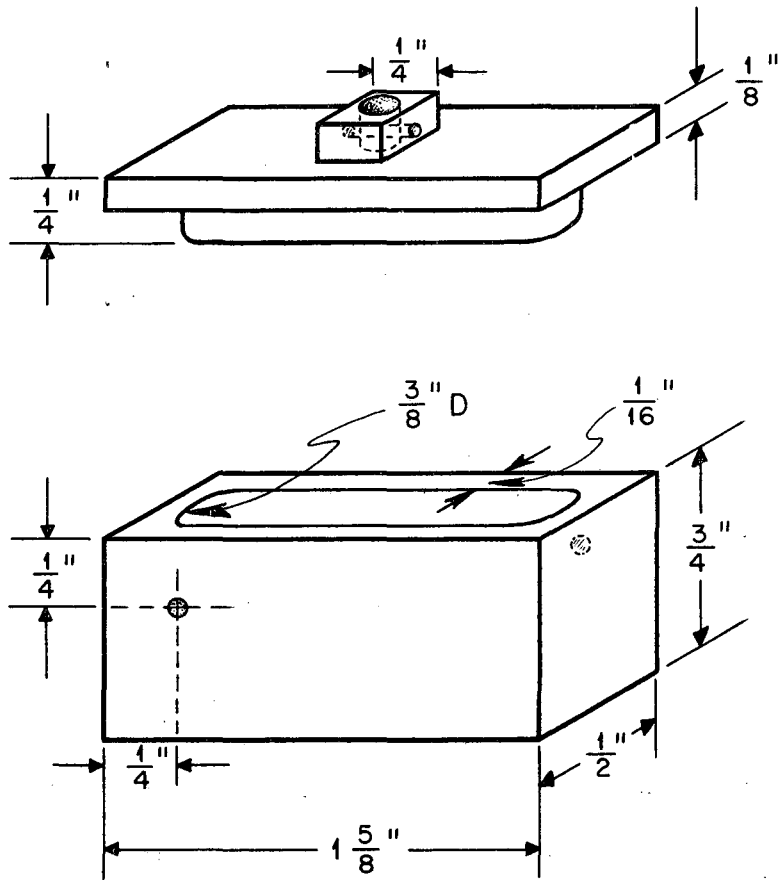

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Fig. 3. Torsion cell.

cell used was tested for leakage before its effusion holes were drilled, by heating the substances whose vapor pressures were to be studied, in the closed cell and noting the deflection. In all cases, no deflection was observed over the entire experiments temperature range. Orifice areas and wall thicknesses at the orifices are given in the Appendix.

Angular deflections resulting from the force of the effusing vapor were determined by returning the suspension system to its original (null) position. To facilitate adjustment to the null position, a light with a sharply focused filament image was beamed into the circular mirror which reflected the image onto a millimeter scale placed directly above the light. Deflection angles could be read from the goniometer to the nearest 0.01 degree.

Vacuum was maintained by a duoseal forepump; an MCF-300 oil diffusion pump with 300 liter/sec capacity and a liquid nitrogen cold trap placed above the diffusion pump. A pressure of less than 10^{-5} mm Hg was maintained in the chamber.

A 10 V secondary of a 30K VA transformer supplied power to the tantalum heating element. Water-cooled, heavy-walled, 1/4 in. copper tubing carried power to the heating element through CGB connectors.

Temperature measurements were made by means of a 20 mil Pt-Pt 10% Rh thermocouple which was located in a dummy cell that was placed just below the torsion cell. To calibrate torsion cell temperatures against temperatures of the dummy cell, another thermocouple, which had been calibrated by measurement of the melting points of gold, tin, and silver was placed inside a second cell. This cell was suspended in the position where the torsion cell is usually located. Figure 4 is a graph of temperature of the permanent dummy cell vs temperature of the second cell.

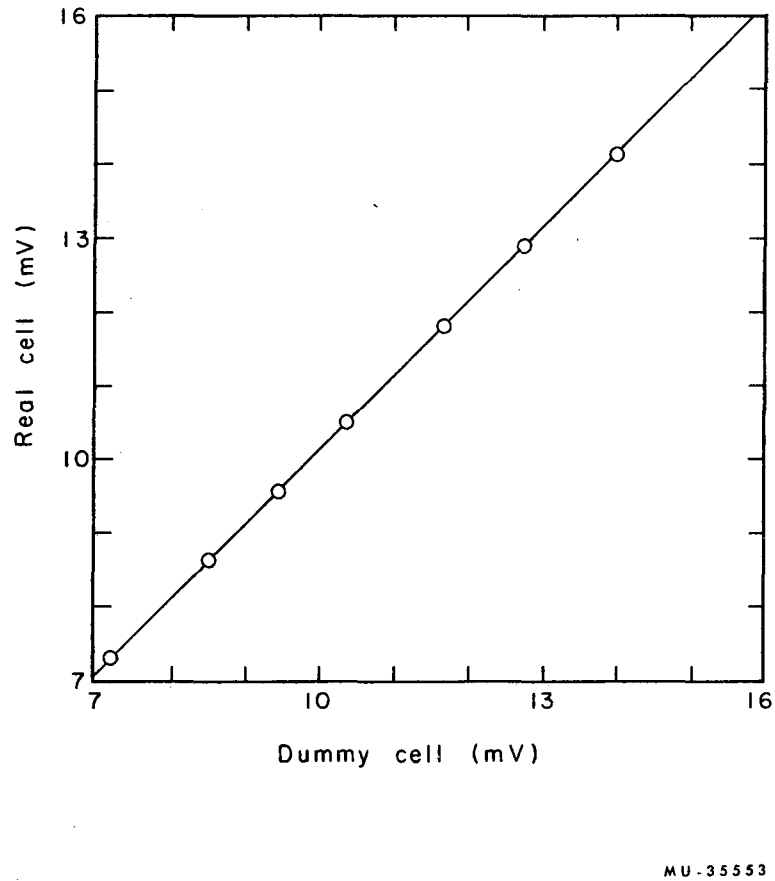

Fig. 4. Comparative thermocouple readings of dummy cell and effusion cell.

The vapor pressure of tin was measured as a check on our experimental methods. Figure 5 gives a graph of our values of the vapor pressure of tin vs $\frac{1}{T}$ as compared with value from the literature.[23] A third law $\Delta\bar{H}_{298}$ of 71.95 kcal/mole was obtained, which agrees closely with the value 71.8 kcal/mole measured by Schulz[22] by the torsion effusion method and reasonably well with 72.2 ± 0.5 calculated by Hultgren et al.[23] from results of earlier studies.

For certain experiments, nitrogen or argon was admitted into the furnace chamber by means of a needle valve. The gases were introduced through a liquid nitrogen cold trap and subsequently through an oxygen getter of copper shavings maintained at 600° C. When the nitrogen was used directly from the tank without passing through the cold trap and oxygen getter, the oxygen impurity in the gas completely converted the magnesium nitride disks to magnesium oxide; and no further deflection was observed, even on strong heating in a vacuum. Upon completion of each sublimation experiment in a foreign gas, the Langmuir vapor pressure in vacuo was checked to insure against oxidation of the sample or to note any irreversible effects. In all cases, the Langmuir pressure was restored within minutes of the restoration of the vacuum.

