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ABSTRACT

Torsion effusion studies confirm earlier reports that effusion cell pressures for sublimation of magnesium nitride are significantly lower than those calculated from thermochemical data for the expected sublimation reaction, $Mg_3N_2(s) = 3Mg(g) + N_2(g)$ even though usual tests imply that equilibrium is obtained in the cell. Free surface sublimation rates range from 2×10^{-2} times the measured effusion pressures at 1000°K to 3×10^{-3} times the measured effusion pressures at 1250°K. Free surface sublimation rates are lowered still further by addition of nitrogen or argon at about 5×10^{-7} atm pressure. The rate of free surface sublimation is apparently limited by adsorption of gases on the sublimation sites. The rate limiting process in effusion is probably different from that for free surface sublimation.

I. INTRODUCTION

Metal nitrides when heated in vacuo decompose to yield as reaction products, diatomic nitrogen gas, and gaseous metal atoms or solids depleted of nitrogen. The measured rates of several of these reactions, notably decomposition of boron nitride and aluminum nitride,[1] gallium nitride[2] and beryllium nitride[3] have been proved to be orders of magnitude lower than the maximum possible rates, which can be calculated from thermodynamic data by use of the Hertz-Langmuir equation.

For the reaction $Mg_3N_2(s) = 3Mg(g) + N_2(g)$, Soulen, Sthapitononda and Margrave[4] have reported Hertz-Knudsen effusion pressures which lie well below pressures that they calculated from thermochemical data. This fact plus an increase in measured pressures when the effusion orifice was decreased suggested that magnesium nitride has a kinetic barrier to decomposition. Soulen et al. considered that they had too few data to permit calculation of the equilibrium pressures or evaporation coefficient.

A company report by Hildenbrand and Theard[5] includes a study of the dependence of measured magnesium nitride dissociation pressures on temperature and on effusion orifice area. By application of the equation[6-9]

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

where P_e is the equilibrium pressure, P_x is the measured pressure, W is the orifice correction factor,[10,11] a is the cross sectional orifice area, α is the evaporation coefficient, and A is the effective sample surface area, Hildenbrand and Theard calculated apparent equilibrium pressures and an upper limit to the evaporation coefficient of 5×10^{-3} over the experimental temperature range. The equilibrium pressures calculated in the study are lower by more than a factor of ten than pressures calculated for the dissociation reaction from data accepted in the JANAF Tables.[12]

Hildenbrand and Theard concluded that either the heat of formation for $Mg_3N_2(s)$ is in error, or the rate of vaporization is limited by a secondary process which leads to false apparent equilibrium pressures when Eq. (1) is applied. They favored the second explanation, largely because thermodynamic quantities calculated from their data were inconsistent with apparently reliable values calculated from independent thermodynamic data. They noted that Kay and Gregory[13] have reported that use of Eq. (1) for effusion data for the reaction $Mg(OH)_2(s) = MgO(s) + H_2O(g)$ yields apparent equilibrium pressures far lower than the known equilibrium pressures.

Since Eq. (1) has come into increasing use for calculation of equilibrium pressures for substances with low evaporation coefficients, the indications reported by Kay and Gregory and by Hildenbrand and Theard that its use may sometimes be invalid are of great concern, and further studies of substances for which the equation may not be valid are of particular importance.

This paper reports a torsion-effusion and torsion-Langmuir study of magnesium nitride. The torsion-langmuir study was made both in vacuo and in controlled pressures of nitrogen and argon gases. The torsion-effusion study provides a direct check of the experimental findings of Hildenbrand and Theard and the torsion-Langmuir study provides an independent means for calculating the evaporation coefficient and temperature dependence and provides evidence on the effects of adsorbed gases on the rate of a sublimation reaction.

II. EXPERIMENTAL

The torsion-effusion and torsion-Langmuir methods as used in this laboratory have been previously described[14,15] and only special features of the present study need be described here.

That leakage from the effusion cells of National Carbon ZT101 grade graphite, caused no deflection was demonstrated by heating magnesium nitride in the cell before effusion holes were drilled. Orifice dimensions for the effusion cells and for the graphite washers behind which wafers were mounted in the torsion-Langmuir experiments and the orifice correction factors used are given in Table I.

