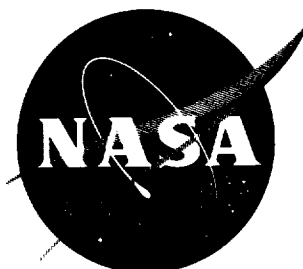


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TECHNICAL NOTE

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INITIAL WEIGHT LOSS OF PLASTICS IN A VACUUM

AT TEMPERATURES FROM 80° TO 500° F

By Hermilo R. Gloria, W. James Stewart,
and Raymond C. Savin

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SUMMARY

Results of tests to determine weight loss rates of plastic materials in a vacuum are presented. The test samples were 2 inches in diameter and varied in thickness from 0.050 to 0.250 inch. The samples were tested at pressures in the range of 3×10^{-7} to 3×10^{-6} mm Hg, at temperatures varying from 80° to 500° F, and for time periods up to 48 hours. Materials tested include polytetrafluoroethylene, polycarbonate, epoxy, and two composite materials, phenolic-nylon and phenolic-silica. Cadmium was also tested to verify the experimental methods employed.

Data obtained for polytetrafluoroethylene are compared to existing experimental data determined from pyrolysis experiments at temperatures above 700° F. The present test data indicate that rates of weight loss are many orders of magnitude higher than would be predicted by an extrapolation of reaction rate constants determined from the higher temperature data. Even so, polytetrafluoroethylene has the lowest rates of weight loss of all the test materials. At 300° F, the rate is about 1.6×10^{-5} lb/ft²-hr. The composite materials have the highest rates which amount to about 1.6×10^{-3} lb/ft²-hr at 300° F. These rates apply to 0.188-inch-thick test samples. The effect of sample thickness on weight loss rate is found to be negligible for polytetrafluoroethylene over the range of thicknesses tested. However, the remaining plastic materials exhibit an order of magnitude increase in rate of weight loss when the sample thickness is decreased from 0.250 to 0.05 inch.

INTRODUCTION

Spacecraft will be subjected to a variety of environmental conditions which can impose limitations on the usability of many materials (see, e.g., refs. 1 and 2). One area of concern is that associated with loss of material by evaporation, or sublimation, due to the high vacuum of space. For elements and some inorganic materials, evaporation rates can be determined by the use of kinetic theory and the usually well-defined vapor pressure data for each material (ref. 3). As noted in reference 4, however, the evaporation of organic materials cannot be

easily determined in this manner. Therefore, actual measurements of evaporation rates in a vacuum are currently necessary for each material of interest.

Numerous experimental studies have been conducted to determine the evaporation rates of organic materials in a vacuum environment. These experiments have been conducted, for the most part, at high temperatures so that a large part of the test sample was volatilized in a relatively short time. For example, in references 5 and 6, experiments were conducted on polytetrafluoroethylene at temperatures greater than about 700° F. These temperatures are considerably higher than the surface temperatures of space vehicles in near-earth orbits. The latter temperatures can range up to about 250° F (ref. 1). Relatively few experiments have been conducted on organic materials at temperatures of engineering interest for spacecraft (refs. 1, 2, 7, and 8). For this reason, much of the low temperature data reported in the literature is based on values extrapolated from results of pyrolysis experiments at high temperatures (see, e.g., ref. 9). The validity of these extrapolations has not been clearly established so that more experimental data at the lower temperatures of practical engineering interest are needed.

The purpose of this paper is to present initial rates of weight loss obtained from vacuum experiments at temperatures up to 500° F for some plastic materials currently of interest for application to space flight. Some considerations on the validity of extrapolating high-temperature data for polytetrafluoroethylene to lower temperatures are also included.

EXPERIMENTAL TECHNIQUES

Test Apparatus

All experiments were conducted in a laboratory-type, high-vacuum, bell-jar system. A photograph of the vacuum system and associated test equipment is shown in figure 1. The glass bell jar, 18 inches in diameter by 30 inches high, was evacuated with an oil vapor diffusion pump backed up with a mechanical vacuum pump. The pump was baffled by water and liquid-nitrogen traps to prevent backstreaming of oil vapor into the test area. Pressure levels in the bell jar were measured by a hot-filament gage mounted in the bell-jar base plate.

