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FREE SURFACE SUBLIMATION OF MAGNESIUM OXIDE

John H. Austin
(M.S. Thesis)

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CONTENTS

Abstract v

I. Introduction 1

II. Significance of Evaporation Coefficients 4

III. Experimental 6

IV. Results 13

V. Discussion 34

Acknowledgments 39

Appendix 42

References 40

FREE SURFACE SUBLIMATION OF MAGNESIUM OXIDE

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ABSTRACT

The free surface sublimation of magnesium oxide was studied utilizing an Atlas mass spectrometer. A total of 75 separate measurements of the Langmuir flux from (001) surfaces of single crystal magnesium oxide were compared to equilibrium data using silver vaporization for calibration. The evaporation coefficient was found to be less than unity but greater than 0.1 in the temperature range 1895-2258°K. In all but one run the apparent activation enthalpy for sublimation was less than the equilibrium enthalpy, indicating that desorption was not rate limiting in those runs. Photomicrographs showed the steady-state surfaces to be covered by pits of octagonal or square cross sections.

I. INTRODUCTION

Despite considerable interest in, and research[1-9] on the sublimation of magnesium oxide, little is presently known about the kinetics of its evaporation. A knowledge of the kinetics is important, not only as a contribution to the theoretical understanding of evaporation, but also because the understanding and control of magnesium oxide evaporation is important in high temperature refractory applications of magnesium oxide.

Past studies that are pertinent to evaluating the evaporation of magnesium oxide can be divided roughly into three categories:

1. Knudsen effusion studies[1-4]
2. Oxygen transpiration measurements[5,6]
3. Flame spectrometry.[7,8]

In 1961 Ackermann and Thorn[10] noted that an accurate determination of the equilibrium pressure of magnesium oxide had not yet been achieved primarily because of its reaction with materials in its environment. Since then, several investigations on the subject have been published. Altman[6] performed Knudsen weight loss experiments in alumina crucibles. He reported the enthalpy for the reaction $MgO_{(s)} \rightarrow Mg_{(g)} + 1/2\ O_{2\ (g)}$ to be 173 kcal/mole and for the reaction $MgO_{(s)} \rightarrow MgO_{(g)}$ to be 158 kcal/mole. The results reconfirmed an earlier mass spectrometric finding by Porter, Chupka, and Inghram[2] that sublimation in vacuum occurs primarily to gaseous magnesium and oxygen. In the latter experiments, it was shown that $Mg^+/MgO^+ > 1000$. Altman[6] and Alexander, Ogden, and Levy[5] performed transpiration experiments with oxygen as the carrier gas in efforts to establish the stability of gaseous oxides. In a mass

spectrometric study Norman, et al.[4] determined the equilibrium pressure of magnesium oxide utilizing an iridium Knudsen cell. At 2000°K the heat of vaporization for the reaction $MgO_{(s)} \rightarrow Mg_{(g)} + O_{(g)}$ was 211.7 ± 9.6 kcal/mole and the ratio of Mg+ to MgO+ was greater than 18,000. These various thermodynamic studies show clearly that under neutral conditions, surfaces that yield near equilibrium fluxes must yield the gaseous elements as the predominate vapor species. Since thermodynamic parameters are not functions of the reaction path, little further information can be obtained from the past studies about the kinetics or mechanisms of sublimation.

One effective means for obtaining kinetic information is to measure Langmuir free surface sublimation rates for comparison with equilibrium data. An evaporation coefficient, α, may be defined by the relation $\alpha = J_{obs}/J_{eq}$ where J_{obs} is the observed free surface flux and J_{eq} is the equilibrium flux.

Apparently the only report in the literature of a free surface vaporization study of magnesium oxide is that of Alcock and Peleg[9] in which a polycrystalline sample was attached to a molybdenum torsion unit and heated at 1900°K. The Langmuir fluxes were lower than the calculated equilibrium fluxes by a factor of four. Since evaporation rates for polycrystalline materials may be markedly influenced by evaporation from pores and grain boundaries,[11] these results may have been an average of low surface fluxes and high fluxes from grain boundary regions.

The purpose of this research is to obtain data for sublimation as a function of temperature from well defined crystal surfaces and from

those data, if possible, to gain better insight into the kinetics of free surface sublimation of magnesium oxide. A mass spectrometer was employed to measure the Langmuir flux. Silver was introduced to serve as a standard for calculation of partial pressures from ion intensities. Silver was chosen since it has a relatively high vapor pressure and a unit evaporation coefficient near its melting point.[12,13]

II. SIGNIFICANCE OF EVAPORATION COEFFICIENTS

Historically, the evaporation coefficient is defined as the ratio of the observed evaporation flux in vacuum to the maximum or equilibrium flux of vaporizing species as calculated from the Hertz-Langmuir[14] equation

$$J_{max} = P_{eq} (2\pi MkT)^{-1/2} \tag{1}$$

where P_{eq} = the equilibrium pressure

k = the Boltzman constant

M = the molecular weight

T = the absolute temperature.

The observed flux is then

$$J_{obs} = \alpha P_{eq} (2\pi MkT)^{-1/2}$$

where the evaporation coefficient is introduced as a correction factor for deviations from proved equilibrium conditions. If instead of monitoring the flux of molecules one were to measure pressures, α would be defined as

$$\alpha = P_{obs}/P_{eq}. \tag{2}$$

The P_{obs} is in this example the observed pressure from free surface sublimation, which may also be called the Langmuir pressure. P_{obs} may then be related to the apparent activation free energy, $\Delta F_v{}^*$ for a condensed species going to the gas phase by the relation

$$P_{obs} = \exp(-\Delta F_v{}^*/RT) = \exp(-\Delta H_v{}^*/RT) \exp(\Delta S_v{}^*/R)$$

where $\Delta H_v{}^*$ and $\Delta S_v{}^*$ are the apparent activation enthalpy and entropy for sublimation, respectively. The equilibrium pressure is related to the standard enthalpy of vaporization, $\Delta H_v{}^\circ$, and to the standard entropy of

vaporization, ΔS_v°, by the relation

$$P_{eq} = \exp(-\Delta H_v^\circ/RT) \exp(\Delta S_v^\circ/R).$$

Accordingly, Eq. (2) may be rewritten

$$\alpha = \frac{\exp(-\Delta H_v^*/RT) \exp(\Delta S_v^*/R)}{\exp(-\Delta H_v^\circ/RT) \exp(\Delta S_v^\circ/R)} \qquad (3)$$

Furthermore, there is such a relation for each vaporizing species. Equation (3) shows that if there is an enthalpy barrier and/or entropy contraint controlling sublimation, α would be less than unity. Such barriers might be bond breaking or making, or reorientation of complex vaporizing molecules on the surface. Measured values of α range from unity for many pure metals and some compounds[15] to 10^{-6} for complex vaporization processes.[16]

III. EXPERIMENTAL

Magnesium oxide single crystals were obtained from the Solid State Division of Oak Ridge National Laboratory. A spectroscopic analysis of the material is given in Table I. The crystals were optically clear but contained numerous microscopic bubbles, possibly of H_2 or H_2O. Since the crystals were grown by the carbon arc process, the bubbles were probably in form and sizes of maximum high temperature stability.

Surfaces for the studies were obtained by cleavage of the as-received magnesium oxide chunk and verified to be the (001) by x-ray diffraction. These cleaved surfaces became end faces of cylinders which were machined from the cleaved pieces without machining the surfaces for which evaporation rates were measured.

A specimen was placed inside an iridium lined tungsten cell. A disk of silver of the diameter as that of the MgO was placed on the MgO surface as depicted in Fig. 1. The free surface was situated approximately 0.8 inch from the shutter so that the point of temperature measurements would be as close to the specimen surface as possible with the existing mass spectrometer design.

TABLE I. ANALYSIS OF MAGNESIUM OXIDE SAMPLE

Element	μgm/gm MgO
Ca	21.
Na	0.2
Pb	< 5.
Ba	<10.
Mn	< 1.
Zr	< 6.
Cr	< 0.6
S	< 2
Fe	2-4
Si	10
Al	12
Ti	2?