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 the torsion cell temperatures against temperatures of the dummy cell, another thermocouple, which had been calibrated by measurement of the melting points of tin and silver was placed inside a second cell. This cell was suspended in the position where the torsion cell is usually located, and the corresponding temperatures of the two thermocouples were measured in the experimental range.

The vapor pressure of tin was measured as a test of our experimental methods. A value of 72.0 kcal/mole for the heat of sublimation at

298°K was obtained by the third law method which agrees well with the value of 71.8 kcal/mole measured by Schulz[16] by the torsion effusion method and with 72.2 ± 0.5 calculated by Hultgren et al.[17] from results of earlier studies.

For experiments on the effect of gases on the rate of sublimation, nitrogen or argon was admitted into the furnace chamber by means of a needle valve. If nitrogen was used directly from the tank, oxygen and water vapor impurities in the gas completely converted the magnesium nitride to magnesium oxide. Accordingly the gases were passed through a liquid nitrogen cold trap and subsequently through an oxygen getter of copper shavings, maintained at 600°C. Upon completion of each sublimation experiment in a foreign gas, the Langmuir pressure in vacuo was measured to insure that oxidation of the sample or other irreversible changes had not occurred. 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 background pressures. The gauge was calibrated against a McLeod Gauge at the higher pressures for argon, air and nitrogen.

The magnesium nitride powder purchased from Metal Hydride Inc., had a guaranteed purity of 99.9%. An x-ray diffraction trace of this material showed only magnesium nitride peaks. A spectrographic analysis of the magnesium nitride, provided by American Spectrographic Laboratories, revealed 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%, Cu 0.0007%, Cr 0.02%, Ba 0.003%. Magnesium nitride disks for the torsion-Langmuir specimens were pressed in a 1/4 in. diameter stainless steel die at 7 tons total load. The pellets retained the yellow color of the powder.

III. RESULTS

Graphs 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. 1. Table II gives measured total pressures and calculated third-law heats of sublimation at 298°K. A least squares calculation of the data for evaporation of magnesium nitride to Mg gas and N_2 gas from cells of 1 mm diameter orifice (near equilibrium) gives for log P_T and log K vs. temperature between 1000° and 1250°K:

$$\log K_{eq} = 4 \log P_T - 0.978 = -\left(\frac{291.38(\pm 8.51)}{4.576}\right)\frac{10^3}{T}$$

$$+ 37.16(\pm 1.61)$$

The quoted errors are the standard deviations from the least squares fit. The second law enthalpies corrected to 298°K are 239.1 ± 16.5, 265.8 ± 18.1 and 218.7 ± 12.9 kcal/mole Mg_3N_2 for 1 mm, 2 mm diameter orifices and Langmuir evaporation, respectively. Application of Eq. (1) to our data yields an apparent equilibrium pressure that differs insignificantly from our measurements with the 1 mm orifices, probably because the effective area of our magnesium nitride powder is higher than that of Hildenbrand and Theard.

When the background pressure of the system was raised by as much as a factor of 10 over the normal background pressure of about 10^{-8}

atm by introduction of either nitrogen or argon there was no measurable effect on the rate of evaporation of magnesium nitride disks. At higher pressures, however, either gas reduced sublimation rates markedly (Fig. 2). Nitrogen appeared to have a slightly greater retarding effect than argon on the evaporation. The fractional reduction in pressure that resulted from a given pressure of either gas increased with increasing temperature.

IV. DISCUSSION

Our effusion pressure measurements are in good agreement with the measurements of Soulen et al.[4] and with the apparent equilibrium pressures calculated by Hildenbrand and Theard[5] (Fig. 1). And the range of evaporation coefficients, 2×10^{-2} at 1000°K to 3×10^{-3} at 1250°K, calculated from the ratio of our Langmuir pressures to our Knudsen pressures has an average near the value which Hildenbrand and Theard calculated by means of Eq. (1).