A CVC Phillips Ionization Gauge was used to measure pressure. Figure 6 gives the calibration of this gauge against a McLeod Gauge at the higher pressures for argon, air, and nitrogen.

The aluminum nitride powder, purchased from Alcoa, had a quoted minimum purity of: 0.08% Si, and less than 0.001% Mg, Fe, Cu, Ca, Na, and Mn. The aluminum nitride disks used for Langmuir evaporation studies were cut from the bottom of a sintered crucible (binder free) made

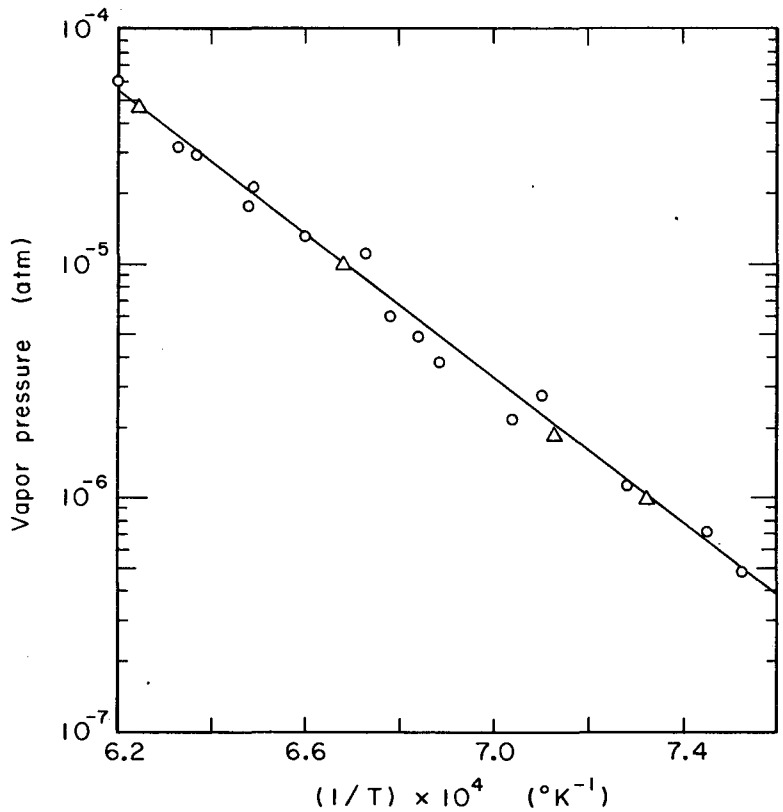

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Fig. 5. Vapor pressure of tin.
o this work
Δ Hultgren et al.

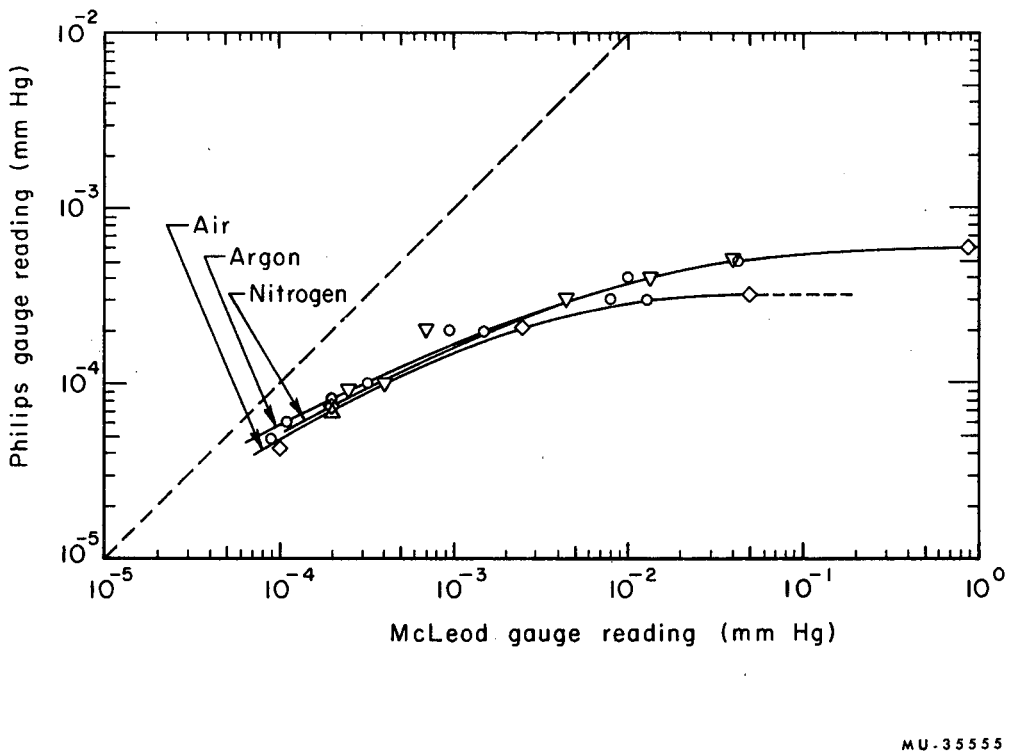

Fig. 6. Phillips Gauge calibration.

of the same powder. An x-ray diffraction trace of this material showed only AlN peaks. A spectrographic analysis of the aluminum nitride performed by American Spectrographic Laboratories detected the following impurities: Mg 0.04%, Si 0.1%, Fe 0.01%, Cu 0.002%, Ni 0.005%, and Ca 0.006%. Figure 7 shows photomicrographs of the pellet surfaces before and after evaporation.

The magnesium nitride powder purchased from Metal Hydride Inc. had a guaranteed purity of 99.9%. An x-ray diffraction trace of this materials showed only magnesium nitride peaks. A spectrographic analysis of the magnesium nitride, done by American Spectrographic Laboratories, detected the following impurities: Al 0.008%, Si 0.007%, Mn 0.025%, Fe 0.05%, Cu 0.003%, Ti 0.08%, Zr 0.1%, Ni 0.02%, Ca 0.0007%, Cr 0.02%, Ba 0.003%. Magnesium nitride disks were pressed in a 1/4 in. diam stainless steel die, at 7 tons total load. The pellets retained the yellow color of the powder. Figure 8 shows pictures of the surfaces of these pressed pellets.

In an attempt to obtain disks of lower porosity, some magnesium nitride powder was pressed at 10^6 psi. The pellets that resulted were very brittle and flew apart when the pressure was released. These pellets were dark grey, apparently because hydrolysis, and perhaps contamination from the steel die, occurred during pressing.

The materials were stored in a vacuum desiccator to prevent them from hydrolyzing. If slight surface hydrolysis occurred, the hydrolyzed layer was removed by driving off water by heating in vacuo and by reaction of the oxide with graphite. Figure 9 shows the vapor pressure of surface-hydrolyzed magnesium nitride powder in a graphite cell vs time of heating.