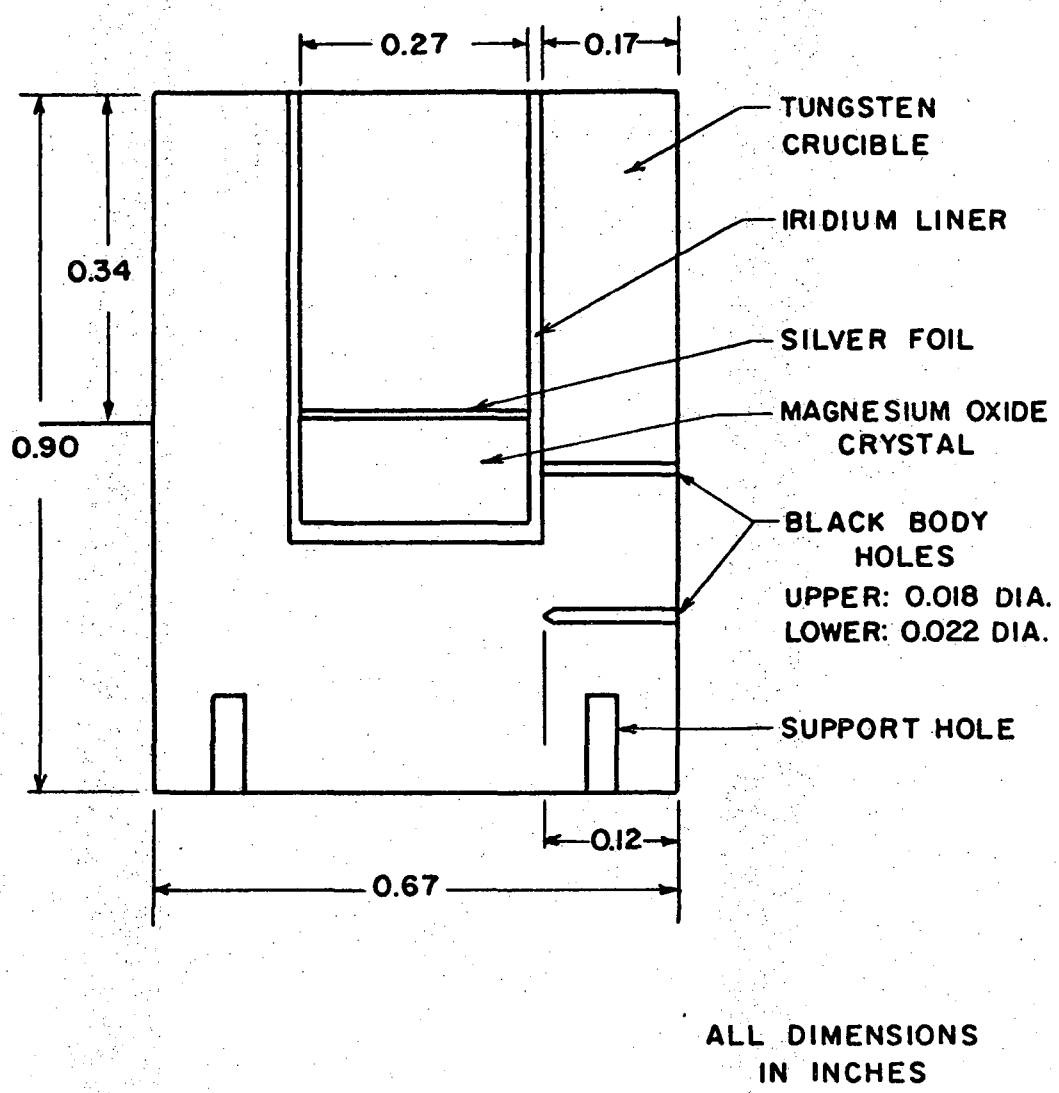

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Figure 1. Free Surface Vaporization Cell.

The shutter orifice served to define a molecular beam for both gaseous silver and gaseous magnesium. Thus, the two measured fluxes were assured to be from the same surface areas and the fluxes could be directly compared for obtaining absolute pressure values.

The Langmuir chamber was evacuated to 1×10^{-6} torr prior to a run, but the pressure rose to a maximum of 1×10^{-5} torr during a run. Differential pumping and a liquid nitrogen cold finger maintained a pressure of $< 1 \times 10^{-7}$ torr in the ionization region.

The crucible was heated by electron bombardment. Tantalum heat shields protected the crucible from radiation losses.

Temperature measurements were obtained with an optical pyrometer calibrated against a standard tungsten-ribbon lamp. Two black-body holes in the side of the tungsten cell were employed. The temperature at the two orifices were within $\pm 5^{\circ}C$ of each other; consequently, only one of the black-body holes was utilized during vaporizations. A magnetically operated shutter was placed before the window to minimize errors due to condensation of material on the port. Temperature corrections for the transmission through the port were made and the port calibration was periodically checked.

A collimated beam emanating from the surface was ionized by 70 ev electrons. A movable shutter intersecting the beam verified that the gaseous species did originate from the Langmuir cell. The ions formed were mass-analyzed in an Atlas CH_4 mass spectrometer (a 24 cm radius, 60° sector, single focusing device). The analyzer was equipped with a 16 stage electron multiplier employing copper-beryllium dynodes. Temperature dependence of ion intensities at mass 107 for silver and

at mass 24 for magnesium were measured over the approximate temperature ranges 1130° - $T_{M.P.}$ and 1900° - 2200°K, respectively. In each particular run the magnitude of the ion intensities was measured at least 15 minutes after each temperature change to ensure that equilibrium was achieved.

The Langmuir partial pressure of magnesium from magnesium oxide was calculated from the ion intensity by use of the relation

$$P_{Mg} = I^{+}_{Mg} \; T_{Mg} \left[\frac{P_{Ag}}{I^{+}_{Ag} \; T_{Ag}}\right] \cdot \left[\frac{\sigma_{Ag}}{\sigma_{Mg}}\right] \left[\frac{\gamma_{Ag}}{\gamma_{Mg}}\right] \left[\frac{\Delta E_{Ag}}{\Delta E_{Mg}}\right]$$

where P = the partial pressure in atmospheres

I^{+} = the isotope corrected shutter intensity

σ = the relative ionization cross section

γ = the multiplier efficiency

ΔE = the difference in energy between the ionizing electrons and appearance potential.

The quantity $\frac{P_{Ag}}{I^{+}_{Ag} T_{Ag}}$ was determined by measuring the ion intensity at mass 107 for several temperatures, making a least squares fit of $I^{+}_{Ag} T_{Ag}$ vs $1/T_{Ag}$, and dividing the accepted equilibrium pressure of silver[7] at the average experimental temperature by the calculated $I^{+}_{Ag} \; T_{Ag}$ value at the same temperature from the least squares fit. The relative ionization cross sections used were Ag = 34.8 and Mg = 15.9.[18] The multiplier efficiency was assumed to be of the form $\gamma = \delta \, M^{1/2}$ where δ is a constant and M is the mass of the impinging ion.[19] The ratio of ΔE's was equated to one since the ionizing electrons were 70 ev and since the appearance potentials of Mg^{+} and Ag^{+} differ by less than 1 ev.[20.21]

Assuming that magnesium oxide sublimes predominately by decomposition to the elements, the following reactions are significant at 2000°K:

$$MgO_{(s)} \rightarrow Mg_{(g)} + 1/2\ O_{2\ (g)}$$

$$K_1 = P_{Mg}\ P_{O_2}^{\ 1/2} \tag{4}$$

$$MgO_{(s)} \rightarrow Mg_{(g)} + O_{(g)}$$

$$K_2 = P_{Mg}\ P_O \tag{5}$$

where the importance of either reaction is determined by

$$1/2\ O_2 \rightleftarrows O$$

$$K_3 = \frac{P_O}{P_{O_2}^{\ 1/2}} \tag{6}$$

For congruent vaporization it is necessary that

$$J_{Mg} = J_O + 2\ J_{O_2}$$

where J = the flux of the individual species as calculated by Eq. (1). The flux equation relates the pressure of magnesium to the pressure of oxygen by the relation

$$\frac{P_{Mg}}{M_{Mg}^{1/2}} = \frac{P_O}{M_O^{1/2}} + \frac{2P_{O_2}}{M_{O_2}^{1/2}} \tag{7}$$

Substituting Eq. (6) into Eq. (7) for P_{O_2} and solving the quadratic equation for P_O leads to an expression for P_O in terms of P_{Mg}, K_3 and the masses. P_O may be eliminated by application of Eq. (5). The equilibrium partial pressure of magnesium over magnesium oxide as a function of temperature was obtained by application of these equations and the existing thermodynamic data for magnesium oxide and oxygen,[22] and magnesium gas.[23]

Because the kinetics of sublimation may be correlated with the

structure of the surface, the morphology of the evaporated surfaces were examined with the aid of an optical microscope.

IV. RESULTS

The results of five runs with a total of 75 separate measurements of the Langmuir partial pressure of magnesium over magnesium oxide are compiled in Tables II through VI. The results of the individual runs are presented below. The silver calibration data is included in the Appendix.

It should be noted that because of instabilities in the electron bombardment system, measurements of the magnesium intensity were never initiated until after at least one hour and up to three hours of heating at about 2000°K. In Runs 1 through 3 the ionization current fluctuated considerably when the beam was shuttered, causing considerable scatter in the data.

The first attempt to measure the evaporation coefficient by the above technique resulted in an evaporation coefficient of about four which is clearly erroneous. The discrepancy was attributed to a faulty silver calibration since the measured silver intensities for this run were about an order of magnitude below those of subsequent runs made under similar conditions. It is believed that in this run the silver disk fell against the wall of the liner while the cell was being tilted and aligned in the spectrometer chamber. With the disk not covering the crystal surface, the silver beam effectively emanated from a smaller-projected surface area than did the magnesium beam. The results of Run 1 have been omitted for this reason.

The results of the second run are presented in Table II and Fig. 2. The straight line in Fig. 2 is the calculated equilibrium partial pressure of magnesium. A least squares fit of the free surface sublimation data yielded the equation

$$\log_{10} P_{atm} = -(1.137 \pm 0.078)\frac{10^4}{T} + 0.187 \pm 0.012$$

for the Langmuir partial pressure of magnesium. The errors are standard variances. The average evaporation coefficient for the temperature range 1895°-2206 °K was calculated to be 0.83.

In the first attempt to reproduce the data with another specimen, an electronic malfunction caused termination of the run after about four hours of heating the crystal at 2000°K and the collection of four data points. The statistically insignificant data was discarded, the same crystal was reinserted with another silver specimen into the cell, and the run was repeated. The results are included in Table III and Fig. 3. A least-squares fit of the data gave

$$\log_{10} P_{atm} = -(2.84 \pm .33)\frac{10^4}{T} + 8.34 \pm 0.93$$

which yields an apparent activation enthalpy of vaporization over twice that of the previous run. The average evaporation coefficient was calculated to be 0.48 in the temperature range 2059-2186°K.