The good agreement obtained for both the apparent equilibrium pressures and the average evaporation coefficient by two somewhat different methods would normally be considered to imply that these quantities are reliably established. However, neither thermochemical data from other sources nor the relative temperature dependences of torsion-Langmuir and torsion-effusion data support the conclusion that equilibrium pressures and valid evaporation coefficients have been measured.

The heat of sublimation at 298°K calculated by the third law method, 242.3 kcal/mole Mg_3N_2, and Hildenbrand and Theard's value of 243.5±0.5

kcal/mole Mg_3N_2, are in marked disagreement with 215.2 kcal/mole calculated from thermochemical data.[12]

It is very doubtful that the reported thermochemical data are in error by 27 Kcal. Furthermore, the heats of sublimation calculated by the third law method in both effusion studies fail to show the temperature independence expected for equilibrium measurements. In this study the values range from an average of 249 kcal at 1050°K to 238 at 1250°K. This variation is far higher than can be explained by reasonable estimates of probable experimental errors. Neither the apparatus used in this investigation nor that of Hildenbrand and Theard has yielded such sharp trends in studies of a variety of other materials. Errors in supporting heat capacity or entropy data could scarcely account for the discrepancy either. For example, the entropy of sublimation would have to be about 50 eu per mole of Mg_3N_2 greater than the accepted value to explain the observed inconsistency on the basis of an entropy error alone.

Agreement between evaporation coefficients calculated from comparison of torsion-Langmuir to effusion rates and evaporation coefficients calculated by Hildenbrand and Theard from reaction 1 may well be fortuitous. The slopes of free surface and effusion plots in Fig. 1 suggest that different surface steps are rate determining under free surface sublimation and effusion conditions. It has been demonstrated theoretically that if effusion and free surface sublimation rates are controlled by the same slow step and if the effusion pressures vary more steeply with temperature than do equilibrium pressures, than the free surface sublimation pressures should vary still more steeply than the effusion pressures with temperature.[18] The predicted behavior is found in beryllium nitride sublimation. But for magnesium nitride sublimation the effusion pressures vary more steeply with temperature than do either the pressures calculated from thermochemical data or the free surface sublimation pressures.

The rate of free surface sublimation is probably limited by adsorption of gas molecules on surface sublimation sites. Both the lower sublimation rates and the steeper temperature dependences of pressures that result from additions of either nitrogen or argon (Fig. 2) are consistent with this hypothesis. Since argon has nearly as marked an effect as nitrogen on the sublimation rate, and since argon would not be expected to strongly adsorb at the temperatures of study, it is probable that water or oxygen, present despite efforts to purify the gas stream, may be the principal adsorbing species in the argon experiments and perhaps in the nitrogen experiments as well.

Nominally the background pressure in free surface sublimation studies was increased about a factor of 50 before significant effects of background gas were noted. However, the true pressures, particularly of impurities, in the region of the cells are difficult to evaluate. Consequently, it is a strong possibility that pressures in the hot zone were higher than recorded, and that if the free surface sublimation were measured under improved vacuum higher sublimation rates would be measured.

The present study reveals serious gaps in our understanding of sublimation reactions, and suggests the need for more careful evaluation of experimental parameters for such reactions. We plan to make in our laboratory detailed studies of the effects of adsorbed gases on rates of sublimation reactions. We also plan a study of the effects of dissolved impurities and introduced gases on the rate of effusion of magnesium nitride from cells in an effort to find an explanation for the apparently false equilibrium pressures yielded for this solid by effusion data.