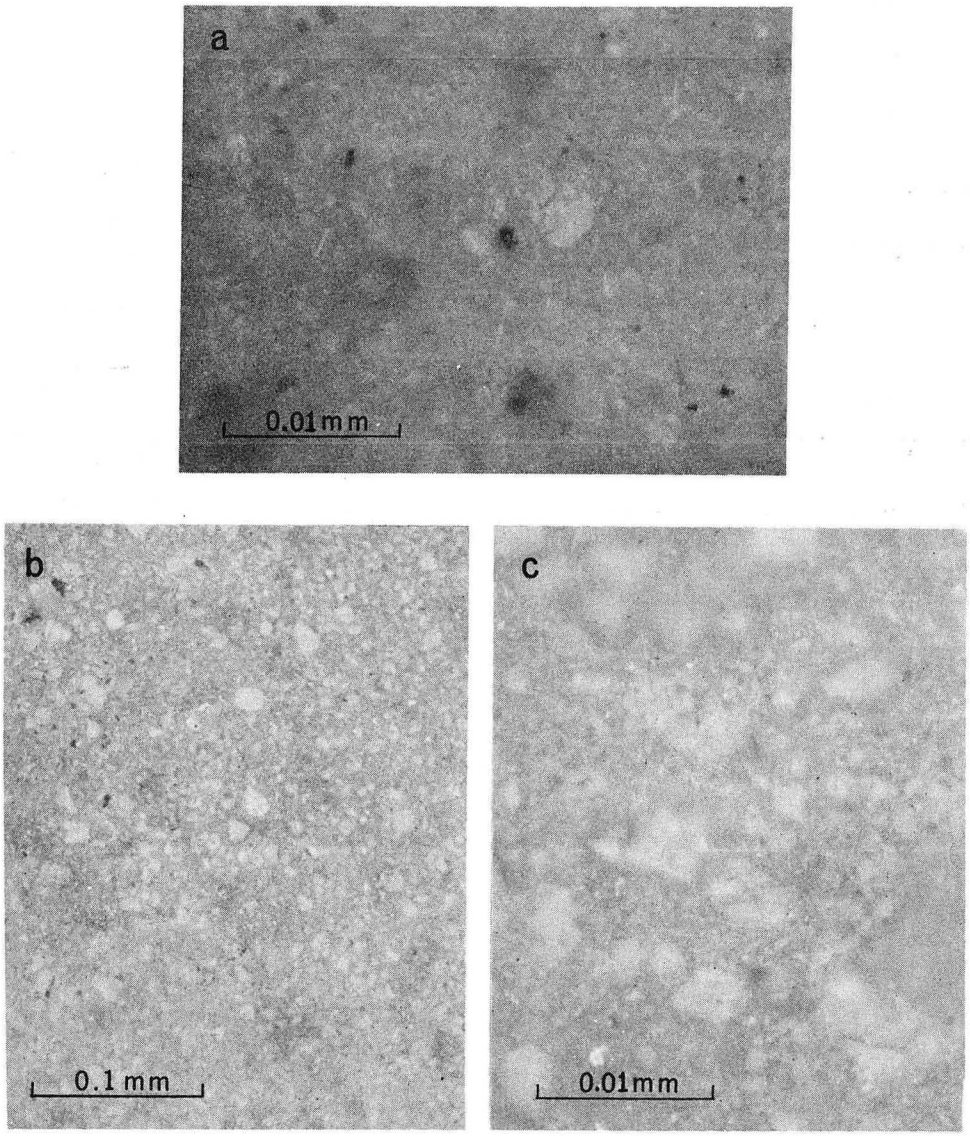

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Fig. 7. Photographs of the aluminum nitride surface.
a. before evaporation
b. and c. after evaporation

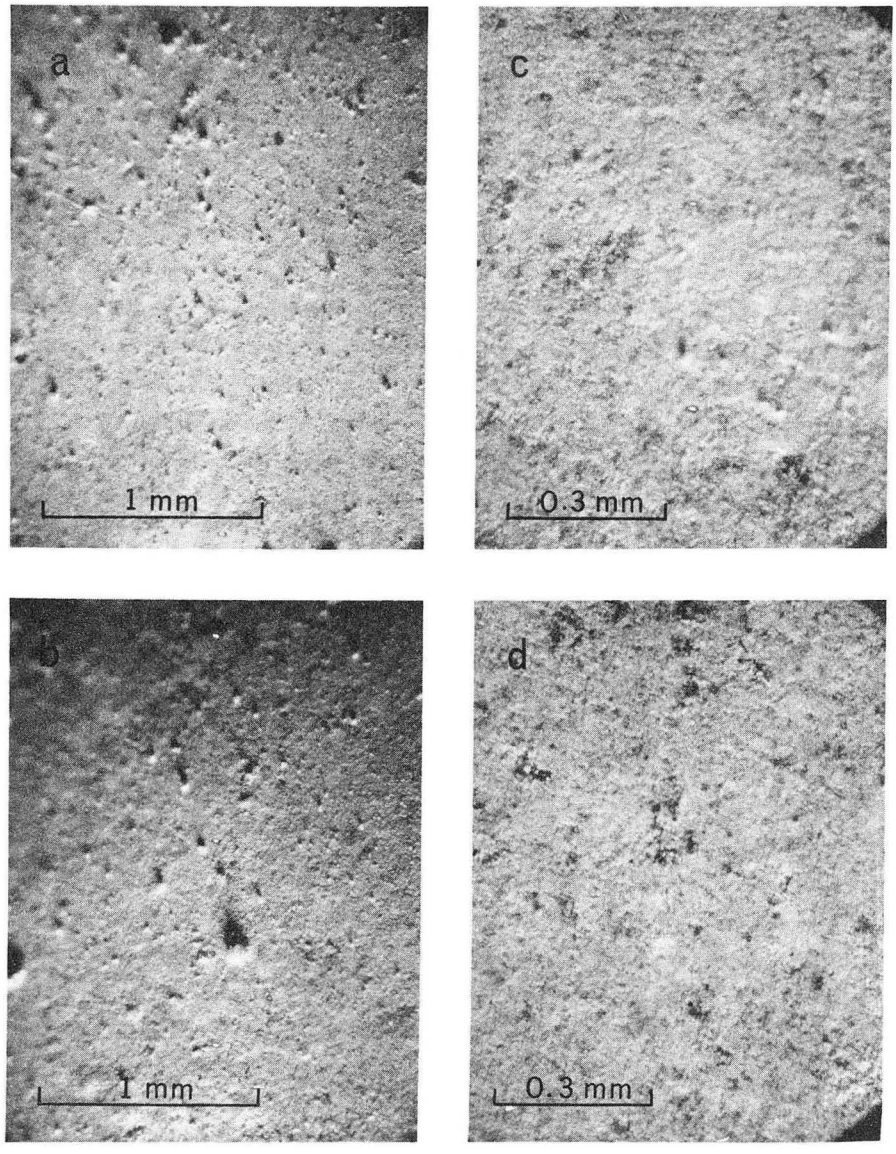

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Fig. 8. Photographs of magnesium nitride pellet surfaces.
a. and c. before evaporation
b. and d. after evaporation

