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THE VAPOR PRESSURE OF MAGNESIUM BETWEEN 223° AND 385°C

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Several investigators have determined the vapor pressure of solid magnesium with fair consistency.(1-3) The Knudsen effusion method and the particular experimental design they used limited the range of useful data obtained to 353° to 500°C, corresponding to the vapor pressure range from 4×10^{-4} to 1×10^{-2} torr. The purpose of this communication is to show that techniques utilizing Langmuir's method(4) of evaporation from a free surface yield reliable data down to 223°C (or 2×10^{-7} torr).

Basically, the experimental procedure consisted in monitoring the rate of weight change, as a function of sample temperature, of a magnesium specimen suspended in a high vacuum by an Ainsworth semimicro vacuum recording balance. The heat source was a collimated light beam from an exterior lamp.

The 1-inch-square magnesium samples were cut from 1/16-inch-thick sheet stock which had a typical spectroscopic impurity analysis (furnished by the supplier) as follows (in percent): Al < 0.005; Ca < 0.01; Cu < 0.001; Fe < 0.0003; Mn < 0.001; Ni 0.0004; Pb < 0.003; Si < 0.001; Sn < 0.01; Zn 0.006. After degreasing and rough finishing, the samples were annealed under argon for 8 hours at 450°C, then finished with No. 000 emery paper and dipped in 6-molar hydrochloric acid for a few seconds. This treatment produced a bright, slightly etched surface.

The prepared sample was suspended approximately 2 feet below the balance pan by a 0.010-inch tungsten wire with its face normal to the light beam (Fig. 1). The automatic recording balance (which could handle a total weight change of 400 mg), with the recording system used, provided reliable data for rates as low as 1 μg per minute. The sample heater was a 1600 watt mercury-xenon lamp with a parabolic reflector and aspheric collimating lens. The beam, and thus the heat input to the sample, could be regulated closely by changing the distance from the lamp to the sample, the power to the lamp, or the focus. The collimating system produced a uniform beam over a 3-inch diameter, as measured with an Eppley thermopile; the beam could generate sample temperatures in excess of 500°C in the vacuum chamber. The chamber, atop a 4-inch oil diffusion pump, consisted of a 4-inch I.D. stainless steel cross with a 4-inch-diameter pyrex port on one horizontal leg. Cryogenic cooling coils (for liquid N_2) wrapped around the cross minimized back reflection of magnesium vapors to the sample. The pyrex window was cleaned only when magnesium condensation seriously affected sample heating, since a clean window was a poor nucleating surface and could cause significant reflection of magnesium back to the sample. The vacuum during a run was maintained at 2×10^{-7} torr or lower. The temperature was monitored with a calibrated iron-constantan thermocouple made of 0.001-inch enameled iron and 0.0008-inch constantan wires, spot-welded to the sample. An insignificant error in weighing was introduced by this wire. The temperature uniformity over the specimens was within 1°C as found by using the apparatus described above but with thermocouples fixed to the front, back, and interior of a calibrating sample. A run also was performed in an 18-inch-diameter vacuum chamber, with room temperature walls, utilizing an ion-gettering pumping system, and the temperature and weight monitoring systems described above, which verified that oil contamination was not influencing the results.

Before an experiment, the system was evacuated to less than 2×10^{-7} torr and the cold walls were charged with liquid N_2. Then the magnesium sample was heated to about 430°C, which served to remove surface impurities hindering sublimation. After clean-up, the samples were tested at various temperatures between 223° and 385°C for periods sufficient to establish mass loss rates.

Sublimation rates were converted to vapor pressures by the Langmuir equation,

$$P = \frac{w}{\alpha}\left(\frac{2\pi RT}{M}\right)^{1/2}$$

where

M	molecular weight, 24.312 g/mole, assuming a monatomic vapor
P	vapor pressure, dynes/cm^2
R	gas constant, 8.31×10^7 dynes cm/mole °K
w	mass loss, g/cm^2-sec
α	sublimation coefficient, equal to 1 for a perfectly clean, pure, smooth surface; assumed to equal 1 for the present experimental conditions

The experimental results for the vapor pressure of magnesium are presented in Fig. 2, along with data from earlier investigations.(1-3) The lines on the plot represent the extent of and the best fit for these earlier data. The present data represent results obtained from four specimens in the manner described above, with sample 4 being run in the ion-pumped vacuum chamber.