Photomicrographs were made of the evaporated surfaces from each run. Fig. 4 depicts the typical coverage of the surface of Run 2 while Fig. 5 shows the morphology of the surface from Run 3. The former surface was characterized by some regions of relatively high surface coverage of pits and some regions of low coverage. The pits were predominately square [possibly (110) walls] with a few having octagonal symmetry [possibly (111) walls]. The surface from Run 3 was characterized by relatively high pit coverage. Many of the pits had octagonal interior walls; some of these pits had octagonal symmetry extending to the top of the pit while others had shapes resembling squares at the surface. Some of the macroscopic pits exhibited square bottoms rotated 45° to the square cross section at the top of the pit.

TABLE II. Langmuir partial pressures and evaporation coefficient of magnesium over magnesium oxide from Run 2.

Temperature (°K)	Intensity (Mv)	Pressure (ATM)	Evaporation coefficient
1895.	0.29	1.67×10^{-6}	2.39
1908.	0.34	2.01×10^{-6}	2.33
1933.	0.29	1.71×10^{-6}	1.33
2007.	0.50	3.11×10^{-6}	0.80
2062.	0.70	4.47×10^{-6}	0.53
2146.	0.86	5.68×10^{-6}	0.22
2056.	0.60	3.82×10^{-6}	0.49
1994.	0.50	3.09×10^{-6}	0.96
2195.	1.58	1.07×10^{-5}	0.23
2133.	1.05	6.94×10^{-6}	0.32
2117.	0.89	5.84×10^{-6}	0.33
2206.	2.24	1.53×10^{-5}	0.29
2140.	1.20	7.96×10^{-6}	0.33
2036.	0.74	4.67×10^{-6}	0.79
1985.	0.49	3.01×10^{-6}	1.07

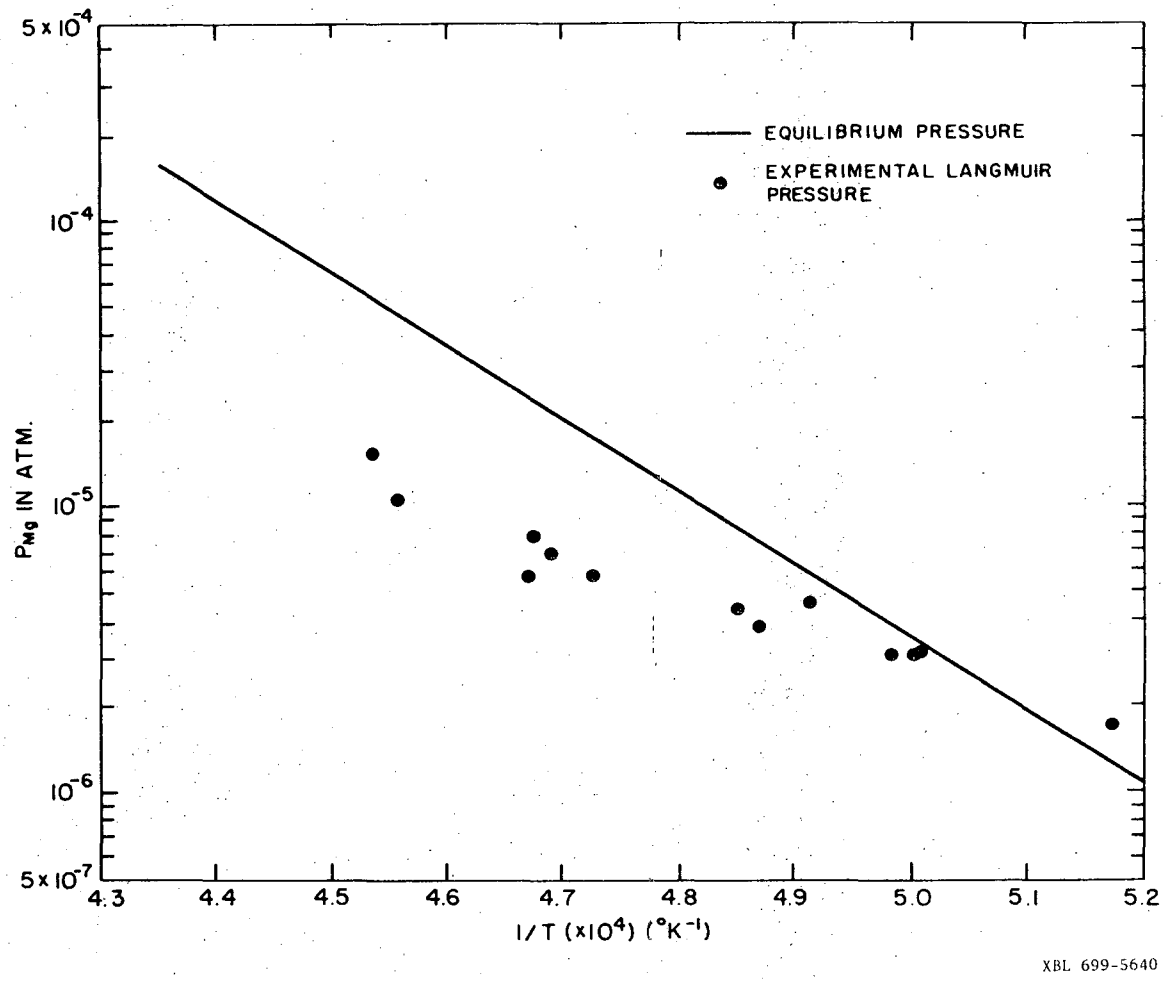

Figure 2. Partial Pressures of Magnesium Over Magnesium Oxide From Run 2.

TABLE III. Langmuir partial pressure and evaporation coefficient of magnesium over magnesium oxide from Run 3

Temperature (°K)	Intensity (Mv)	Pressure (ATM)	Evaporation coefficient
2059.	0.43	2.95×10^{-6}	0.36
2102.	0.89	6.22×10^{-6}	0.43
2180.	1.89	1.37×10^{-5}	0.35
2106.	0.88	6.18×10^{-6}	0.40
2141.	1.00	7.17×10^{-6}	0.30
2149.	1.75	1.25×10^{-5}	0.47
2166.	2.69	1.94×10^{-5}	0.59
2155.	2.06	1.48×10^{-5}	0.52
2134.	1.61	1.15×10^{-5}	0.52
2103.	1.23	8.63×10^{-6}	0.59
2178.	2.05	1.49×10^{-5}	0.39
2186.	3.33	2.43×10^{-5}	0.58
2148.	2.26	1.62×10^{-5}	0.62
2173.	2.94	2.13×10^{-5}	0.59

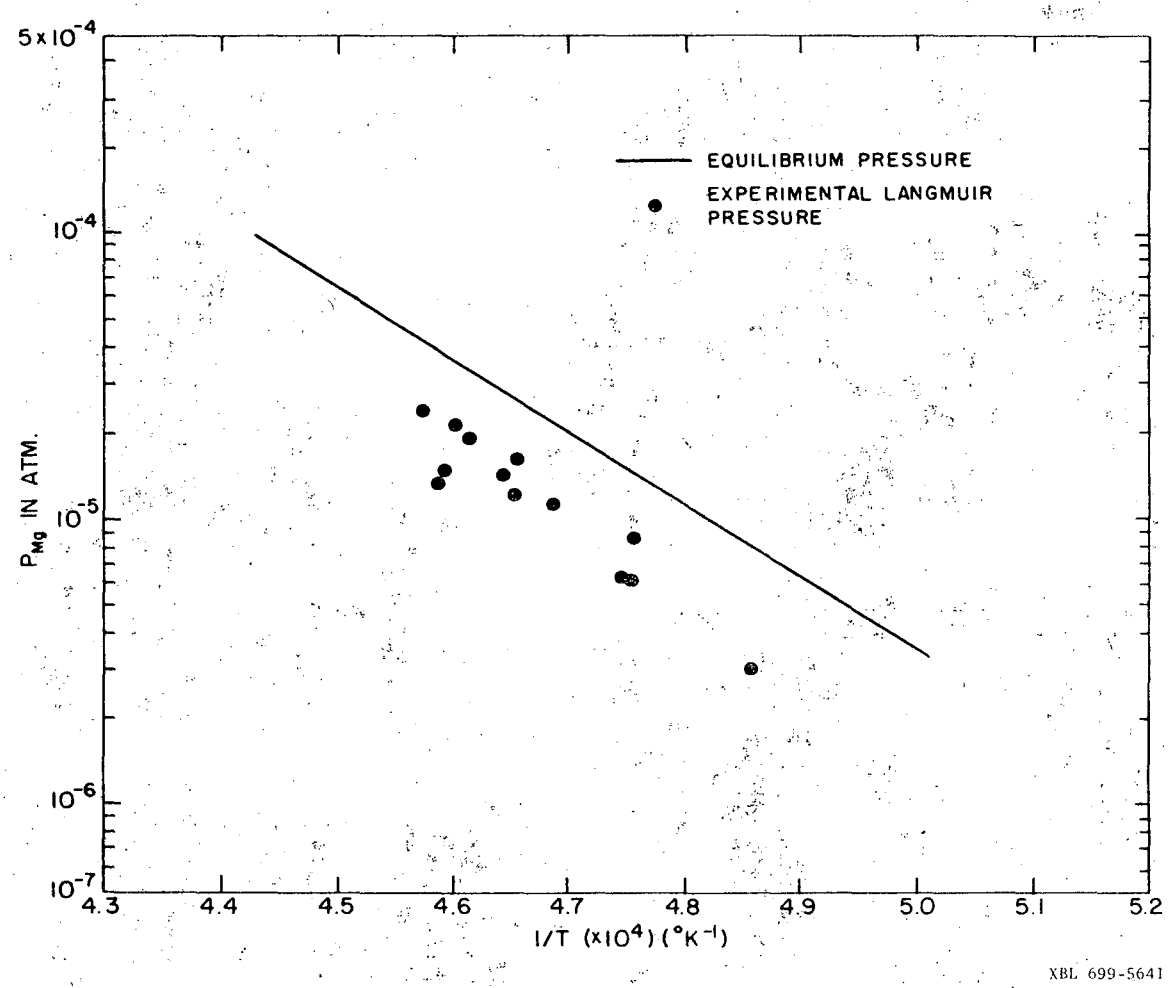

Fig. 3 Partial Pressures of Magnesium Over Magnesium Oxide From Run 3.