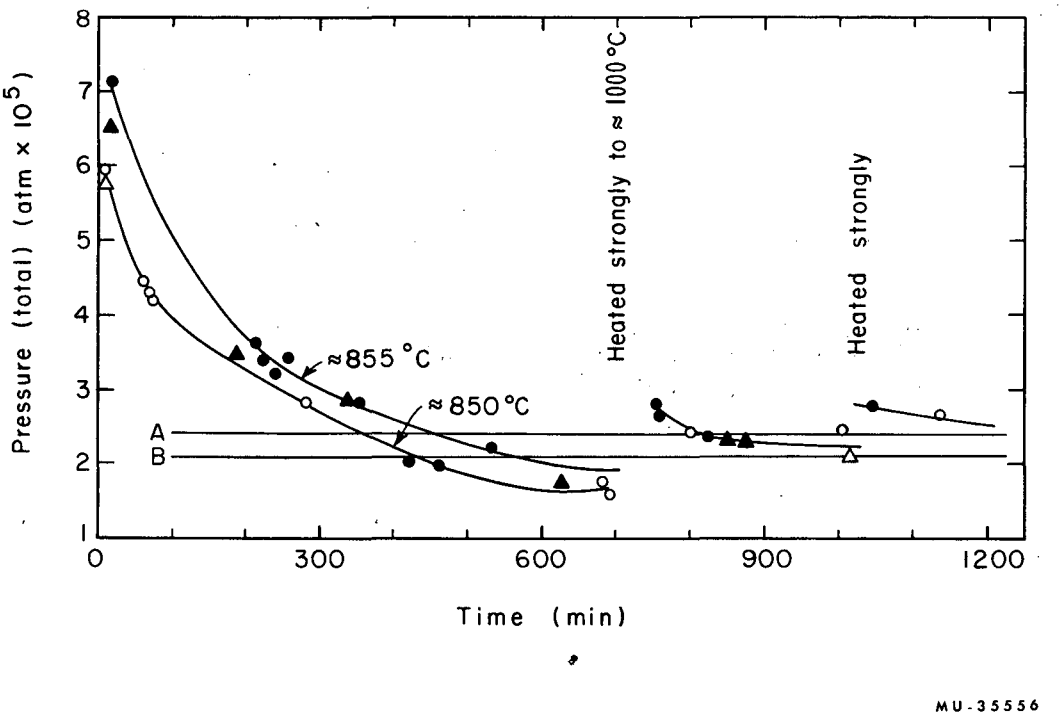

Fig. 9. Dehydration of hydrated magnesium nitride powder.

The equilibrium pressure is reached after heating for about 10 h. Our materials were heated at high temperature to insure the removal of any oxidized material before data were taken.

III. RESULTS

Vapor pressures were calculated from the torsion effusion data by means of the equation $P = \frac{2D\phi}{(q_1 a_1 f_1 + q_1 a_1 f_2)}$, where P is the pressure in atmospheres, D is the torsion constant of the wire in dyn-cm, ϕ is the angle of deflection of the suspension in radians, q_1 and q_2 are perpendicular distances from the center of the effusion holes of the axis of rotation (cm), a_1 and a_2 are areas of the effusion holes (cm^2), and f_1 and f_2 are Freeman and Searcy's force correction factors.

Figure 10 gives plots of log P vs 1/T for the Langmuir and Knudsen evaporation of aluminum nitride from our experiments and from experiments of Dreger and of Hoch and White. Table I gives the temperature, total pressure, $\log K_{eq}$, and the third-law enthalpy of sublimation of aluminum nitride. Data for the thermodynamic calculation were obtained for nitrogen and for aluminum nitride from the JANAF Tables[15] and for aluminum from Hultgren.[23]

A least squares fit of the data for 1 mil diam orifices gives an equation for $\log K_{eq}$ at any temperature between 1450 and 1750°K for the reaction $AlN(s) \rightarrow Al(g) + \frac{1}{2} N_2(g)$:

$$\log K_{eq} = \frac{3}{2} \log P_T - 0.3150 = -\left(\frac{145.516 \pm 9.429}{45.76}\right) \frac{10^4}{T} + 11.277 \pm 1.270 ,$$

where P_T is the total pressure. The errors are the standard deviations from the least squares fit. The 2 mil orifice data yield a very nearly parallel line, despite the rather high degree of scatter in the data.

Equilibrium pressures were calculated from the least squares plots for 1 mil and 2 mil orifice data by substitution in Eq. (1) described in the introduction.

Table I. Aluminum nitride vapor pressures, log K_{eq}, and third-law enthalpies of vaporization

T °K	P_T	$-\log K_{eq}$	ΔH°_{298}
1 mil diam orifice			
1706	2.08×10^{-5}	7.3380	153.2 kcal/mole AlN
1655	1.34×10^{-5}	7.6243	150.9
1631	7.52×10^{-6}	8.0007	151.5
1611	4.99	8.2679	151.7
1581	2.02	8.8571	153.2
1579	1.475	9.0620	154.5
1561	1.03	9.3134	154.5
1619	4.90	8.2799	152.5
1675	1.22×10^{-5}	7.6856	153.1
1689	1.55×10^{-5}	7.5296	154.4
1536	1.08×10^{-6}	9.2649	151.8
1584	3.55	8.4897	150.8
1621	5.13	8.2499	152.5
1652	7.83	7.9745	153.3
1670	1.07×10^{-5}	7.7711	153.4
1713	1.475	7.5620	155.6
1668	8.55×10^{-6}	7.9172	154.3
1598	2.34	8.7366	153.9
1641	4.32	8.3618	155.2
1626	3.72	8.4593	154.5
1606	2.43	8.7366	154.7
1579	1.44	9.0776	154.6
1561	1.26	9.1646	153.5
2 mil diam orifice			
1678	7.5×10^{-6}	8.0024	155.8
1676	7.1	8.0380	155.9
1657	4.34	8.3589	156.6
1638	2.87	8.6283	156.9
1615	1.89	8.9004	156.7

Table I. (continued)

T °K	P_T	$-\log K_{eq}$	ΔH°_{298}
2 mil diam orifice (continued)			
1582	9.82×10^{-7}	9.3269	156.7 kcal/mole AlN
1552	4.16	9.8865	157.7
1516	2.63	10.1852	156.2
1486	1.18	10.7228	156.8
1685	4.83×10^{-6}	8.2892	158.7
1665	3.51	8.4971	158.4
1643	2.30	8.7725	158.4
1624	1.65	8.9889	158.3
1687	4.34	8.3589	159.4
1636	1.91	8.8935	158.7
1600	1.06	9.2771	158.1
1575	7.66×10^{-7}	9.4887	157.2
1547	5.10	9.7537	156.3
1698	5.72×10^{-6}	8.1791	159.0
1672	3.59	8.4825	159.0
1637	2.08	8.8380	158.4
1597	1.10	9.2531	157.6
1589	9.43×10^{-7}	9.3533	157.5
1562	7.07×10^{-7}	9.5409	156.3
1543	6.29	9.6171	154.9
1457	1.96	11.4236	158.5
1493	3.93×10^{-8}	10.4432	152.7
1677	7.13×10^{-6}	8.0355	156.0
1692	9.78	7.8296	155.8
1670	4.84	8.2878	157.3
1650	3.07	8.5865	157.7
1622	1.60	9.0089	158.2
1590	7.15×10^{-7}	9.5336	159.0
1564	4.36	9.8559	158.7
1530	3.42	10.0122	156.4

Table I. (continued)