The final treatment of the data is shown in Table 1. A least-squares analysis of the data produced values for b and m, coefficients of the vapor pressure equation, log $P_{torr} = b + (m/T)$. The values of b and m which best fit the data between 496° and 658°K were +8.6047 and -7560.3, respectively.

The enthalpy change for the reaction Mg (solid) → Mg (gas) at 298.15°K, ΔH_s^o (298.15), was calculated for each experimental point by the 3rd law method.(5) Values for the free energy functions were taken from the recent compilation by McBride et al.(6) The resultant value for ΔH_s^o (298.15), 35.3 ± 0.4 Kcal/mole, corresponds closely to (all in Kcal/mole) 35.3,(1) 34.5,(2) 34.99 + 0.7,(3) derived from data obtained at higher temperatures by other workers using variants of the Knudsen effusion method.

Several experiments (not shown) yielded unexpectedly low rates of sublimation. In all these cases visual examination of the surface showed marked roughening, indicative of uneven sublimation. The cause of this unevenness was not definitely determined, but it is assumed to have been due to imperfect cleaning of the test surface, with perhaps some residual layer of oxide occurring in the areas which did not vaporize. Upon examination of one specimen, which gave such low results, loss was found to have occurred only from the edges and places of attachment of the thermocouple and support. No attempt was made to estimate effective surface area for these samples and, as stated, the test results were rejected. The geometrical area was always taken as the true area and no correction made for any surface roughening which may have occurred due to sublimation. As shown in Fig. 2, each individual run has good internal consistency; the slight variance between runs was probably due, primarily to the fact that the assumed area differed slightly from the true surface area. All runs, including those rejected, produced nearly identical slopes (activation energies) on plots like Fig. 2, which indicate that a constant fraction of the surface was causing nearly all the weight loss.

It was necessary to evaporate several mg/cm^2 from the magnesium sample before reasonably true sublimation rates were obtained. Since the initial oxide film has an areal density of less than 1 $\mu g/cm^2$,(7) it seems reasonable that the relatively large mass of magnesium leaving the surface could carry away the oxide or cause it to break into fine particles and fall away. Although the results obtained in the ion-pumped chamber (sample 4) did not differ from the other runs performed in the oil diffusion-pumped system, it was noted that in the former less initial evaporation was required before satisfactory sublimation rates were found. This is probably due to a somewhat lower working pressure and a difference in gaseous species present.

A study by Addiss into the oxidation of single crystals of magnesium at low pressures indicates the role of oxide in hindering the sublimation of magnesium.(7) He was able to measure net weight gains, due to oxidation, at temperatures where mass loss from sublimation should have occurred. His work at 400° and 440°C was probably just below the point at which magnesium oxide may be displaced by the subliming magnesium. Oxidation rates of evaporated films given by him at oxygen pressures of 2×10^{-7} torr indicate that interference with sublimation rates would possibly occur at our lower temperatures. Although the partial pressure of oxygen in our system was about one-tenth the measured total pressure, zero or positive weight changes were sometimes noted below

250°C. An induction period of several minutes noted by Addiss for the oxidation of magnesium at 10^{-6} to 10^{-7} torr of oxygen coupled with our lower oxygen partial pressures most likely accounts for the fact that good results were obtained by us at these lower temperatures in several runs.

The Langmuir method is capable of sensitivity several magnitudes greater than Knudsen's effusion method. However, since certain factors affecting the sublimation coefficient, α, are usually more troublesome in Langmuir's method than Knudsen's, the latter method is generally employed with its sensitivity being extended through use of radio tracers. In the present case no suitable isotope exists; thus, for magnesium, Langmuir's method is probably the best available for determining low vapor pressures. As shown above, our results agree well with those predicted from results using Knudsen's methods at higher temperatures.