The test equipment contained within the bell jar is shown schematically in figure 2. The test sample was suspended from one leg of a semimicroanalytical balance as shown in figure 2(a). The balance was magnetically damped and was equipped with a visual read-out which provided a continuous indication of test sample weight over a range of 200 milligrams. The test samples were heated by infrared radiation from a resistance heating element located below the test sample as shown in detail in figure 2(b). The test sample temperatures were determined by means of a dummy sample instrumented with thermocouples and located as

shown in this figure. In addition, a movable thermocouple probe was used to monitor surface temperatures. The power to the heater was automatically controlled to maintain the sample temperatures at various predetermined levels. As also indicated in figure 2(a), the region of the test sample was enclosed by a cold wall which was cooled by liquid nitrogen. The liquid-nitrogen flow was also controlled automatically for the duration of the test. The various shields shown in figures 2(a) and 2(b) were employed to minimize the heat load to the cold wall and to minimize the changes in temperature of the balance.

Materials and Test Specimens

Five organic materials and one element were used in the present investigation. They are listed in the following table with their respective densities:

Material	Density, lb/ft ³
Polytetrafluoroethylene (Teflon)	137
Polycarbonate (Lexan)	75
Nylon-phenolic composite (50-percent nylon)	74
Silica-phenolic (70-percent silica; Astrolite 1201P)	102
Epoxy, casting type (Epon 821)	88
Cadmium, 99.95-percent pure plating type	540

Teflon and Lexan are relatively pure thermoplastic materials. Nylon-phenolic and silica-phenolic are typical of high-temperature composite materials of current interest in heat-shield applications for spacecraft. Epoxy is a relatively pure thermoset material. The materials were obtained from commercial suppliers.

Disks 2 inches in diameter and of thickness varying from 0.050 inch up to 0.25 inch were machined from these materials. The samples were cleaned with a solution of 5-percent tin-chloride and sodium-hydroxide, rinsed with distilled water, and stored in a dessicating box at room temperature. After drying, the organic samples were weighed, placed in a silver plating bath, and given a flash coating of silver to make them electrically conductive. All samples, including the cadmium, were then given a 1-mil thick coating of copper followed by a 2- to 3-mil thick plating of nickel on all surfaces. After plating, the samples were stored in a dessicating box at 150° F.

The dummy samples used for temperature instrumentation had an annular shape with an outer diameter of 3 inches and an inner diameter of 2.50 inches. Each dummy sample was 0.188 inch thick and was plated in the same manner as the test samples.

Test Procedure

For the tests the plating was removed from one surface of the test sample and dummy sample. Each sample was installed in such a manner that the single vaporizing surface would not "see" the heater (see fig. 2(b)). No attempt was made to degas the samples prior to the measurements of the actual weight losses.

Tests were run at constant temperatures at pressure levels ranging from 3×10^{-7} to 3×10^{-6} mm Hg for periods up to 48 hours, or for a total sample weight change of 200 milligrams, whichever occurred first. Sample temperatures ranged from 80° F to a maximum of 500° F. Maximum temperature differences through the dummy samples ranged from 10° F for the cadmium and composite samples (at 300° F) to 25° F for the Teflon sample (at 500° F). Equilibrium cold-wall temperatures ranged from -250° to -290° F. Balance temperatures ranged from 80° to 90° F.

Weight changes during each test were recorded by a 16-mm movie camera using time-lapse techniques. Strip-chart recordings of dummy sample temperatures, cold-wall temperatures, balance temperatures, and bell-jar pressures were obtained simultaneously with the photographic records. A new test sample was used for each test and the sample was not removed from the test chamber until the test was concluded. A single dummy sample of each material was used throughout the tests.

Accuracy of Measurements

Since the ionization gage used for pressure measurements was calibrated for nitrogen only, the species evaporating from the test samples could affect the pressure readings. However, test runs were made with and without test samples in the vacuum chamber, and the pressure levels remained essentially the same in both cases.