T °K	P_T	$-\log K_{eq}$	ΔH°_{298}
Langmuir evaporation			
1632	1.47×10^{-8}	12.0641	182.0 kcal/mole AlN
1683	6.26	11.1201	180.3
1719	2.59×10^{-7}	10.1963	176.8
1745	5.17	9.7448	175.9
1757	6.51	9.5946	175.8
1683	1.54	10.5338	175.8
1719	4.04	9.9054	174.5
1728	4.12	9.8927	175.3
1740	5.54	9.6998	175.0
1752	6.75	9.5711	175.2
1668	8.23	10.9419	177.4
1645	1.57	12.0221	183.1
1637	2.60×10^{-8}	11.6928	179.8
1668	1.06×10^{-7}	10.7783	176.1
1682	1.36	10.6148	176.3
1690	1.86	10.4108	175.6
1665	9.44×10^{-8}	10.8525	176.4
1648	7.29	11.0210	175.9
1631	6.17	11.1296	174.9
1613	9.69×10^{-9}	12.3356	181.9

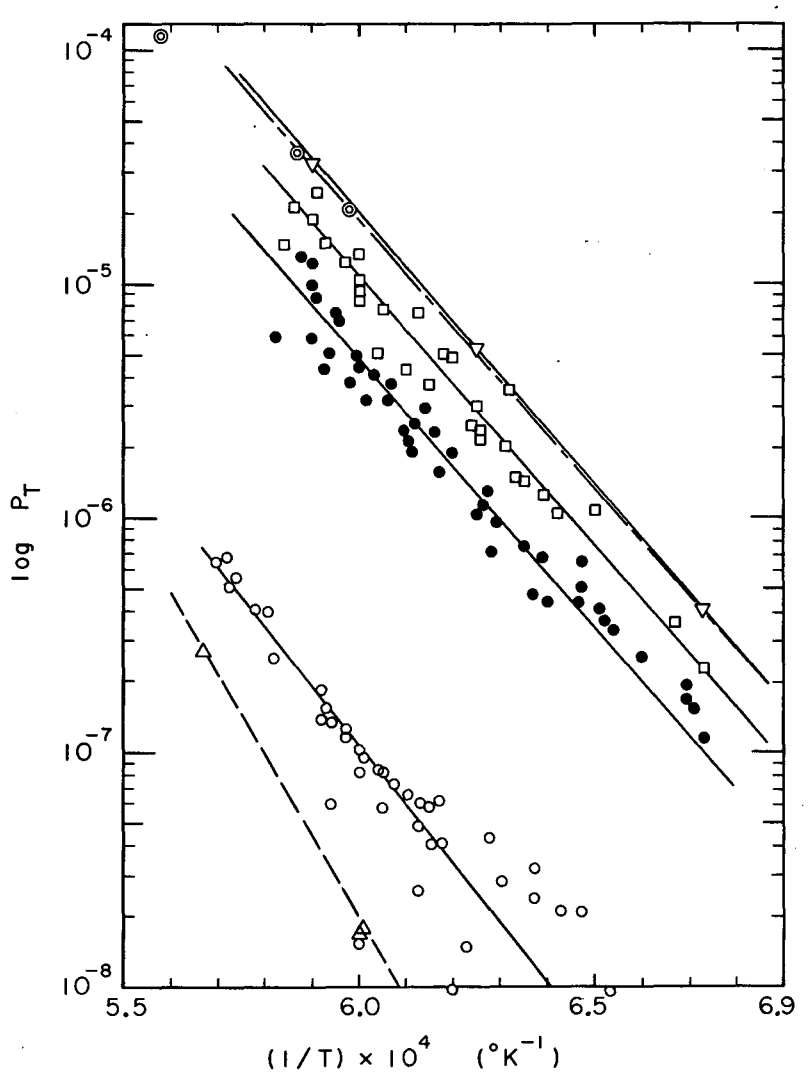

Fig. 10. Vapor pressure of aluminum nitride.
▽ This work (extrapolation to zero orifice)
□ This work (effusion diam 1 mm)
● This work (effusion diam 2 mm)
o This work Langmuir evaporation
—— —— —— Dreger et al.[3]
———— Equilibrium[15]
⊙ Hoch and White[4] (P_{eq})

The second-law heat and entropy were obtained from a plot of $\Sigma = -R \ln K_{eq} + \Delta a \ln T + \frac{\Delta b}{2} T - \frac{\Delta c}{2T^2}$ vs $1/T$, where Δa, Δb, and Δc are the differences of the constants in the heat capacity equation for the products and the reactants.[1] Now $\Sigma = \Delta H_I^\circ + I$, where ΔH_I° and I are constants so that the slope of the plot is equal to ΔH_I° and the intercept to I. The value of ΔH_T° could then be calculated from ΔH_I° from the expression $\Delta H_T^\circ = \Delta H_I^\circ + \Delta a\, T + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{T}$, and the second-law entropy could be calculated from: $\Delta S_T^\circ = \Delta a + \Delta b\, T + \Delta a \ln T + \frac{\Delta c}{2} T^{-2} - I$.

The second-law heat of sublimation for aluminum nitride is 150.4 ± 9.4 kcal/mole for 1 mil diam orifice, 150.12 ± 4.6 for a 2 mil orifice, and 150.8 ± 12.1 kcal/mole AlN for the Langmuir vaporization. The second-law entropies are 58.4, 55.6, and 45.0 cal/°K/mole AlN for 1 mil, 2 mil diam orifices and Langmuir evaporation, respectively. Plots of $\log P_T$ vs $1/T$ for both Knudsen and Langmuir evaporation of magnesium nitride, as found in the present and earlier studies, are given in Fig. 11. Table II gives T, P_T, $\log K_{eq}$ for vaporization of magnesium nitride, and calculated third-law heats of sublimation at 298°K. A least squares calculation of the data for the evaporation of magnesium nitride to Mg gas and N_2 gas from cells of 1 mil diam orifice (near equilibrium) gives the following equation for $\log P_T$ and $\log K_{eq}$ vs temperature between 1000° and 1250°K:

$$\log K_{eq} = 4 \log P_T - 0.978 = -\left(\frac{245.979 \pm 16.64}{45.76}\right) \frac{10^4}{T} + 28.733 \pm 3.162$$

The quoted errors are the standard deviations from the least squares fit. The second-law enthalpies at 298°K are 239.1 ± 16.5, 265.8 ± 18.1,

Table II. Magnesium nitride vapor pressure, log K_{eq}, and third-law enthalpies of vaporization