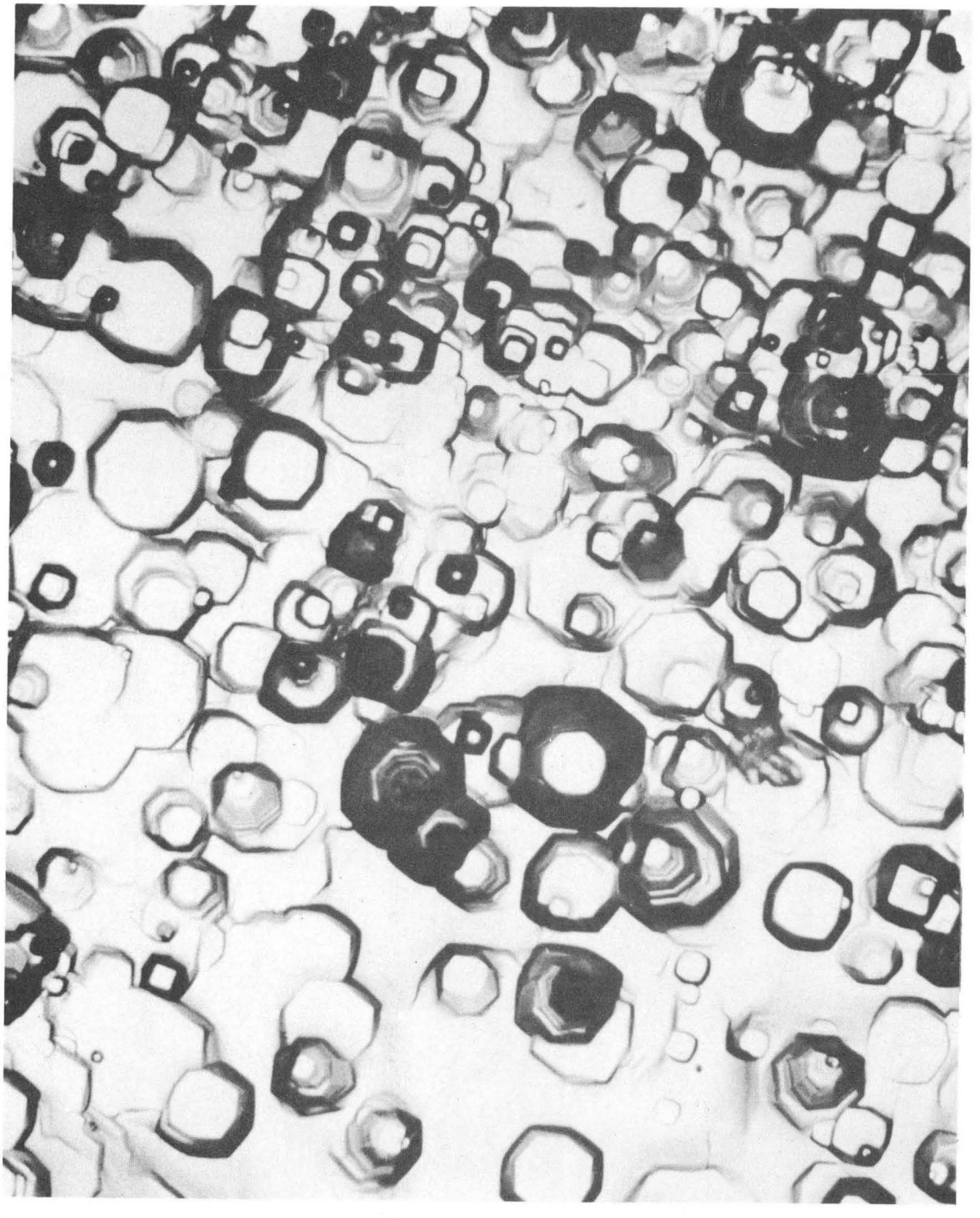

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Fig. 4 Typical Surface of Magnesium Oxide After Run 2 Evaporation (At 63X).

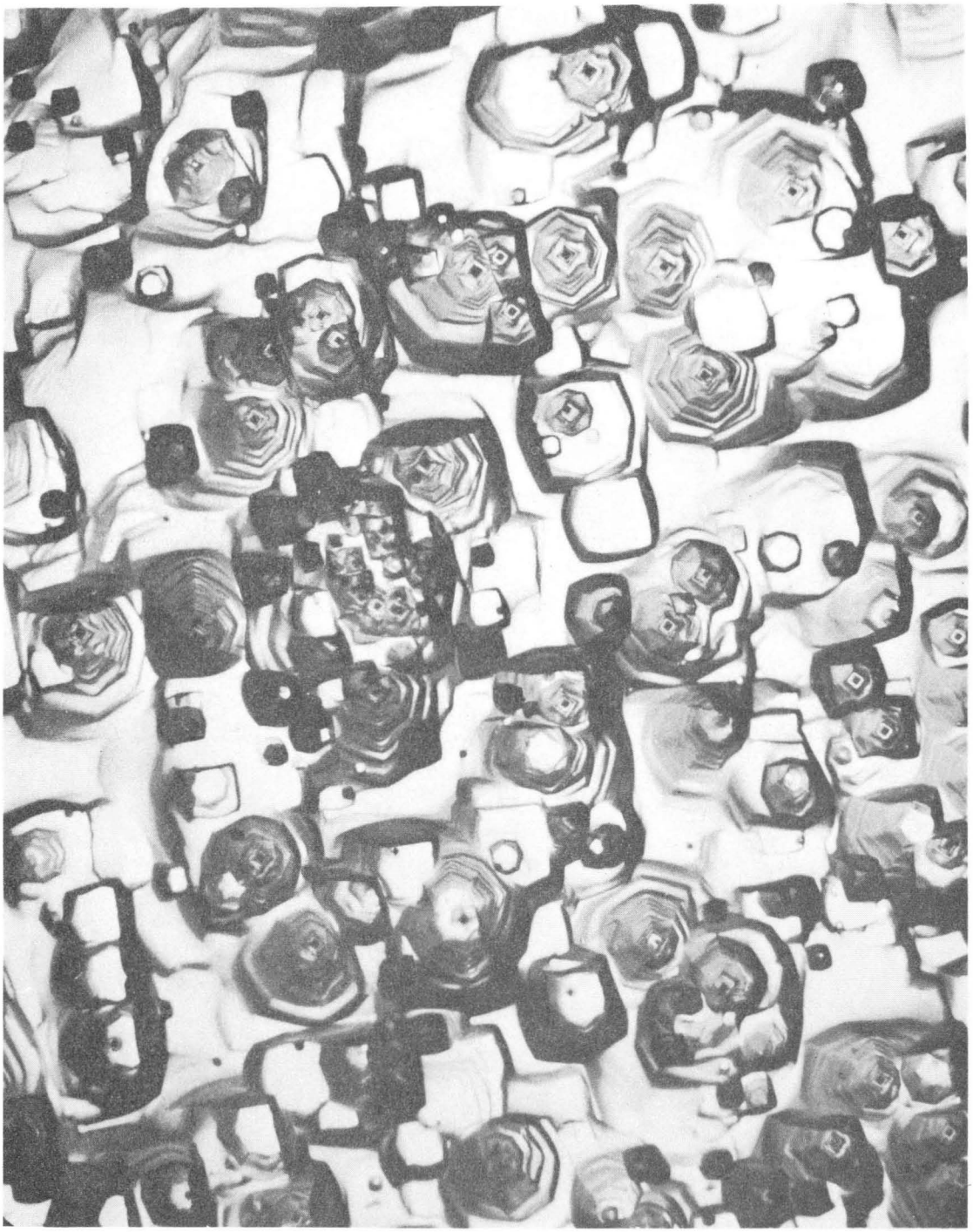

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Fig. 5 Typical Surface of Magnesium Oxide After Run 3 Evaporation (At 63X).

Another crystal was prepared and degassed at approximately 2000°K for two hours before data was collected. In this time, the intensity of mass 24 increased and seemed to level off. Photomicrographs of the surface showed that small square pits had formed. The crystal was placed again into the cell with a silver disk and the evaporation procedure repeated. Table IV and Fig. 6 present the results. A least squares fit of the data yielded the equation

$$\log_{10} P_{ATM} = -(1.056 \pm 0.066) \frac{10^4}{T} - 0.328 \pm 0.017$$

which is in good agreement with Run 2. The average evaporation coefficient was calculated from the data to be 0.50 for the temperature range 1947°-2185°K. The microscopic detail of the evaporated Langmuir surface is depicted in Fig. 7. More than half of the surface had been covered by thermal pits. The outstanding feature of the surface is the square symmetry at the bottom of many of the pits which is rotated 45° with respect to the square walls at the surface. Little indication of octagonal walls is evident. Figure 8 shows the cluster of thermal pits associated with a macroscopic ledge on the surface.