The surface temperature of each dummy sample was controlled to within $\pm 5^{\circ}$ F of each prescribed test temperature. The surface temperature of the test sample, as monitored, indicated temperatures that were within the deviation quoted for the dummy sample.

The balance was capable of directly indicating changes in weight up to 200 milligrams with resolution to ± 0.1 milligram. The 16-mm film records of the weight changes could be read to ± 0.2 milligram. Random vibration of the bell-jar system induced deviations in the balance

readings up to 0.5 milligram. As a result of these deviations it is estimated that the maximum probable error in the rates of weight loss derived is ± 10 percent.

RESULTS AND DISCUSSION

In the present tests, only a small fraction of the initial test sample weights was lost. To insure that the test conditions were adequate to determine maximum rates of weight loss for each material, it was deemed desirable to obtain a check on the reliability of the test techniques employed. This was done by testing cadmium under the same environmental conditions as those under which the organic materials were tested. Cadmium was chosen for this purpose because its vapor pressure and molecular weight are well known so that its maximum evaporation rate can be determined with confidence from kinetic theory. (See, e.g., refs. 3 and 4.) Thus a comparison of theoretical and experimental rates obtained for this material should provide a measure of the reliability of the experimental techniques employed.

Evaporation Rate of Cadmium

Time histories of the change in weight obtained on cadmium samples 0.188 inch thick at surface temperatures of 180° , 210° , 250° and 300° F are shown in figure 3. The linearity with time of these data is typical of that obtained for all the test materials.

The rate at which molecules leave the surface of an inorganic material in a perfect vacuum is given by the Langmuir equation (ref. 3).

$$w = \frac{p_v}{17.14} \sqrt{\frac{M}{T}} \quad (1)$$

where

w rate of evaporation, gram/cm²-sec

p_v vapor pressure of the material, mm Hg

M molecular weight of the material in the gas phase

T temperature, $^\circ$ K

For cadmium $M = 112.4$, and the dependence of vapor pressure on temperature is (ref. 10)

$$\log_{10} p_v = 8.564 - \frac{5693.1}{T} \quad (T \leq 600^\circ \text{ K})$$

The rates of evaporation calculated from equation (1) are shown in figure 4 as a function of the reciprocal of the absolute temperature in degrees Kelvin. Also shown, as data points, are evaporation rates obtained from the slopes of the data shown in figure 3. Data for cadmium presented in reference 8 are also shown in figure 4 for comparative purposes. The agreement between the calculated and experimental results shown in this figure indicates that good reliability has been achieved in the present over-all test techniques.

Initial Weight Loss Rate of Polytetrafluoroethylene (Teflon)

Rates of weight loss of Teflon were derived from experimental time-history data similar to that presented in figure 3 for cadmium. As mentioned earlier, the rates were essentially constant over the test period at each test temperature. Results obtained for samples 0.188 inch thick over a temperature range of 150° to 500° F are presented in figure 5 as a function of the reciprocal of the absolute temperature in degrees Kelvin. Also shown are data obtained from tests of Teflon samples exposed to vacuum conditions similar to those of the present tests and reported in references 7 and 8. The differences in rates obtained from the various tests at the higher temperatures cannot be explained at the present time. They may be due to the variability of commercial materials or perhaps to differences in test techniques.

A relatively large amount of experimental work has been done to establish reaction rates and mechanisms of degradation of Teflon in a vacuum at temperatures above 700° F such as reported in references 5 and 6. It is interesting to compare the results of the present tests and those of reference 8 with data compiled from references 5 and 6. The comparison is made in figure 6 in the form of an Arrhenius plot. The reaction rate constant, k , is related to the absolute temperature by the Arrhenius equation (see, e.g., ref. 11)

$$k = Ae^{-E/RT}$$

where

A frequency factor, sec^{-1}

E activation energy, cal/mole

R universal gas constant, cal/mole-°K

T temperature, °K

The reaction rate constant is also related to the rate of evaporation by (see, e.g., ref. 11)

$$k = \frac{1}{W} \frac{dW}{dt}$$

where W is the polymer weight in grams and dW/dt is the weight loss rate in grams per second. Therefore, once k as a function of T has been determined from experiment, the activation energy and frequency factor can be determined from the slope and intercept, respectively, of a logarithm plot of the data similar to that shown in figure 6 for the data of references 5 and 6. The solid line in figure 6 represents a least squares fit to these data as determined by Friedman in reference 12 and is defined by