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Table 1.- Coefficients of the vapor pressure equation and heat of sublimation of magnesium

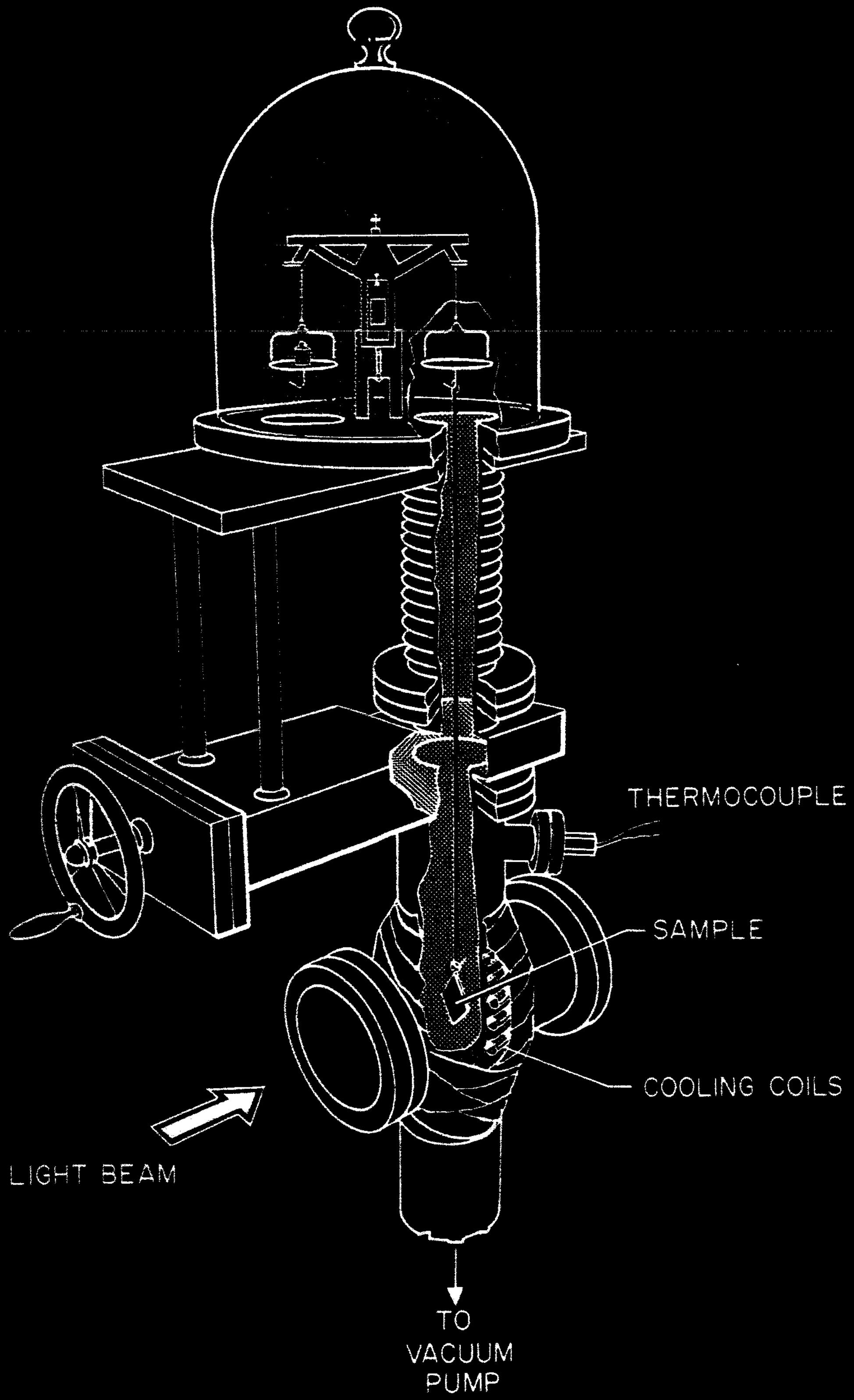
Sample	Temperature range (^{o}K)	b	m	ΔH_s^o (298.15)* (Kcal/mole)
1	529 - 635	8.4514	-7403.8	35.05 ± 0.17
2	502 - 658	8.6322	-7660.4	35.73 ± 0.13
3	496 - 623	9.3774	-7906.1	34.95 ± 0.50
4	504 - 576	7.9579	-7271.0	35.61 ± 0.10
mean		8.6047	-7560.3	35.33 ± 0.4

*Determined by the 3rd law method.(5)

FIGURE TITLES

Fig. 1.- Schematic drawing of vacuum balance and test chamber.