The two following runs were performed under as nearly identical electronic settings of the spectrometer as possible to the previous run. Accordingly, the observed magnesium intensities were compared to the silver intensity of that run.

The fifth run was with a crystal prepared in the same manner as those before. The specimen was heated to 2000°K for one hour before data were collected. Table V and Fig. 9 present the results which followed the equation

$$\log_{10} P_{ATM} = -(1.141 \pm .057) \frac{10^4}{T} - 0.124 \pm .005$$

TABLE IV. Langmuir partial pressure and evaporation coefficient of magnesium over magnesium oxide from Run 4.

Temperature (°K)	Intensity (Mv)	Pressure (ATM)	Evaporation coefficient
1947.	2.57	2.16×10^{-6}	1.36
2063.	3.76	3.36×10^{-6}	.39
1993.	3.14	2.71×10^{-6}	.85
2100.	4.83	4.39×10^{-6}	.31
1907.	1.62	1.34×10^{-6}	1.58
2132.	5.64	5.20×10^{-6}	.24
2105.	5.19	4.73×10^{-6}	.31
2163.	7.44	6.96×10^{-6}	.22
2124.	5.94	5.46×10^{-6}	.28
2185.	7.68	7.26×10^{-6}	.17
2048.	3.15	2.79×10^{-6}	.40
2149.	5.89	5.48×10^{-6}	.21
2014.	2.54	2.21×10^{-6}	.51
2056.	3.38	3.01×10^{-6}	.39
2142.	5.80	5.38×10^{-6}	.22

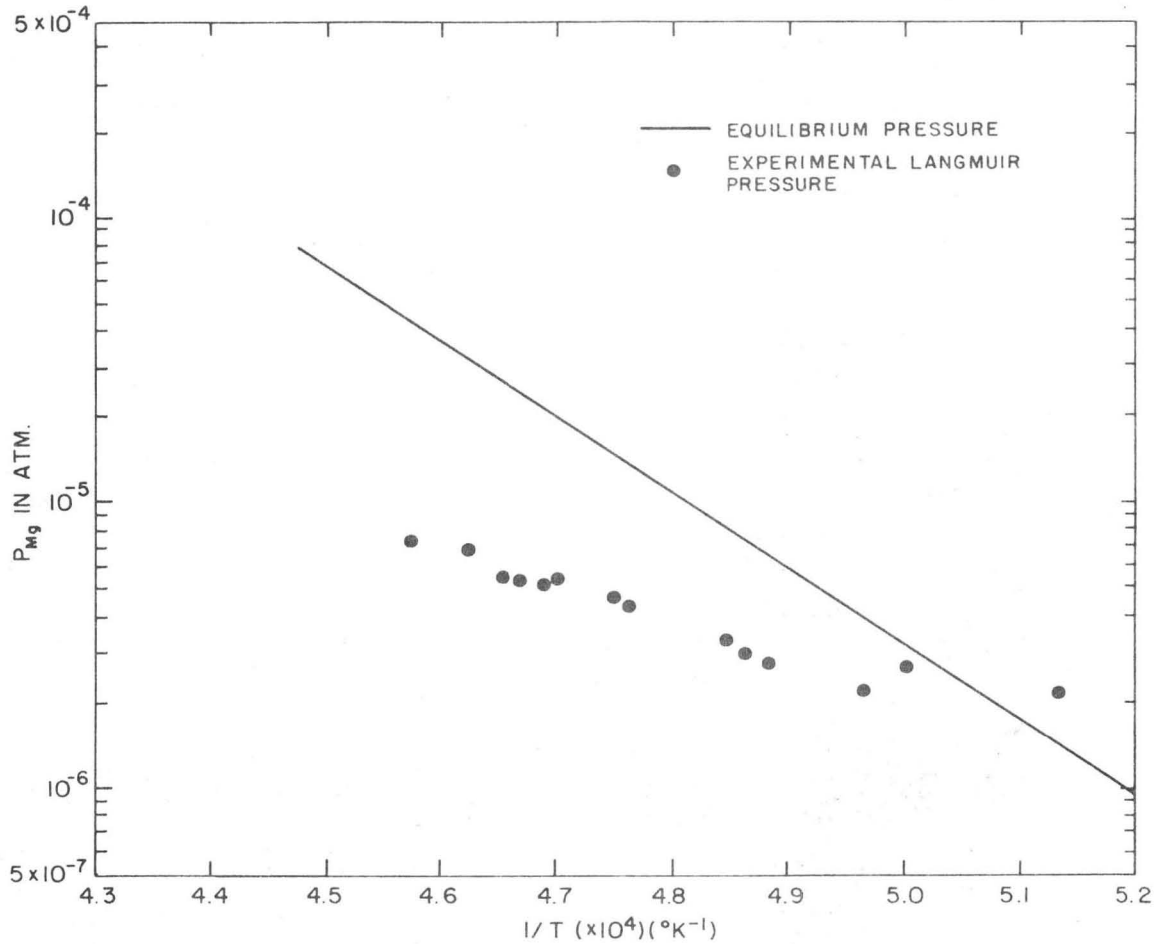

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Fig. 6 Partial Pressures of Magnesium Over Magnesium Oxide From Run 4.

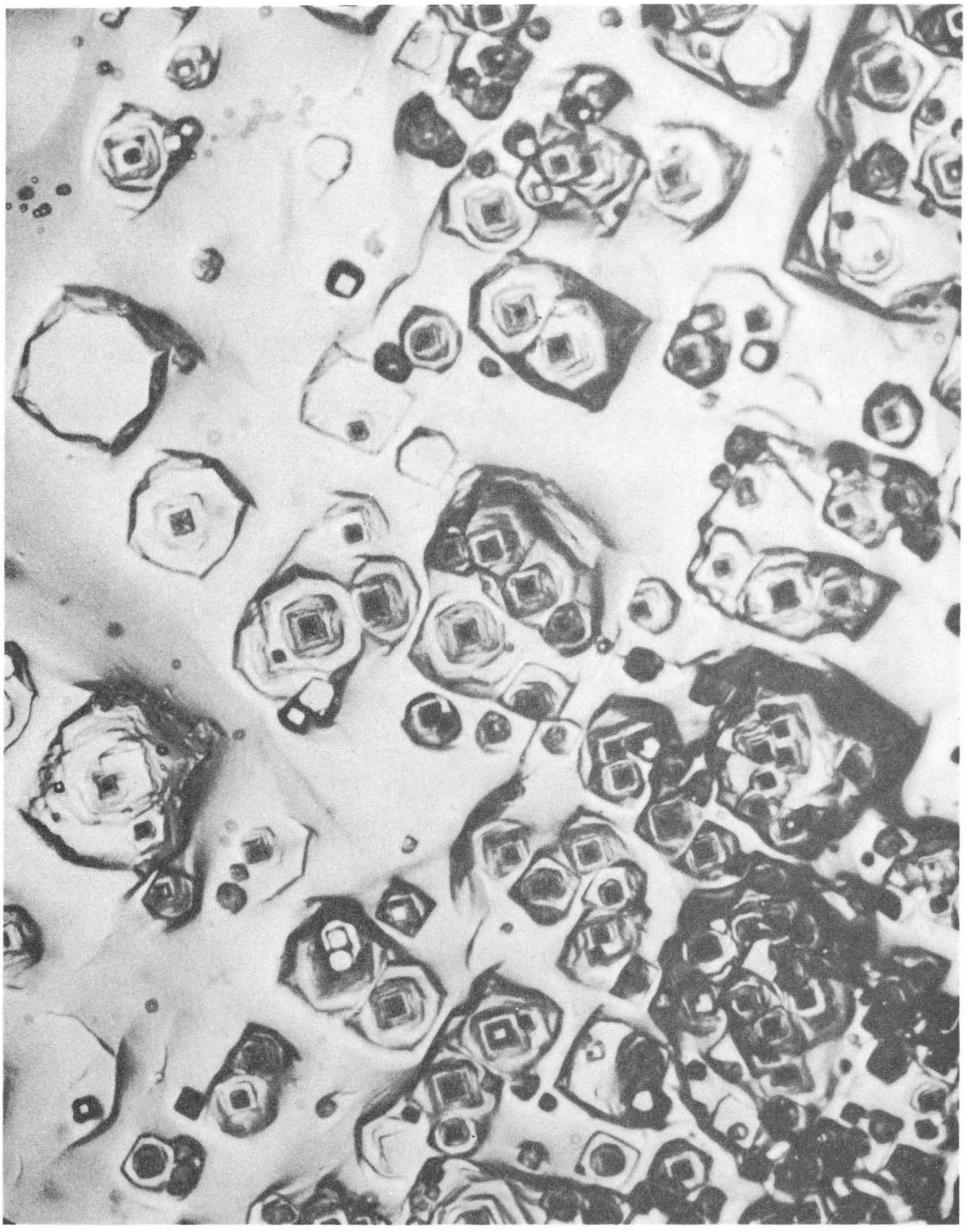

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Fig. 7 Thermal Pits of Magnesium Oxide After Langmuir Evaporation (At 63 X).