$$k = 9.4 \times 10^{18} e^{-81,400/RT} \text{ sec}^{-1} \quad (2)$$

The frequency factor of $9.4 \times 10^{18} \text{ sec}^{-1}$ and activation energy of 81,400 cal/mole are consistent with the values obtained for these quantities by the authors of references 5 and 6 from their respective experiments. It might be noted that the dissociation energy of C-C bonds is about 76,000 calories per mole (ref. 6). This is consistent with the value of 81,400 cal/mole obtained from the slope of the solid line shown in figure 6, which indicates that there is scission of the C-C bonds. On the other hand, the slopes of the dashed lines representing the lower temperature data are considerably lower. This would indicate that a homogeneous breakdown of C-C bonds did not occur in the lower temperature tests. The vertical dashed line in figure 6 represents the temperature at which a Teflon sample was visually observed to change color and become transparent although no apparent dimensional change of the sample occurred. In view of the fact that this phase change occurred in the temperature range where there appears to be a marked change in the variation of evaporation rate ($T \approx 600^\circ \text{ F}$), it may be significant. Details of this phase change have been described by others (see, e.g., ref. 13).

The mechanism of degradation of Teflon at low temperatures is not understood. The weight losses obtained in the present tests may be due to absorbed gases and water. In any event, one important thing to note from figure 6, from an engineering standpoint, is that extrapolation to lower temperatures of high temperature data for the weight loss rate of Teflon is questionable.

Initial Weight Loss Rates of Polycarbonate (Lexan), Epoxy, Nylon-Phenolic, and Silica-Phenolic

Initial rates of weight loss for these materials were also determined from time histories of tests on samples 0.188 inch thick at various temperatures up to 300° F . Again, these rates were constant for the test period in each case. There was no apparent change in the physical appearance of any of the test samples up to their respective heat distortion temperatures. Because of the possible engineering significance of the rates obtained, these rates are presented in figure 7 in terms of pounds per square foot-hour as a function of the temperature in degrees Fahrenheit. Data for Teflon are also shown for purposes of comparison. The thermoplastic materials, Teflon and Lexan, have the lowest rates of weight loss. The homogeneous thermoset material, epoxy, has a rate about an order of

magnitude greater and the reinforced phenolics have rates about two orders of magnitude greater than the thermoplastics.

Effect of Sample Thickness On Weight Loss Rate

Test results presented up to this point were for samples 0.188 inch thick. To determine the effect of sample thickness on weight loss rates, samples of thicknesses ranging from 0.050 to 0.250 inch were also tested. Results of these tests are presented in figure 8. The rate of weight loss of Teflon, like cadmium, was not measurably affected by changes in sample thicknesses. This result implies that the reaction occurring for Teflon is effectively a surface phenomenon. In contrast, there is an order of magnitude increase in weight loss rates for all the other organic materials tested when the sample thickness is reduced from 0.250 to 0.050 inch. This suggests that the diffusion of the reaction products through the bulk of these latter materials may be a controlling factor in the weight loss process. It is also indicated in figure 8 that the weight loss rates of these materials may not change significantly for thicknesses greater than about 0.25 inch.

SUMMARY OF RESULTS

On the basis of the agreement of the results obtained for cadmium from kinetic theory and from experiment, the experimental methods employed in this investigation were shown to be reliable.

Initial rates of weight loss obtained for Teflon at temperatures of 500° F and lower were found to be many orders of magnitude higher than would be predicted from an extrapolation of pyrolysis data obtained by other investigators at temperatures greater than 700° F. It was further indicated that the degradation mechanism may be different at temperatures up to about 600° F from that which occurs at higher temperatures. Further experiments such as longer exposure times and mass spectra analyses to determine the mechanism of weight loss at lower temperatures would, therefore, appear to be warranted.