Acknowledgments-

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REFERENCES

1. L. H. Dreger, V. V. Dodope and J. L. Margrave, J. Phys. Chem., 66, 1556 (1962).
2. Z. A. Munir and A. W. Searcy, J. Chem. Phys., 42, 4223 (1965).
3. R. E. Yates, M. A. Greenbaum and M. Farber, J. Phys. Chem., 18, 2682 (1964).
4. J. R. Soulen, P. Sthapitononda and J. L. Margrave, J. Phys. Chem., 59, 132 (1955).
5. D. L. Hildenbrand and L. P. Theard, ASTIA Unclassified Report 258410, 1961, Aeronutronic Report U-1274.
6. R. Speiser and H. L. Johnston, Trans. Am. Soc. Metals, 42, 283 (1950).
7. C. I. Whitman, J. Chem. Phys., 20, 161 (1952); ibid., 21, 1406 (1953).
8. K. Motzfeldt, J. Phys. Cehm., 59, 139 (1955).
9. G. M. Rosenblatt, J. Electrochem. Soc., 110, 563 (1963).
10. P. Clausing, Ann. Physik, 12, 961 (1932).
11. R. D. Freeman and A. W. Searcy, J. Chem. Phys., 22, 762 (1954).
12. D. R. Stull, et al., JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan.
13. E. Kay and N. W. Gregory, J. Phys. Chem., 62, 1079 (1958).
14. A. W. Searcy and R. D. Freeman, J. Am. Chem. Soc., 76, 5229 (1954).
15. Z. A. Munir and A. W. Searcy, J. Chem. Phys., 42, 4223 (1965).
16. D. A. Schulz, Ph.D. Thesis, University of California, Berkeley (1961).
17. R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley and Sons, Inc., New York (1963).
18. C. L. Hoenig and A. W. Searcy, submitted for publication J. Am. Ceram. Soc.

Table I. Cell measurements and related information

	a_1 (= a_2) cm^2	q_1 cm	q_2 cm	L/r
1 mm diam orifice	7.85×10^{-3}	1.05	1.06	3
2 mm diam orifice	3.14×10^{-2}	1.57	1.59	1.5
Langmuir	6.25×10^{-3}	1.34	1.35	Knife-edged

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

Temperature °K	Total Pressure (atm)	Apparent Heat of Reaction at 298°K
1 mm diam orifice		
1056	1.98×10^{-6}	250.8 kcal/mole Mg_3N_2
1122	1.98×10^{-5}	245.8
1169	7.56	243.4
1193	1.42×10^{-4}	242.3
1211	2.62	240.0
1237	4.77×10^{-4}	239.2
1202	1.86	241.6
1181	1.07	242.7
1159	5.05	245.1
1178	1.62×10^{-4}	238.2
1231	4.68	238.2
1036	3.06×10^{-6}	242.7
1162	8.84×10^{-5}	240.6
1212	2.78×10^{-4}	239.7
1087	1.15×10^{-5}	243.0
1252	7.04×10^{-4}	238.1
1231	4.18	239.3
1223	3.57	238.1
1221	3.14	240.2
1168	8.72×10^{-5}	241.9
1105	2.70×10^{-5}	239.5
1213	2.51×10^{-4}	240.8
1193	1.40×10^{-4}	242.5
1182	1.03	243.2
1166	6.48×10^{-5}	244.3
1161	5.40	244.9
1146	3.72	245.2

Table II. Continued

1125	1.94	246.6
1105	9.06×10^{-6}	249.0
1096	7.22	248.7
1063	3.51	247.3
1052	1.85	250.4
2 mm diam orifice		
1206	2.74×10^{-4}	238.6 kcal/mole Mg_3N_2
1190	2.33	237.1
1164	1.97	233.6
1110	1.33×10^{-5}	246.8
1067	3.22×10^{-6}	249.4
1004	1.73	247.7
1101	3.06×10^{-5}	248.1
1151	5.90	248.1
1171	2.34×10^{-4}	246.2
1204	2.36	239.7
1212	2.47	240.8
1181	1.98	236.9
1125	1.25×10^{-5}	250.6
1107	1.17	247.2
Typical Langmuir evaporation data		
1254	3.30×10^{-6}	292.0
1222	1.36	293.3
1194	7.44×10^{-7}	292.4
1141	3.56	286.3
1122	1.94	237.1
1064	9.79×10^{-8}	278.3
1305	9.16×10^{-6}	293.0
1293	6.20	294.4
1258	4.42	290.0
1110	1.09×10^{-7}	289.2
1068	6.08×10^{-8}	233.3
1026	3.14	277.8