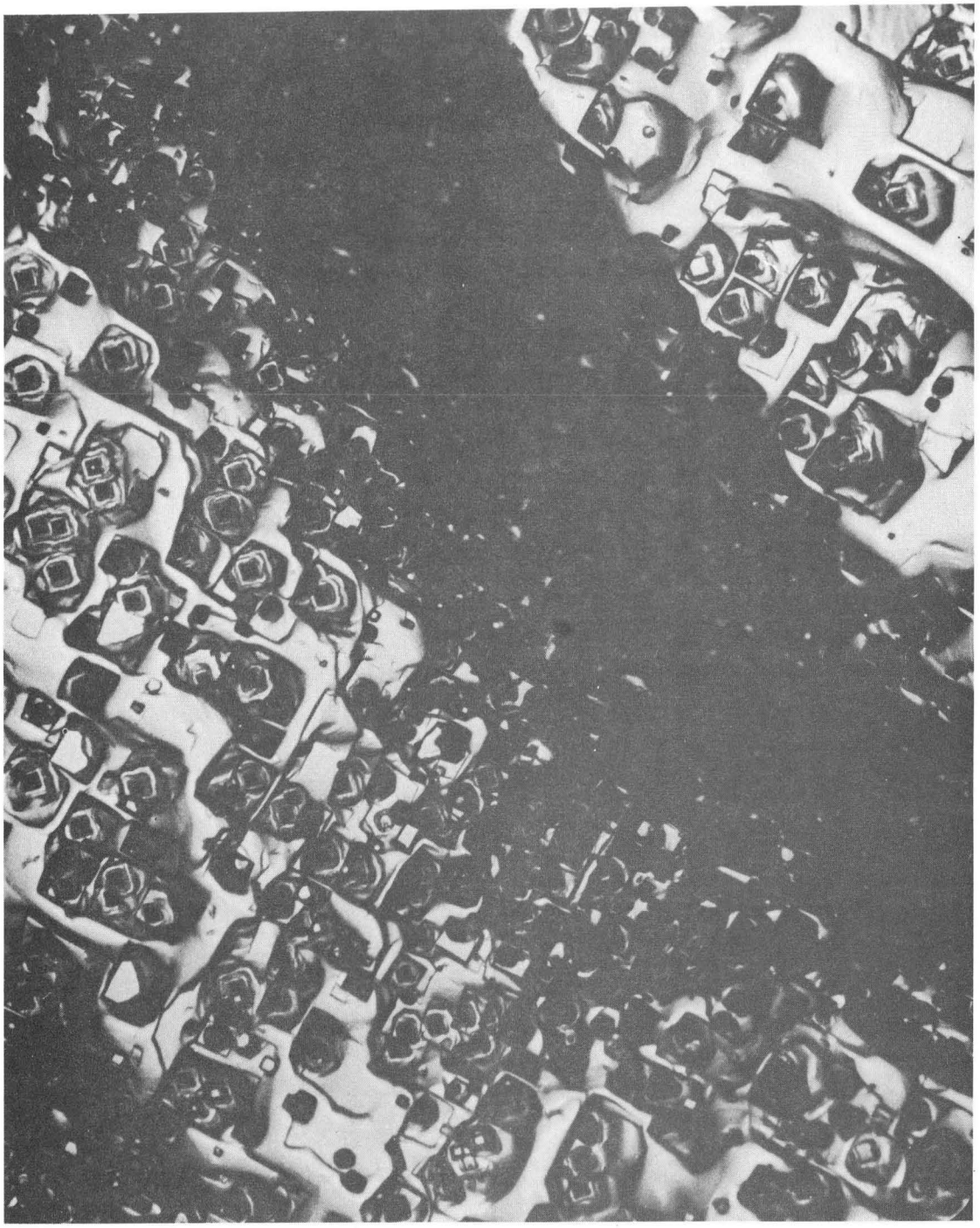

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Fig. 8 Cluster of Pits Associated with Macroscopic Ledge on Surface (At 63 X).

for the Langmuir pressure. The temperature dependence of the pressure was within experimental error in agreement with Runs 2 and 4. The average calculated evaporation coefficient was 0.25 over the temperature range 1982°-2125°K. Figure 10 depicts the typical appearance of the evaporated surface. The photomicrograph is of the surface near the edge of the specimen. The outstanding feature of the surface was the lack of pits. Although the temperature dependence of the Langmuir partial pressure was in excellent agreement with Run 2, the morphology of the evaporated surfaces of Runs 2 and 5 were quite different. Figure 4 shows that the Run 4 surface was covered with pits while Fig. 10 shows that the Run 5 crystal surface had very few observable thermal pits. Note in Fig. 10 at the upper left corner, the apparent rounding of the crystal edge.

Because the morphology of the evaporated crystal surface from Run 2 most closely resembled the surface developed in Run 3, the former crystal was utilized to investigate the effect of further heating on the behavior of the thermal pits and to see if octagonal pits would develop. The crystal had been heated near 2000°K for approximately 3 hours; Fig. 4 shows the appearance of the surface. The specimen was again placed in the spectrometer and evaporated. The results are given in Table VI and in Fig. 11. A least squares fit of the Langmuir data yielded the equation

$$\log_{10} P_{ATM} = -(1.66 \pm 0.08) \frac{10^4}{T} + 2.34 \pm 0.10$$

The average evaporation coefficient was calculated to be 0.17 over the temperature range 2024-2258°K.

TABLE V. Langmuir partial pressure and evaporation coefficient of magnesuim over magnesium oxide from Run 5.

Temperature (°K)	Intensity (Mv)	Pressure (ATM)	Evaporation coefficient
2096.	2.79	2.53×10^{-6}	0.19
2049.	2.14	1.90×10^{-6}	0.27
2146.	4.02	3.73×10^{-6}	0.15
2034.	2.37	2.09×10^{-6}	0.36
2166.	4.50	4.22×10^{-6}	0.13
2083.	2.49	2.44×10^{-6}	0.20
2117.	3.08	2.82×10^{-6}	0.16
2063.	2.50	2.23×10^{-6}	0.26
2192.	5.37	5.09×10^{-6}	0.11
1982.	1.63	1.40×10^{-6}	0.52
2110.	3.02	2.76×10^{-6}	0.17
2027.	1.98	1.74×10^{-6}	0.33
2125.	3.50	3.22×10^{-6}	0.16
1998.	1.67	1.41×10^{-6}	0.42

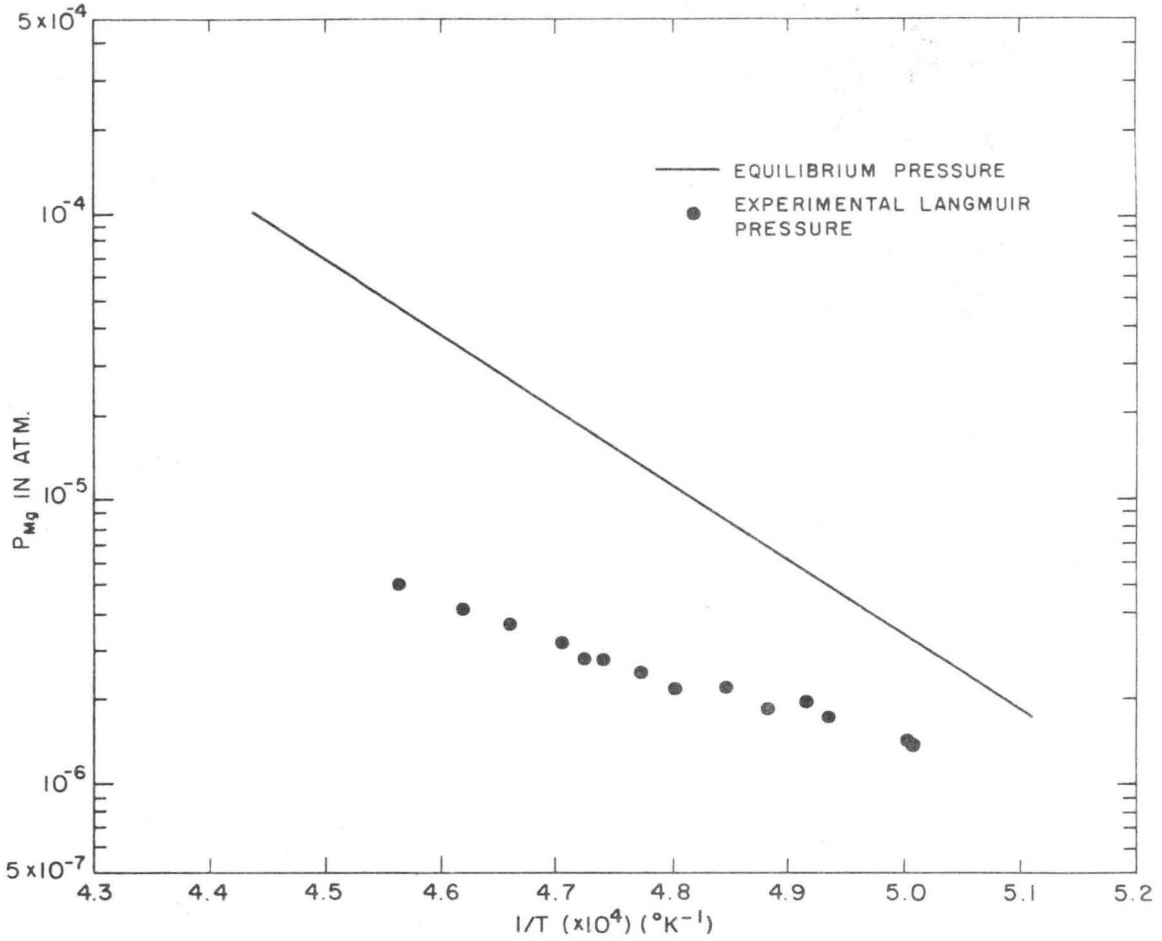

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Fig. 9 Partial Pressures of Magnesium Over Magnesium Oxide From Run 5.