No effect of material thickness on the initial rate of weight loss of Teflon was found at a surface temperature of 300° F for thicknesses ranging from 0.05 to 0.25 inch. It is concluded, therefore, that at this temperature the reaction is effectively a surface phenomenon. The initial rates of weight loss of Lexan, epoxy, nylon-phenolic, and silica-phenolic were found to increase significantly with decreasing material thickness, indicating that the diffusion of the reaction products through the bulk of the material was a controlling factor in the weight loss process of these materials.

Finally, the test results indicate that material loss may be significant at temperatures which might be attained by spacecraft and that rates of weight loss may be especially high for thin films. Here again, however, tests of several hundred hours duration are needed to establish this point.

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Moffett Field, Calif., Mar. 29, 1962

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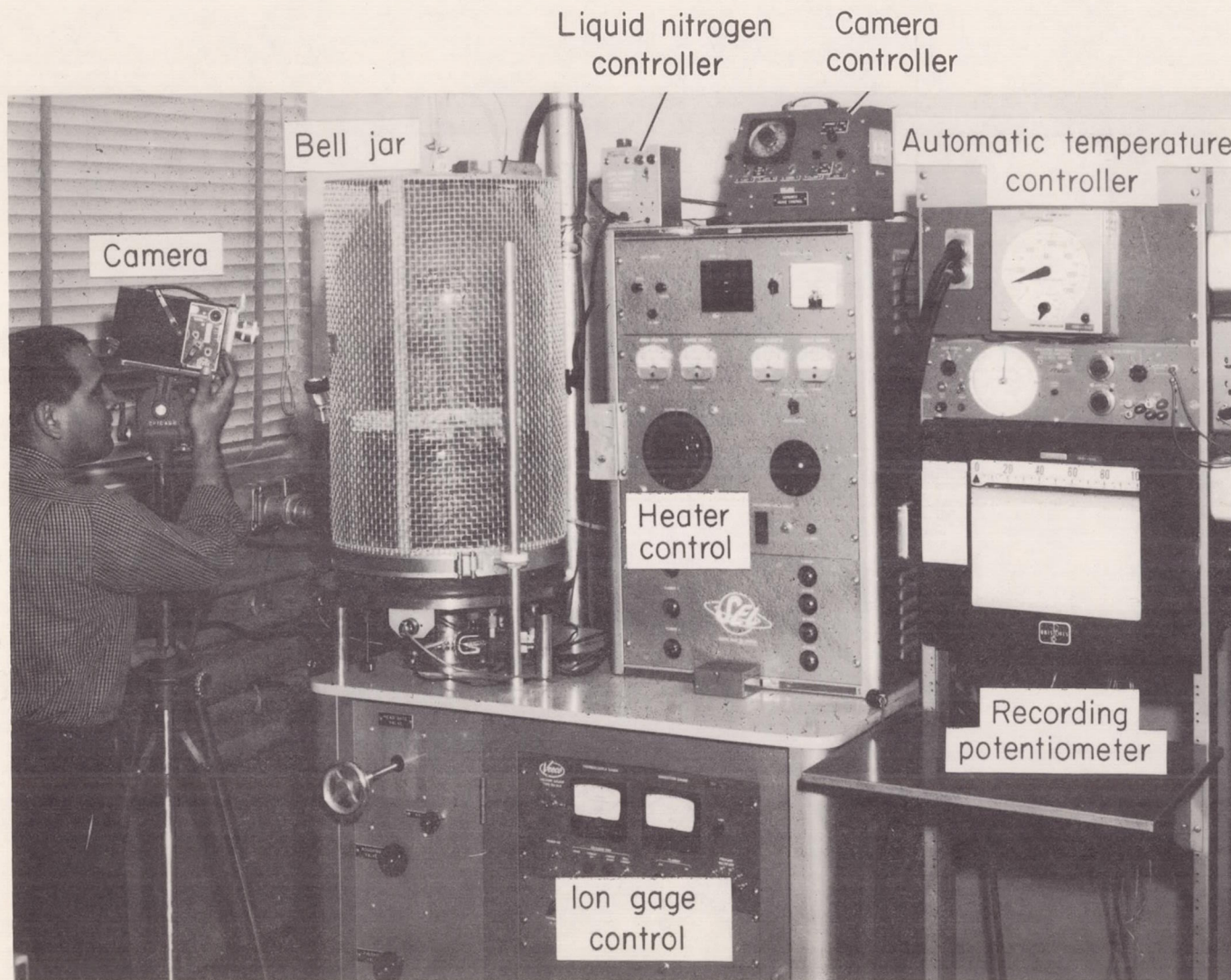
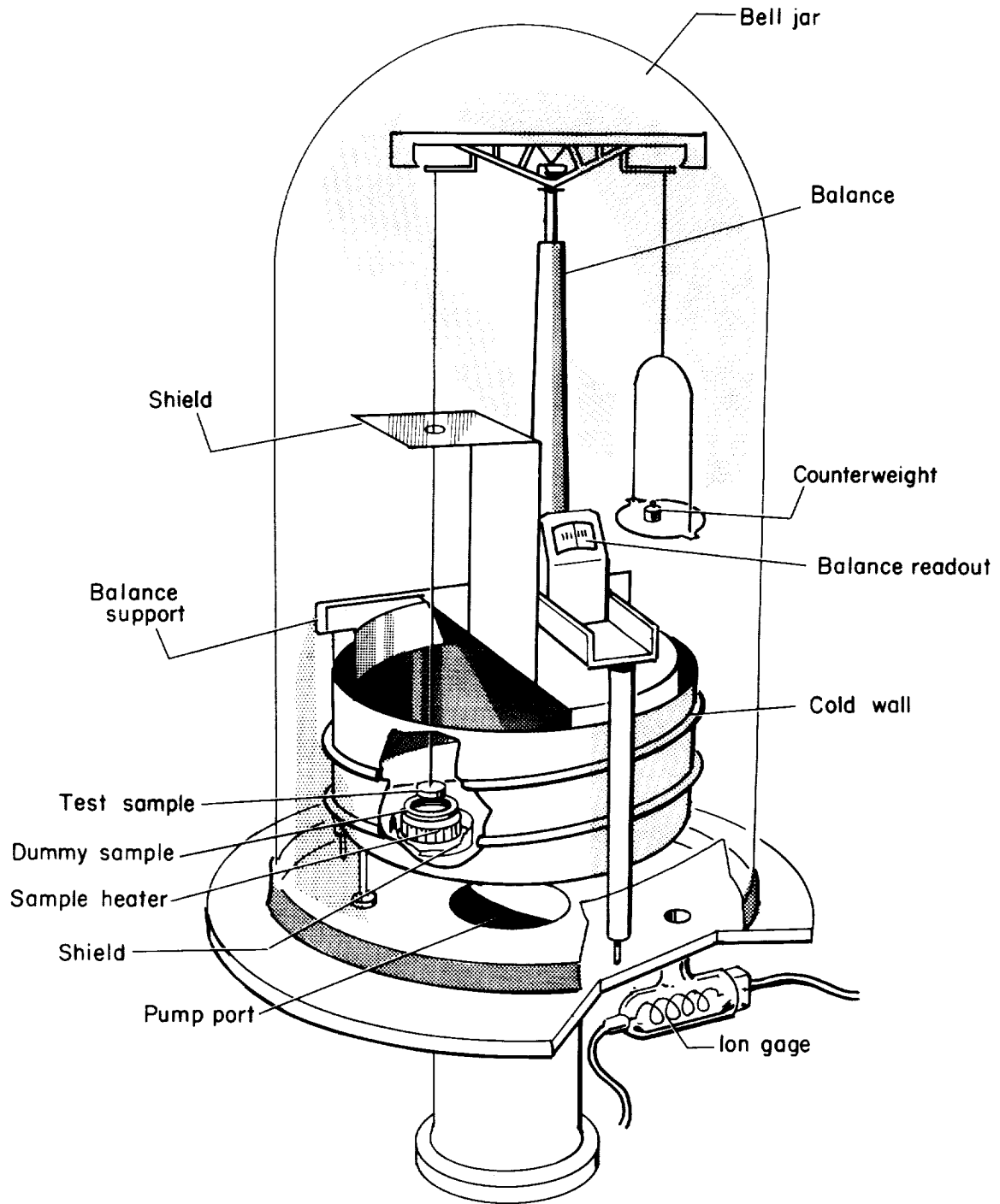