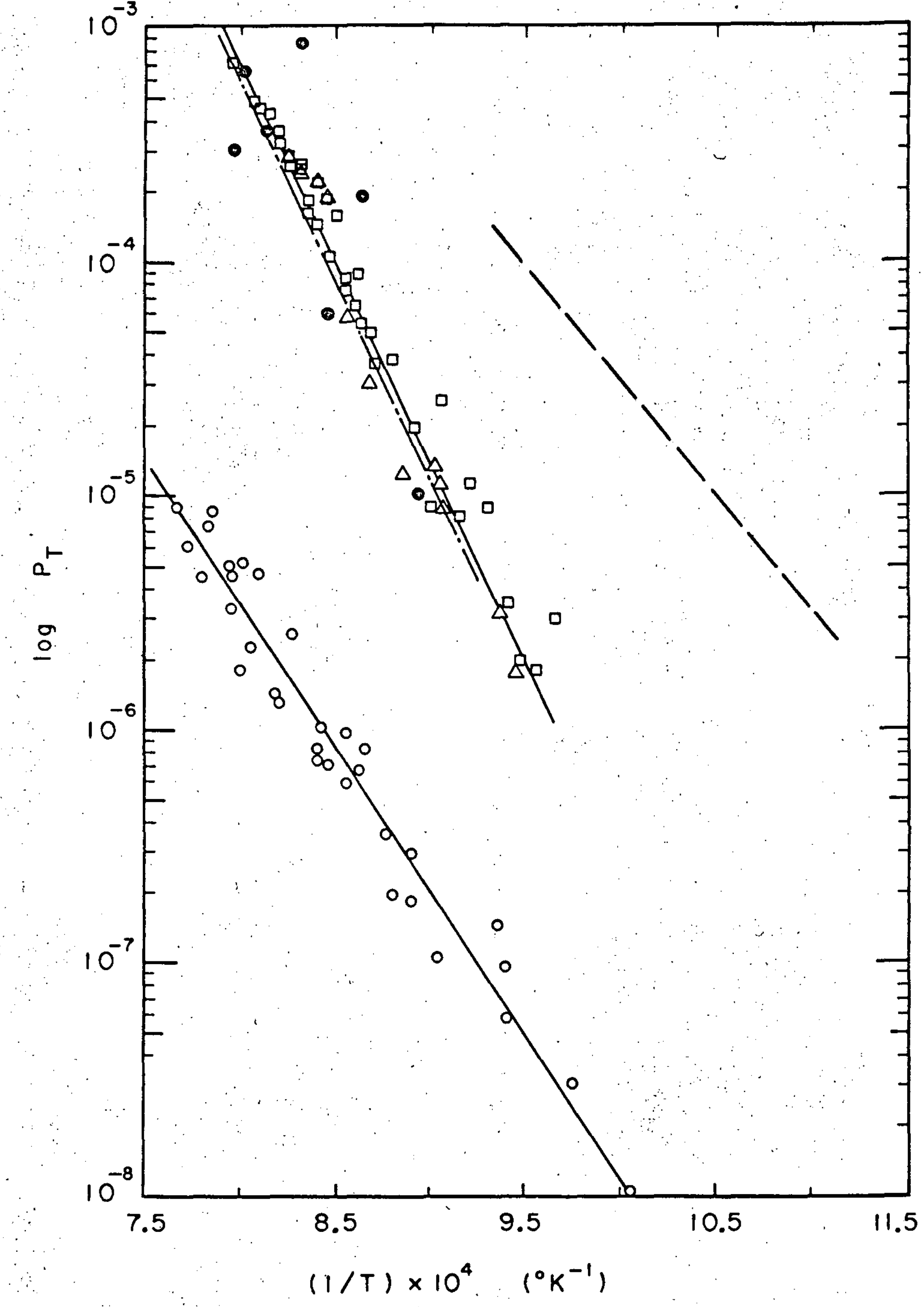

Fig. 1

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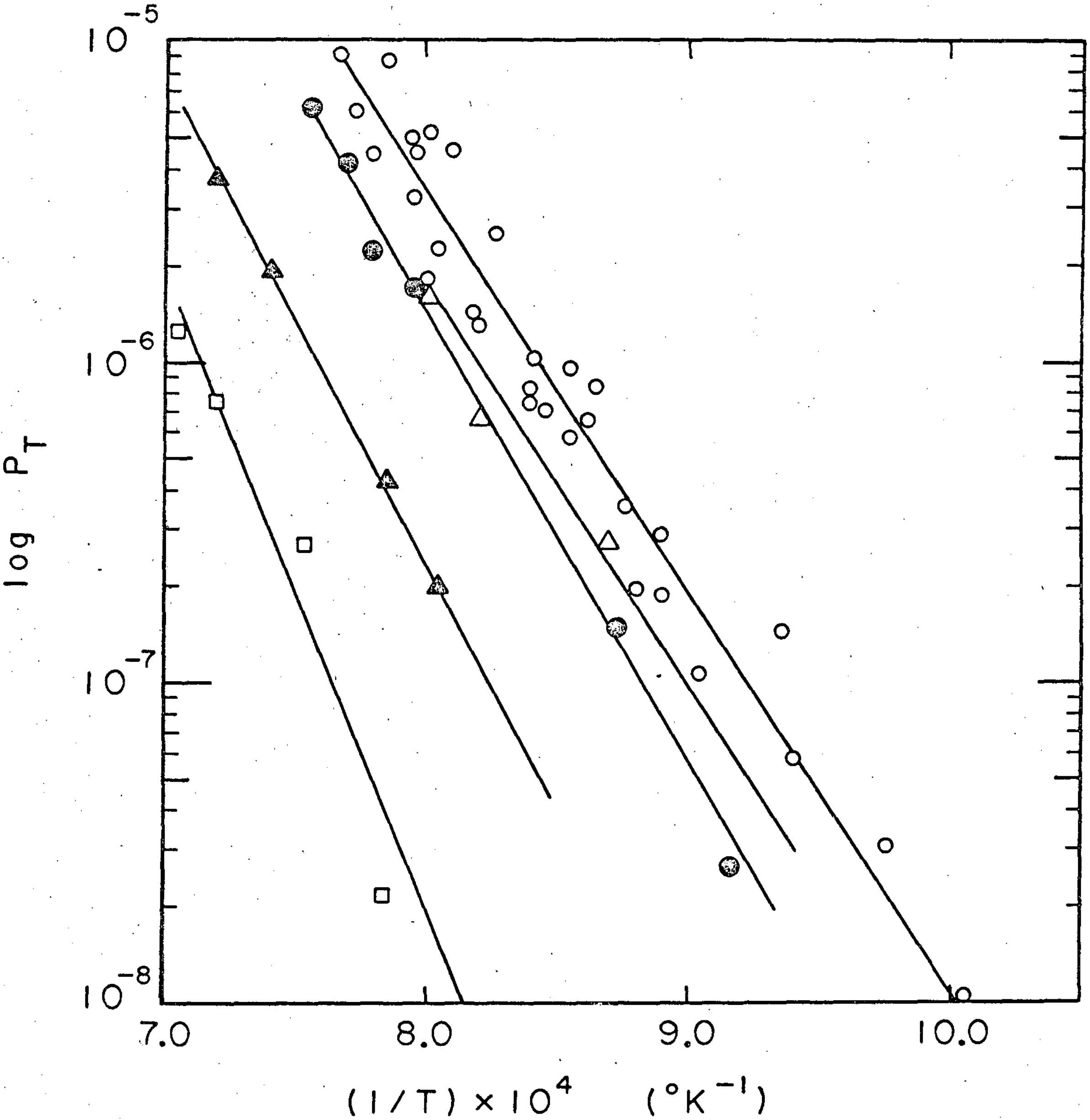

Fig. 2

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FIGURE CAPTIONS

Fig. 1 Vapor pressure of magnesium nitride.

□ Effusion diam 1 mm

△ Effusion diam 2 mm

○ Langmuir vaporization

— — — Equilibrium calculated from thermal data

o-o-o- Hildenbrand and Theard calculated equilibrium pressure

● Soulen et al.[4] Knudsen measurements.

Fig. 2 Langmuir vaporization of magnesium nitride in vacuo, argon, and nitrogen.

○ in vacuo 10^{-8} atm

△ 5×10^{-7} atm argon

● 5×10^{-7} atm nitrogen

▲ 7×10^{-7} atm argon

□ 6.5×10^{-7} atm nitrogen