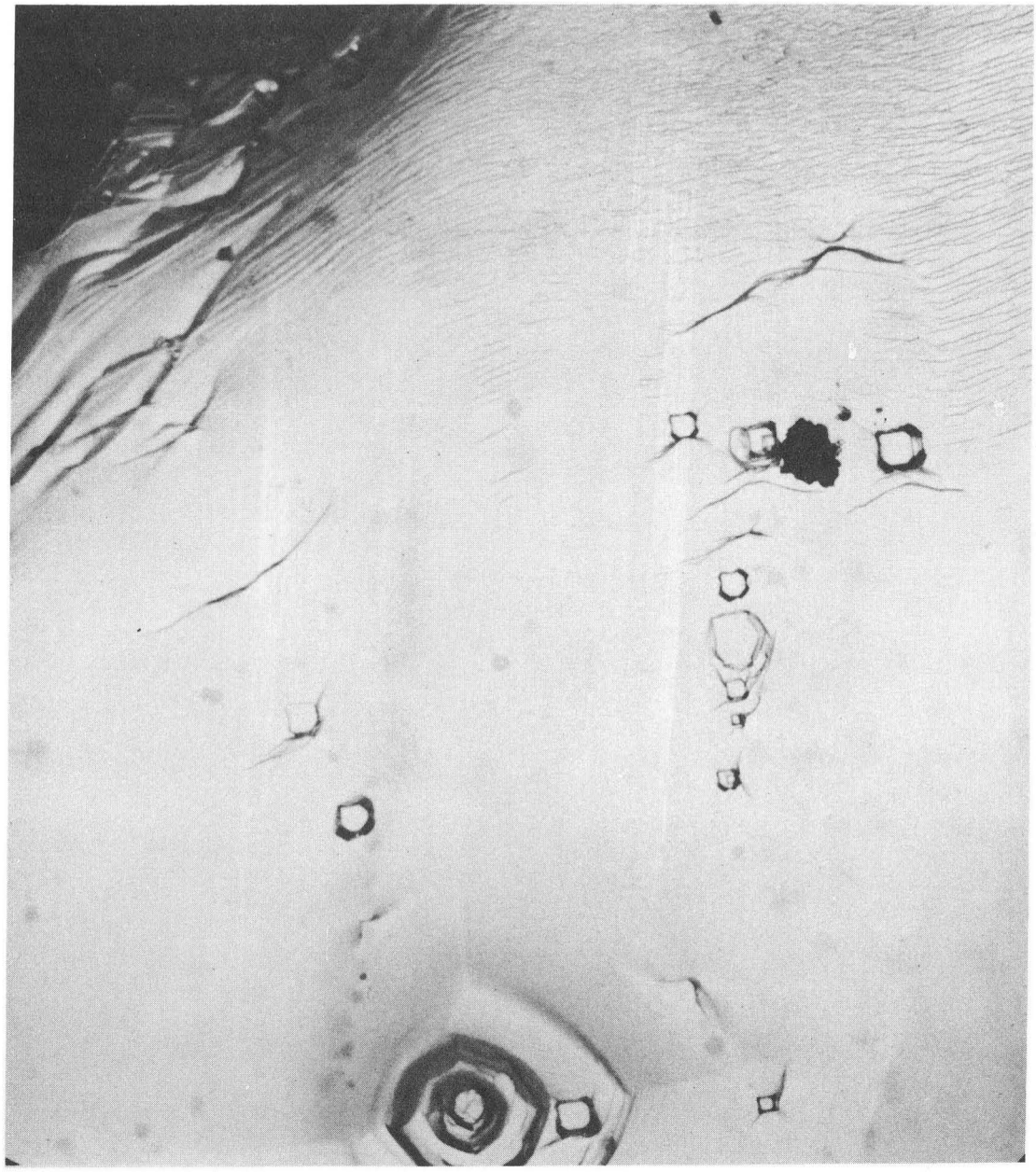

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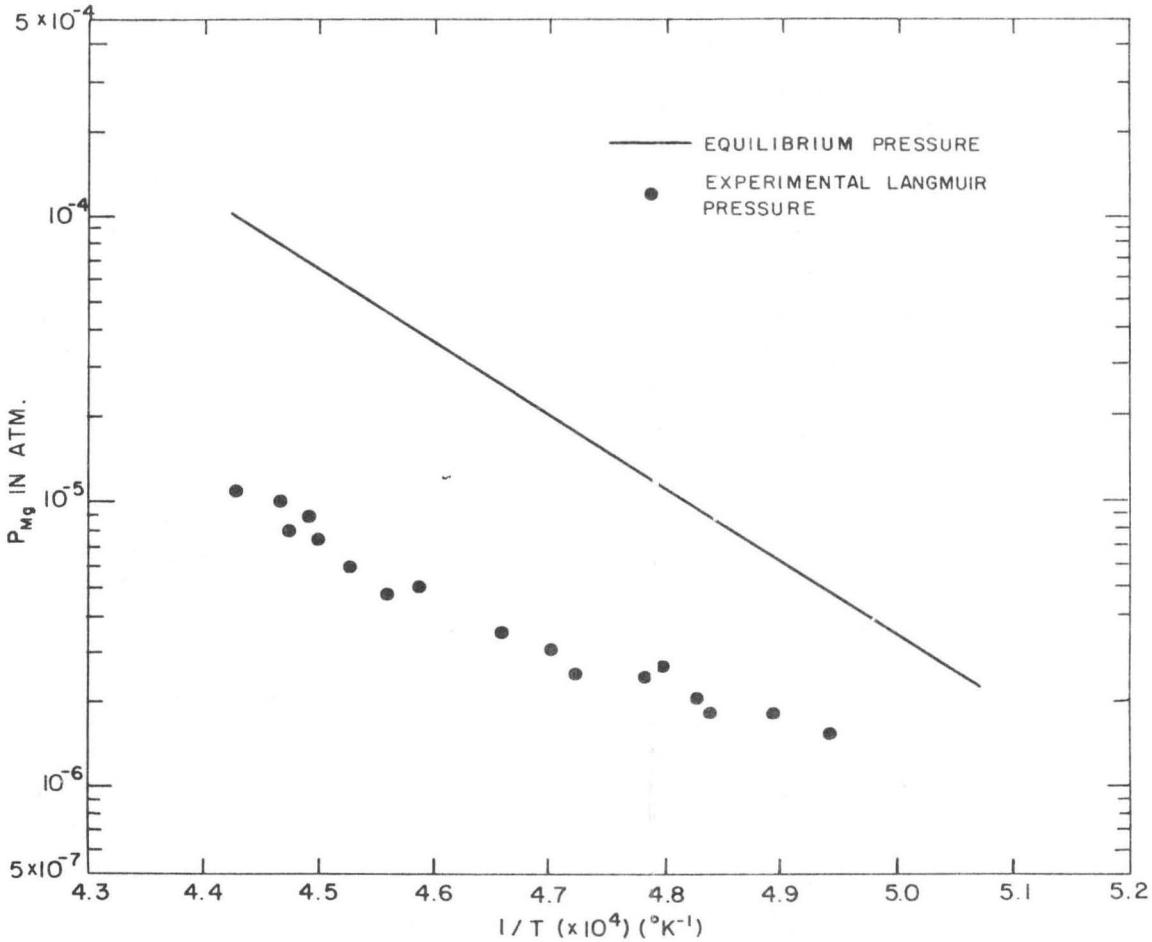
Fig. 10 Magnesium Oxide Surface After Evaporation (63 X).

TABLE VI. Langmuir partial pressure and evaporation coefficient of magnesium over magnesium oxide from Run 6.

Temperature (°K)	Intensity (Mv)	Pressure (ATM)	Evaporation coefficient
2067.	2.09	1.87×10^{-6}	0.21
2194.	5.10	4.84×10^{-6}	0.10
2146.	3.85	3.58×10^{-6}	0.14
2209.	6.29	6.01×10^{-6}	0.11
2118.	2.75	2.52×10^{-6}	0.14
2235.	8.29	8.02×10^{-6}	0.11
2084.	3.00	2.71×10^{-6}	0.24
2239.	10.50	1.03×10^{-5}	0.13
2223.	7.89	7.59×10^{-6}	0.12
2258.	11.31	1.11×10^{-5}	0.11
2092.	2.75	2.49×10^{-6}	0.20
2181.	5.43	5.12×10^{-6}	0.13
2071.	2.43	2.18×10^{-6}	0.23
2227.	9.43	9.09×10^{-6}	0.13
2044.	2.12	1.88×10^{-6}	0.28
2127.	3.47	3.19×10^{-6}	0.16
2024.	1.81	1.59×10^{-6}	0.32



XBL 699-5642

Fig. 11. Partial Pressures of Magnesium Over Magnesium Oxide From Run 6.

Visual inspection of the evaporated surface revealed that a single macroscopic pit covered approximately 1/10 of the surface. The size indicated that it may have acted as an opening for a micro-effusion cell in which the equilibrium flux could possibly have been achieved. Figure 12 shows the typical pit coverage of the surface. Comparison of Fig. 12 with Fig. 4 shows that, in general, the pits grew in size with further heating, but that new pits were not obviously being formed. Some of the pits had converged while part of the surface area had no well-defined depression. No general trend in the geometry of the pits is evident.

XBB 698-5676

.g. 12 Surface of Crystal From Run 2 After Second Evaporation (At 63 X).