T °K	P_T	$-\log K_{eq}$	ΔH°_{298}
1 mil diam orifice			
1056	1.98×10^{-6}	23.7916	250.8 kcal/mole Mg_3N_2
1122	1.98×10^{-5}	19.7916	245.8
1169	7.56	17.4640	243.4
1193	1.42×10^{-4}	16.3692	242.3
1211	2.62	15.3048	240.0
1237	4.77×10^{-4}	14.2640	239.2
1202	1.86	15.9000	241.6
1181	1.07	16.8656	242.7
1159	5.05	18.1652	245.1
1178	1.62×10^{-4}	16.1456	238.2
1231	4.68	14.2972	238.2
1036	3.06×10^{-6}	23.0352	242.7
1162	8.84×10^{-5}	17.1924	240.6
1212	2.78×10^{-4}	15.2020	239.7
1087	1.15×10^{-5}	20.7356	243.0
1252	7.04×10^{-4}	13.5880	238.1
1231	4.18	14.4936	239.3
1223	3.57	14.7676	238.1
1221	3.14	14.9904	240.2
1168	8.72×10^{-5}	17.2160	241.9
1105	2.70×10^{-5}	19.2560	239.5
1213	2.51×10^{-4}	15.3796	240.8
1193	1.40×10^{-4}	16.3936	242.5
1182	1.03	16.9268	243.2
1166	6.48×10^{-5}	17.7320	244.3
1161	5.40	18.0488	244.9
1146	3.72	18.6960	245.2
1125	1.94	19.8268	246.6
1105	9.06×10^{-6}	21.1496	249.0
1096	7.22	21.5440	248.7
1063	3.51	22.7968	247.3
1052	1.85	23.9096	250.4

Table II. (continued)

T °K	P_T	$-\log K_{eq}$	ΔH°_{298}
2 mil diam orifice			
1206	2.74×10^{-4}	15.2272	238.6 kcal/mole Mg_3N_2
1190	2.33	15.5088	237.1
1164	1.97	15.8020	233.6
1110	1.33×10^{-5}	20.4892	246.8
1067	3.22×10^{-6}	22.9468	249.4
1004	1.73	25.7320	247.7
1101	3.06×10^{-5}	21.1400	248.1
1151	5.90	19.0352	248.1
1171	2.34×10^{-4}	17.8948	246.2
1204	2.36	15.4864	239.7
1212	2.47	15.4076	240.8
1181	1.98	15.7916	236.9
1125	1.25×10^{-5}	20.5904	250.6
1107	1.17	20.7056	247.2
Langmuir evaporation			
1254	3.30×10^{-6}	22.9040	292.0
1222	1.36	24.4440	293.3
1194	7.44×10^{-7}	25.4920	292.4
1141	3.56	26.7724	286.3
1122	1.94	27.8316	287.1
1064	9.79×10^{-8}	29.0152	278.3
1305	9.16×10^{-6}	21.1308	293.0
1293	6.20	21.8088	294.4
1258	4.42	22.3964	290.0
1110	1.09×10^{-7}	28.8316	289.2
1068	6.08×10^{-8}	29.8424	283.3
1026	3.14	30.9904	277.8

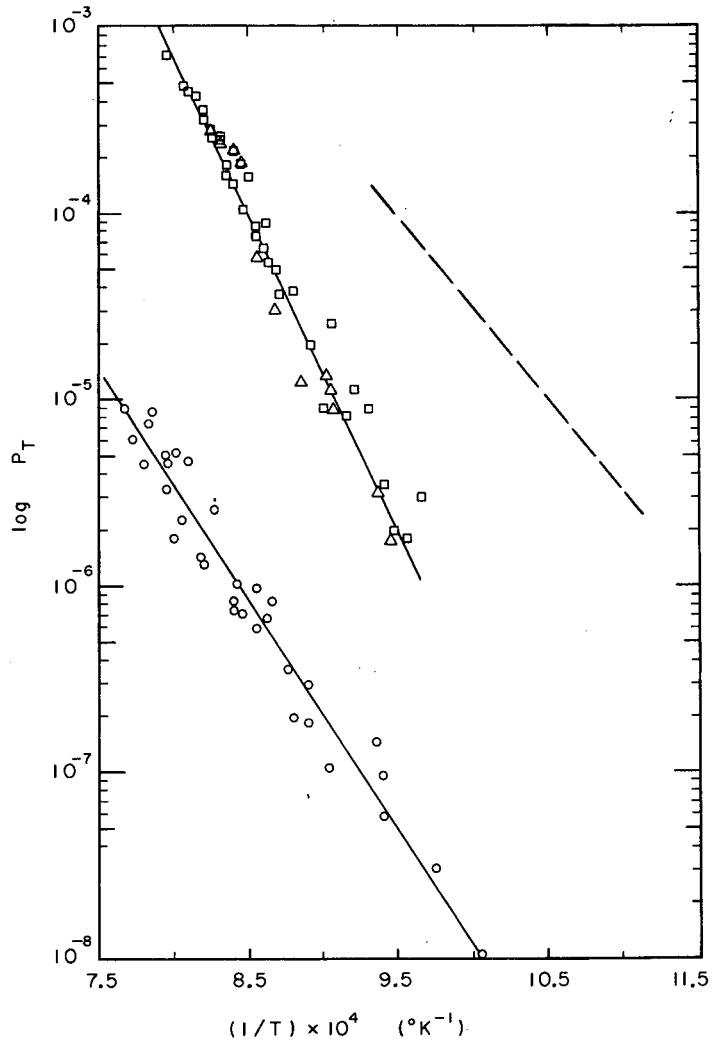

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Fig. 11. Vapor pressure of magnesium nitride.
□ Effusion diam 1 mm
△ Effusion diam 2 mm
o Langmuir vaporization
—— —— —— Equilibrium[15]

and 218.7 ± 12.9 kcal/mole Mg_3N_2 for 1 mil, 2 mil diam orifices and Langmuir evaporation, respectively; and the corresponding entropies of vaporization are 121.6, 144.4, and 66.4 cal/°K/mole Mg_3N_2. The heat of formation of solid magnesium nitride calculated from our 1 mil orifice data is -136.8 kcal/mole Mg_3N_2. Pressures measured with the 2 mil orifice agree with those obtained with the 1 mil orifice near the upper end of our temperature range, but appear to deviate systematically toward lower pressures at low temperatures. The deviations appear too close to our random scatter to warrant use of Eq. (1) for extrapolation to obtain equilibrium pressures or values of α .

Background pressures of 10^{-7} atm of either argon or nitrogen had no measurable effect on the rate of evaporation of magnesium nitride disks. In one atmosphere of argon or nitrogen, the torque produced by evaporation became immeasurable even when the rear face of each nitride disk was not vented upward (the practice was to vent the rear face in normal Langmuir sublimation studies) but fitted flat against a graphite surface. Plots of log P vs 1/T for free surface evaporation of magnesium nitride in nitrogen and argon atmospheres are shown in Fig. 12. Nitrogen appeared to have a greater retarding effect than argon on the evaporation. The apparent third-law and second-law enthalpies of sublimation and the apparent second-law entropies of sublimation for magnesium nitride in Langmuir experiments in vacuo and in nitrogen and argon atmospheres are summarized below:

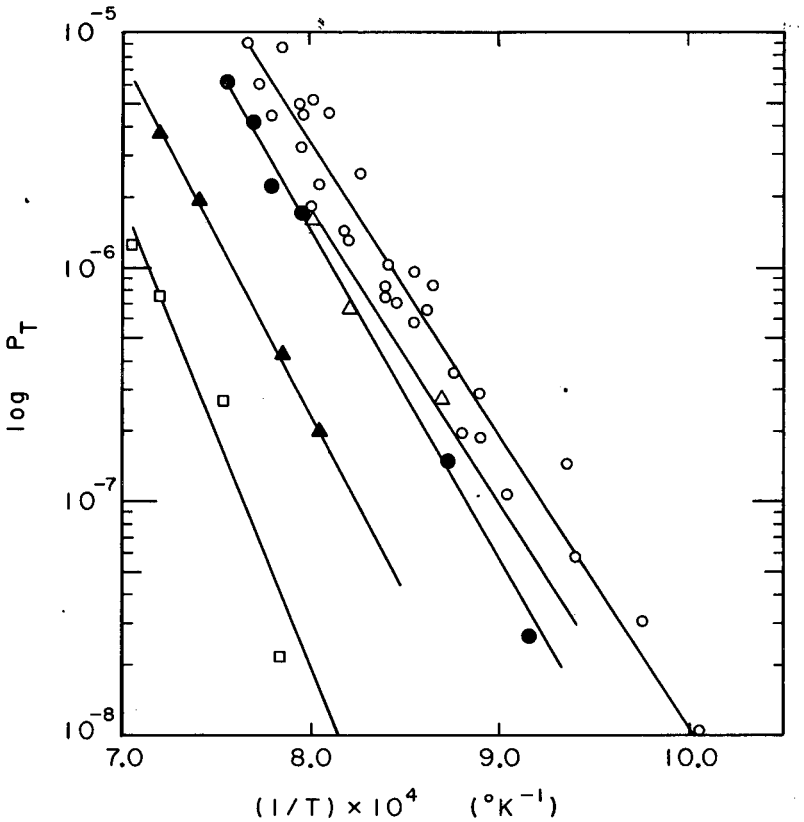

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Fig. 12. Langmuir vaporization of magnesium nitride in vacuo, argon, and nitrogen.
- o in vacuo 10^{-8} atm
- △ 5×10^{-7} atm argon
- o 5×10^{-7} atm nitrogen
- △ 7×10^{-7} atm argon
- □ 6.5×10^{-7} atm nitrogen

		3rd law ΔH°_{298} °K kcal/mole Mg_3N_2	2nd law ΔH°_{298} °K kcal/mole Mg_3N_2	ΔS°_{298} cal/°K/mole
Vacuum	10^{-8} atm	286.3	218.7 ± 12.9	66.3
Argon	4×10^{-7}	295.1	193.0 ± 54.1	38.5
Nitrogen	3.5×10^{-7}	297.6	259.8 ± 6.9	92.0
Argon	$.7 \times 10^{-7}$	316.3	252.2 ± 14.1	73.0
Nitrogen	6.5×10^{-7}	338.4	377.5 ± 65.8	150.6

IV. DISCUSSION OF RESULTS

The evaporation coefficient α measured for aluminum nitride varied from 3×10^{-3} to 8×10^{-3}. The power supply to the furnace, which provided a maximum temperature of 1460°C, limited the range in which reproducible Langmuir measurements could be obtained. Within experimental error, a constant value of $\alpha = 5 \times 10^{-3}$ can be assigned, although on theoretical grounds α can be expected sometimes to be temperature-dependent. Dreger et al.[5] measured Langmuir pressures that were a factor of 3 to 5 lower than those that were found in this work. Unless pore-free surfaces are used—and we were unable to obtain pore-free material, Langmuir studies can lead only to upper limits to the value of α. But the difference between Dreger's results and ours probably reflects a layer of hydration product (Al_2O_3) on Dreger's samples which would serve to lower the apparent pressure. Our highly sintered pellets being less porous than Dreger's compressed powder wafers would show a lower Langmuir vapor pressure if the difference observed were a porosity effect.

Our Knudsen results, which require only a relatively short extrapolation using Eq. (1), yield $\Delta H^\circ_{subl\ 298} = 153.2$ kcal/mole AlN which is in close agreement with 155.1 ± 12.5 kcal reported by Dreger et al.,[5] who used an $\alpha = 2.32 \times 10^{-3}$ to correct his Langmuir pressures to equilibrium pressures. Since the calculation of Dreger et al. involved the choice of α to force agreement between the Langmuir and equilibrium data, this agreement only demonstrates agreement between our data and the thermochemically calculated heat of sublimation.

The heat of formation at 298 °K for aluminum nitride calculated by the third-law method from our data extrapolated to zero orifice area is -73.3 kcal/mole AlN compared to -73 reported by Hildenbrand and Theard as a preliminary result and 71.9 kcal/mole that we calculate from measurements of Hoch and White. These values are all in reasonable agreement with the average of the two apparently most reliable calorimetric measurements 76 ± 1 kcal/mole.[7,8] Furthermore, there is good agreement between the second-law enthalpy of sublimation, 150.4, and the third-law enthalpy, 153.2 kcal/mole. The close agreement between the heat of activation for evaporation and the heat of the equilibrium reaction indicates that the rate of evaporation is controlled by a low rate of transmission of atoms from crystal sites from which evaporation occurs, rather than by the passage of atoms over an energy barrier that exceeds the energy change in the equilibrium reaction. The rate-determining step thus appears different from that in gallium nitride sublimation for which Munir and Searcy[3] found the heat of activation for $GaN(s) = Ga(g) + \frac{1}{2} N_2(g)$ to exceed the heat of the equilibrium reaction by 45.6 kcal/mole.

The evaporation coefficient of magnesium nitride apparently varies from 2×10^{-2} at 1000°K to 3×10^{-3} at 1250°K if our Langmuir data are compared to the pressures measured with the 1 mil orifice. Hildenbrand and Theard's[6] and Soulen's[12] equilibrium pressure curves are in good agreement with ours as can be seen from Fig. 13; and Hildenbrand's evaporation coefficient 5×10^{-3} obtained by use of Eq. (1) falls in the middle of our range (2×10^{-2} to 3×10^{-3}).