Fig. 2.- Vapor·pressure of magnesium vs. reciprocal of absolute temperature.



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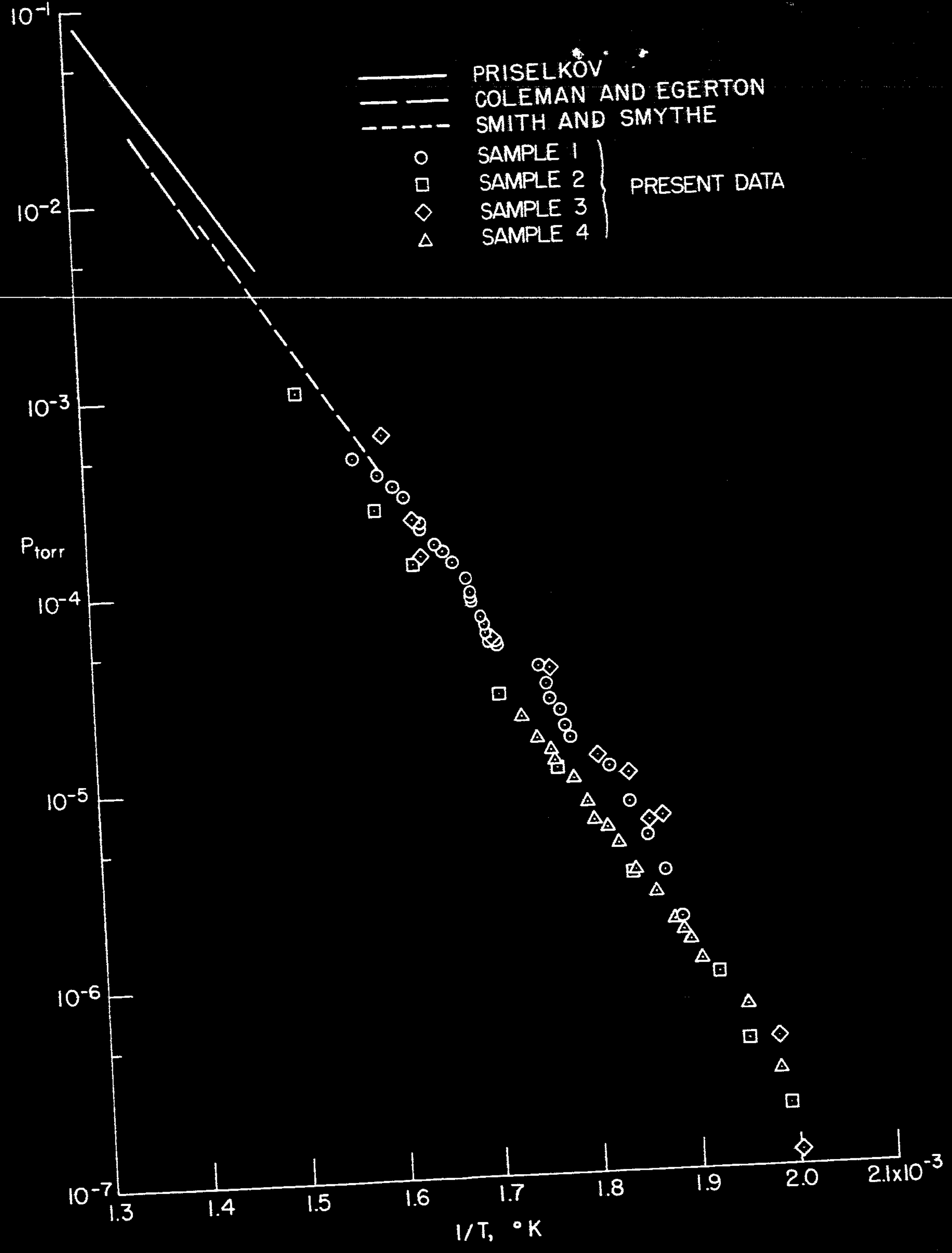

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