V. DISCUSSION

The Langmuir pressure results are summarized graphically in comparison with the equilibrium line in Fig. 13. A least squares calculation yielded the apparent enthalpies and entropies of activation listed in Table VII. These should be compared to the standard equilibrium enthalpy and entropy of sublimation; namely, ΔH_v^o = 115.9 kcal/mole and ΔS_v^o = 32.99 kcal/mole at the average experimental temperature and based on the partial pressure of magnesium only. The silver calibration slopes are different from the value accepted by Hultgren, et al.[17] Consequently, the magnesium partial-pressure slopes have been corrected by the factor necessary to align the silver data with the accepted value. The corrected heats and entropies are also listed in Table VII. Several generalizations can be made on the experiments.

Coloration or reaction products were observed in runs with conventional Langmuir cells using either tantalum or molybdenum lids over the single crystals. Since the intensity of mass 24 was masked by the reduction of the magnesium oxide by the latter materials, the results were not of value in this study and have been omitted. With the use of an iridium liner, no reduction of the magnesium oxide by the liner was observed.

In general, the right cylindrical crystals become rounded at the free surface edges upon vaporization. This suggests that edges of the crystal served as sources for ledges of atoms from which vaporization may occur via stepwise mechanism in accordance with the well-known theory set forth by Volmer.[24] This point is most evident in Fig. 10. Evaporation ledges can also form readily at pit sources; generally

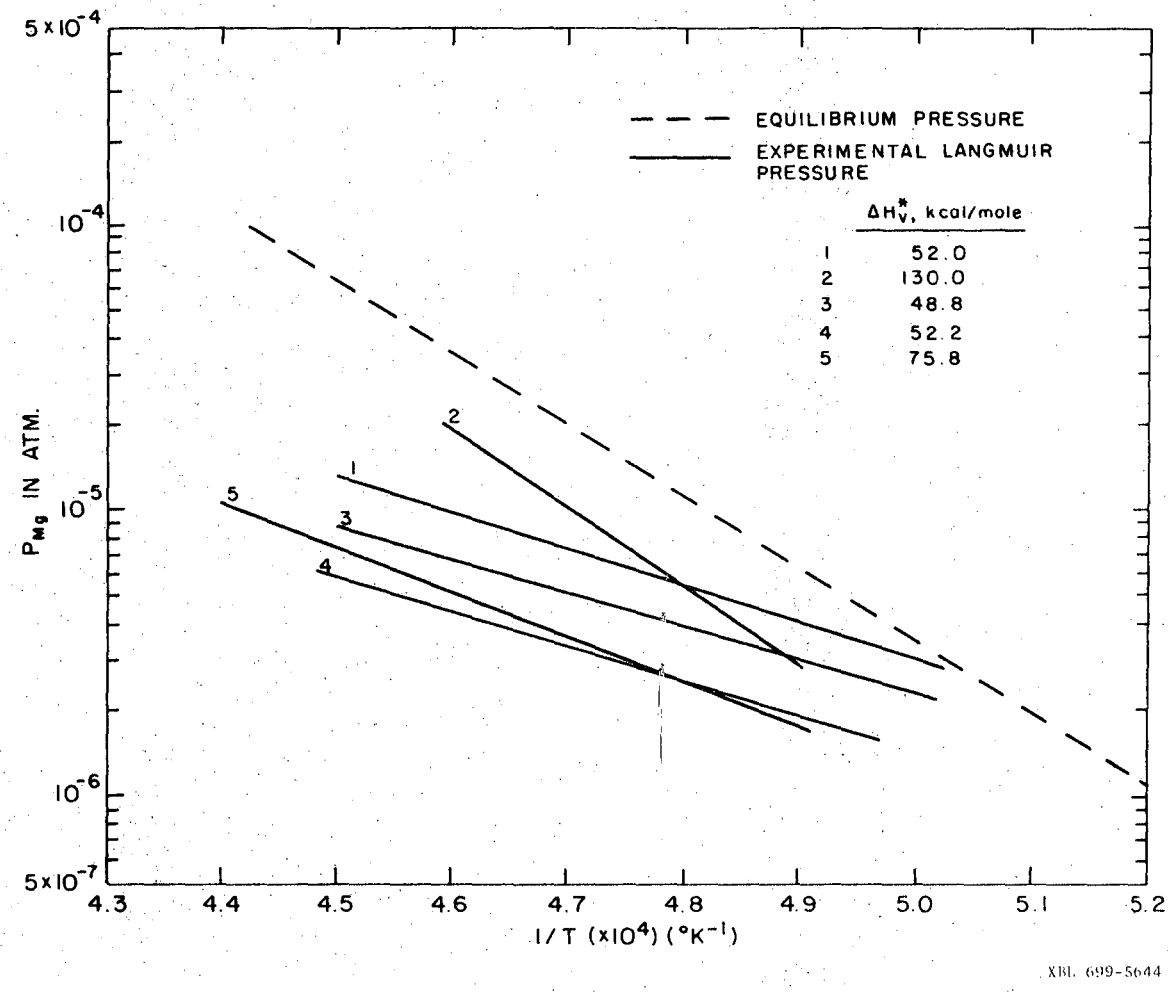


Fig. 13 Partial Pressures of Magnesium Over Magnesium Oxide.

TABLE VII. Apparent enthalpy and entropy of activation for free surface sublimation

Run	Apparent Enthalpy of Activation (Kcal/mole)	Apparent Entropy of Activation (eu)	Average Evaporation Coefficient	Temperature Range (°K)	Corrected Enthalpy of Activation (Kcal/mole)	Corrected Entropy of Activation (eu)
2	52.0 ± 3.6	0.855 ± 0.056	0.83	1895. - 2206.	53.9	1.78
3	130. ± 15.	38.2 ± 4.3	0.48	2059. - 2186.	132.	39.4
4	48. ± 3.0	-1.50 ± .07	0.50	1907. - 2185.	53.3	.906
5	52.2 ± 2.6	-0.57 ± .02	0.25	1998. - 2192.	59.7	2.83
6	75.9 ± 3.9	10.7 ± .5	0.17	2024. - 2258.	82.4	13.6

thermal pits are related to dislocations. However, the sublimation rate of magnesium oxide does not seem to be directly dependent upon the number of pits as is apparent in the comparison of Fig. 4 with Fig. 10.

Microscopic examination of the evaporated surfaces did not reveal a reproducible development of surface morphologies from run to run. Some evaporated surfaces were covered with thermal pits, others were not; some crystals developed octagonal pits while some developed square pits. Probably undetectably small differences in dislocation densities or impurity concentrations are enough to noticably change the relative importance of dislocation endings and edges as sources of atoms in the chemisorbed layer from which vaporization occurs.

The Langmuir pressures of Tables II - VI indicate that single crystal magnesium oxide does have a low evaporation coefficient. The average α of each run ranges from 0.17 to 0.83 with an overall average of 0.46 in the temperature range 1895-2258°K. Because of inherent uncertainties in mass spectrometric measurements, only a lower limit of 0.1 for α can be set in the experimental range.

That single crystal magnesium oxide has a low evaporation coefficient is of considerable interest. Alcock and Peleg's data for polycrystalline magnesium oxide indicated an $\alpha \approx 0.2$.[9] Evidently the only other study of the evaporation coefficient of an alkaline earth oxide is that of polycrystalline beryllium oxide which within experimental error is unity.[25] Also tungsten trioxide,[26] hafnium dioxide,[9] thorium dioxide,[27] and zirconium dioxide are oxides that have reported evaporation coefficients near unity for polycrystalline samples. All of these oxides probably have high concentrations of undissociated molecules

in the vapor[10] whereas magnesium oxide vaporizes by dissociation.

Of the few experimentally determined evaporation coefficients of solid oxides that sublime by dissociation the values of α tend to be less than unity. Zinc oxide ($\alpha \approx 10^{-3}$),[28] stannic oxide ($\alpha \leqslant 0.1$)[29] and silica ($\alpha \approx 0.03$)[25] are examples of this class.

The measured evaporation coefficient of less than unity indicates that there is an enthalpy barrier and/or entropy constraint limiting the rate of free surface sublimation of single crystal magnesium oxide. The spread in the experimental values of the apparent activation quantities, however, prohibits a conclusive analysis of the mechanistic implications of the low evaporation rate. In all but one of the runs, the apparent activation enthalpy was less than the standard equilibrium enthalpy for sublimation implying that the desorption of the magnesium and oxygen atoms from the surface is not the rate limiting step.

Although only the partial pressure of magnesium was measured, the rate limiting step may involve an oxygen atom or molecule since the sublimation of magnesium oxide is congruent.

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APPENDIX

LANGMUIR PRESSURES FOR SILVER

Run	Temperature (°K)	Intensity (Millivolts)	Pressure (ATM)
2	1241.	.00324	4.094×10^{-6}
	1231.	.00223	2.795×10^{-6}
	1193.	.00100	1.125×10^{-6}
	1214.	.00186	2.299×10^{-6}
	1201.	.00164	2.005×10^{-6}
	1220.	.00199	2.472×10^{-6}
			ΔH°_{v}=62,300 kcal/mole
3	1246.	.00332	4.533×10^{-6}
	1226.	.00184	2.472×10^{-6}
	1201.	.00136	1.790×10^{-6}
	1239.	.00279	3.788×10^{-6}
	1219.	.00160	2.137×10^{-6}
	1225.	.00234	3.141×10^{-6}
	1234.	.00286	3.868×10^{-6}
	1244.	.00307	4.185×10^{-6}
			ΔH°_{v}=64,980 kcal/mole
4	1144.	.00253	4.116×10^{-7}
	1159.	.00365	6.016×10^{-7}
	1204.	.00990	1.695×10^{-6}
	1209.	.01044	1.795×10^{-6}
	1193.	.00759	1.288×10^{-6}
	1133.	.00221	3.561×10^{-7}
			ΔH°_{v}=60,450 kcal/mole

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