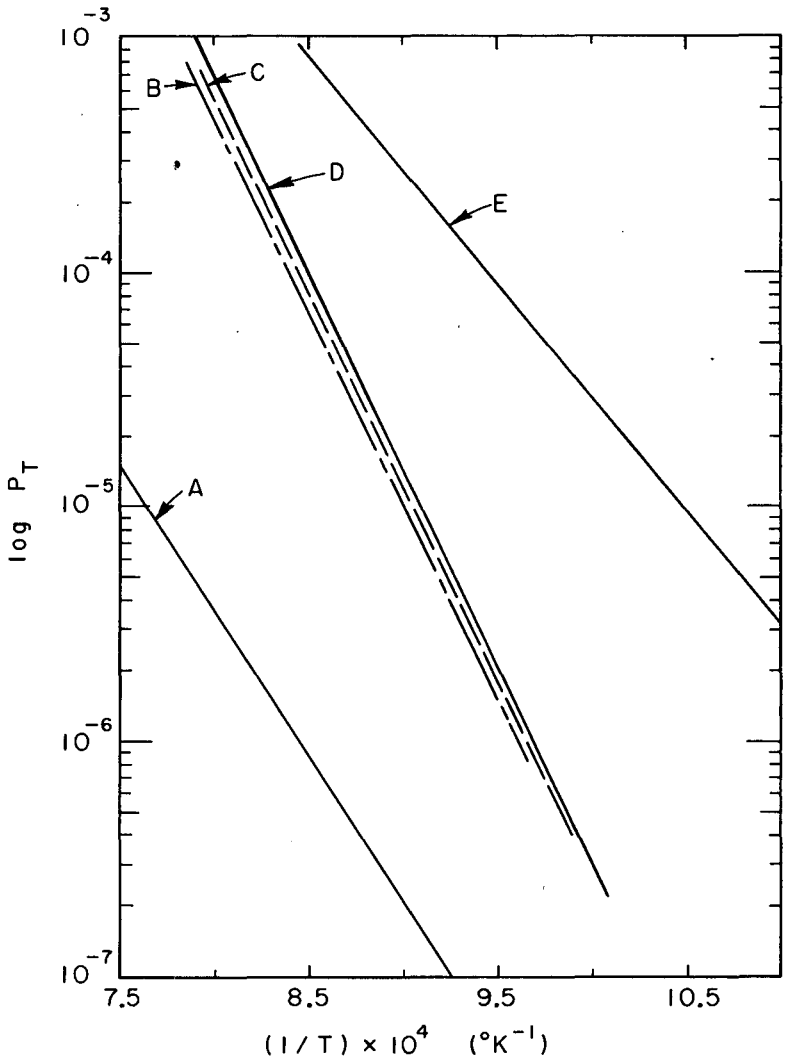

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Fig. 13. Comparison of magnesium nitride data.
A. This work Langmuir evaporation
B. Soulen et al.[9] Knudsen "
C. Hildenbrand and Theard[6]
D. This work Knudsen evaporation
E. Equilibrium[15]

Very good agreement was obtained between our average value calculated for the heat of sublimation at 298°K by the third-law method 242.3 kcal/mole and Hildenbrand's value 243.5 ±0.5 kcal/mole Mg_3N_2. Figure 13 shows a comparison of our data with Hildenbrand's and Soulen's along with the equilibrium pressure calculated from data in the JANAF Tables.[15] A comparison of our second-law ΔH°_{298} = 239.1 ± 16.5 shows satisfactory agreement between the second- and third-law methods.

We confirm, therefore, Hildenbrand and Theard's conclusion that direct determinations yield apparent equilibrium pressures that are more than an order of magnitude below dissociation pressure calculated from the accepted heat of formation of magnesium nitride[15, 16] and from the well-known heat of sublimation of magnesium.[23]

The heat of formation calculated from our 1 mil orifice data is -136.8 kcal/mole using heats of vaporization of magnesium from Hultgren's Tables.[23] This value agrees closely with the heat of formation calculated by Hildenbrand and Theard, -136 kcal/mole and disagrees seriously with the value -110.240 ± 0.275 accepted in the JANAF Tables.[15] Hildenbrand and Theard[6] speculated that the discrepancy between measured and calculated pressures could result either from establishment of a metastable equilibrium in the Knudsen cell (such an effect has been hypothesized by Kay and Gregory[24] to explain the anomalous evaporation behavior of $Mg(OH)_2$), or from errors in the calorimetric measurements.

A possible metastable equilibrium might be that for the reaction $Mg_3N_2(s) \rightarrow Mg(g) + Mg_2(g) + N_2(g)$. This hypothesis is consistent with the report of Soulen et al.,[12] that the broadening of the magnesium line in the optical spectra of the vapor of magnesium nitride indicates

the presence of $Mg_2(g)$. However, if this reaction were the case, the log vapor pressure vs 1/T curve expected from the calculated dissociation pressure of $Mg_2(g)$ would be approximately four orders of magnitude below the observed Knudsen vapor pressure with a slope less steep than even the calculated equilibrium dissociation to Mg(g) and $N_2(g)$ shown on Fig. 11.

Experiments designed to provide further insight are clearly desirable. Mr. E. G. King of the Pacific Experimental Station of the U. S. Bureau of Mines intends to investigate the heat of formation of magnesium nitride by direct nitridation in a bomb. For aluminum nitride the heat of formation which was measured from the heat of solution has been shown to be considerably less negative than the heat of formation measured by direct nitriding of aluminum, while the direct nitriding experiments yielded results that agreed closely with that calculated from effusion pressure measurements.

To determine whether or not vapor species other than magnesium atoms and nitrogen molecules may contribute significantly to the pressures observed in the Knudsen cell experiments, a mass spectrometer investigation of the vapor species will be made.

Somorjai and Jepsen[25] have investigated the effects of beams of sulfur and Cd of various intensities on the rate of sublimation of cadmium sulfide single crystals. They found that sulfur vapor at low impingement rates had no observable effect, but when the impingement rate became of the same order of magnitude as that of the evaporation rate of CdS, the sulfur beam lowers the evaporation rate. For high sulfur flux the evaporation rate of CdS was inversely proportional to

the square root of the S_2 impingement rate. As far as we are aware, no other investigation of the effect of gas pressure on the kinetics of sublimation of a substance that displays a low evaporation coefficient has been reported.

In the present study the influence of both nitrogen gas and argon gas at known pressures was investigated. When argon or nitrogen that had not been carefully dried and purified of oxygen, an oxide layer formed that greatly reduced the evaporation rate. The layer was not removed even by heating for long periods in vacuo. However, the effects of the purified nitrogen and argon gases were reversible, the Langmuir pressure that was characteristic under vacuum being re-established within minutes of re-establishment of the vacuum.

We found that the nitrogen and argon had no apparent retarding effect on evaporation unless their pressures were the same order of magnitude as the evaporating species or higher, but the fractional reduction in pressure that resulted from a given pressure of either gas was somewhat greater at low temperatures than at higher temperatures.

The retardation of evaporation might be a consequence of either the decreased mean free path that results from the presence of a background gas or of the adsorption of molecules of the gas on the active sites of the surface. We think that adsorption was responsible for most of the retardation, because a relatively large decrease in rate of evaporation occurred on introducing the background gas at levels which should produce negligible changes in the measured pressures if decrease in mean free path was responsible. The marked reduction in evaporation

rate in the presence of argon must arise from inhibition of a surface step of the evaporation reaction that results from occupancy by argon of surface sites. Nitrogen had a retarding effect an order of magnitude greater than that of argon at background pressures of 7×10^{-7} atm. The difference, while marked, may simply reflect greater physical adsorption of nitrogen in comparison to argon to reduce by a factor of ten the surface sites available for a critical reaction step. One way to distinguish between this possibility and the possibility that nitrogen gas acts in a more specific manner to reverse a reaction step may be to investigate the effects of additional inert gases in order to see if the inhibition of the reaction by these gases in comparison with nitrogen can be correlated with their expected degrees of adsorption. We hope to carry out such an investigation.

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APPENDIX

A. Cell Measurements and Related Information

Method	a_1 (= a_2) cm^2	q_1 cm	q_2 cm	L/r	f
Torsion-effusion					
1 mil diam orifice	7.85×10^{-3}	1.05	1.06	3	0.47203
2 mil diam orifice	3.14×10^{-2}	1.57	1.59	1.5	0.64260
Langmuir	$.625 \times 10^{-2}$	1.34	1.35	0	1

B. Calibration of Torsion Wire

Annealed wires of tungsten with 2 mil diam were calibrated to obtain a torsion constant. The torsion constant D is calculated (from the period t, of the suspension system alone, and the period t_w, with a weight of known moment of inertia I_w added to the system) with the aid of the following equation:

$$D = \frac{4 \pi^2 I_w}{(t_w{}^2 - t^2)}$$

D_2 mil wire used = 2.74.

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