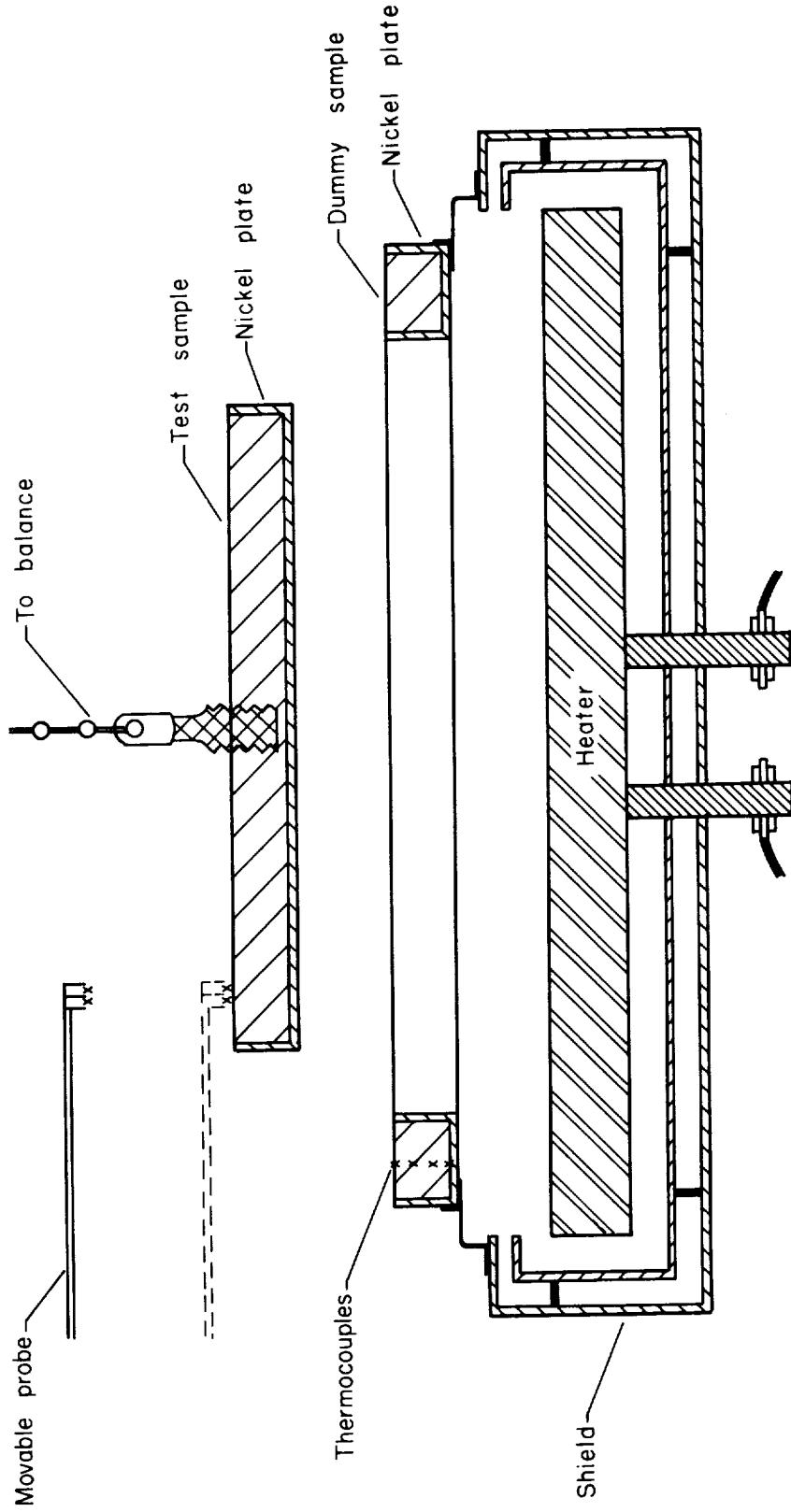
Figure 1.- Photograph of vacuum system.

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(a) General arrangement.

Figure 2.- Vacuum chamber test equipment.



(b) Arrangement of samples and heater.

Figure 2.- Concluded.

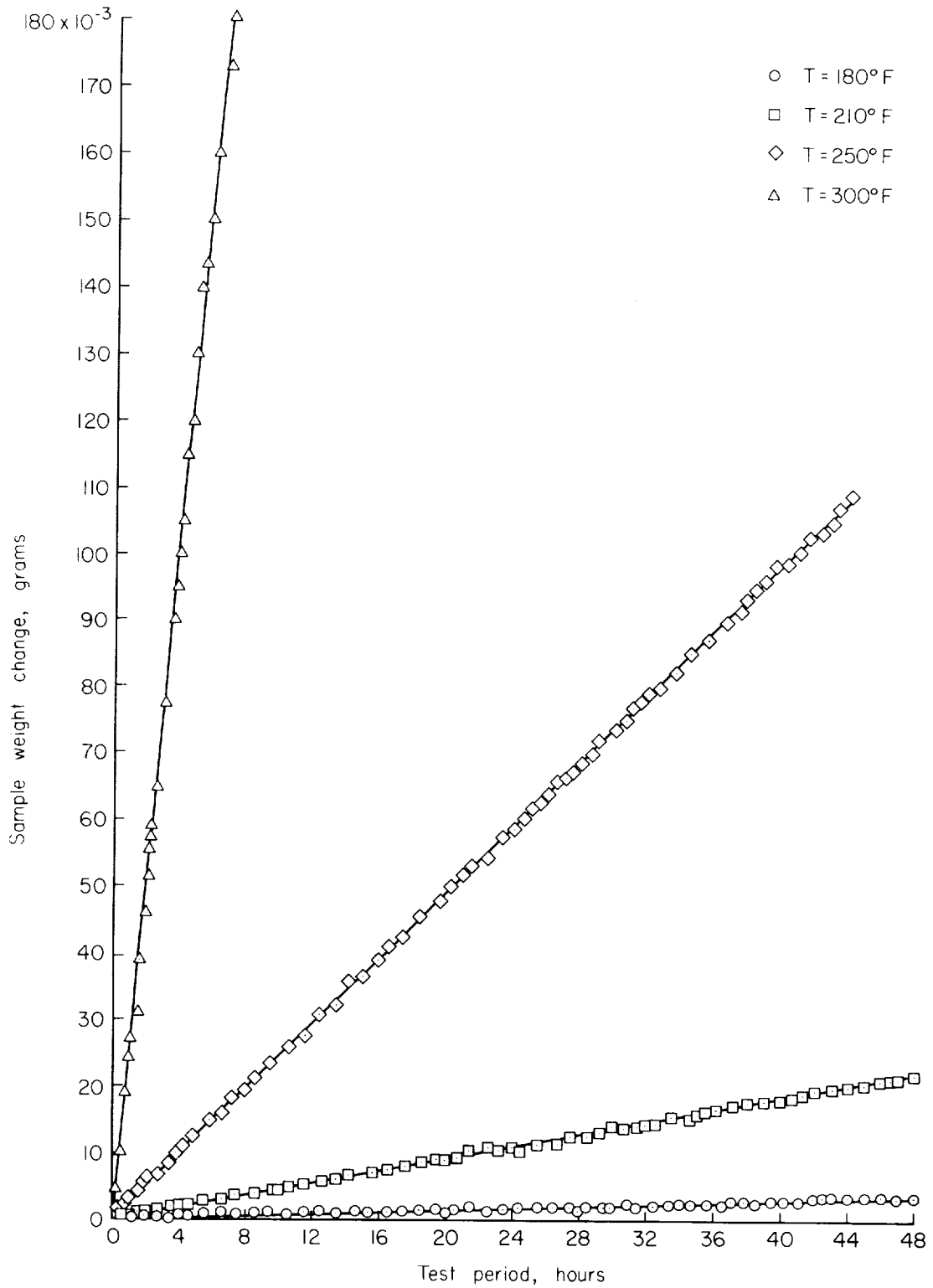


Figure 3.- Evaporation of cadmium.

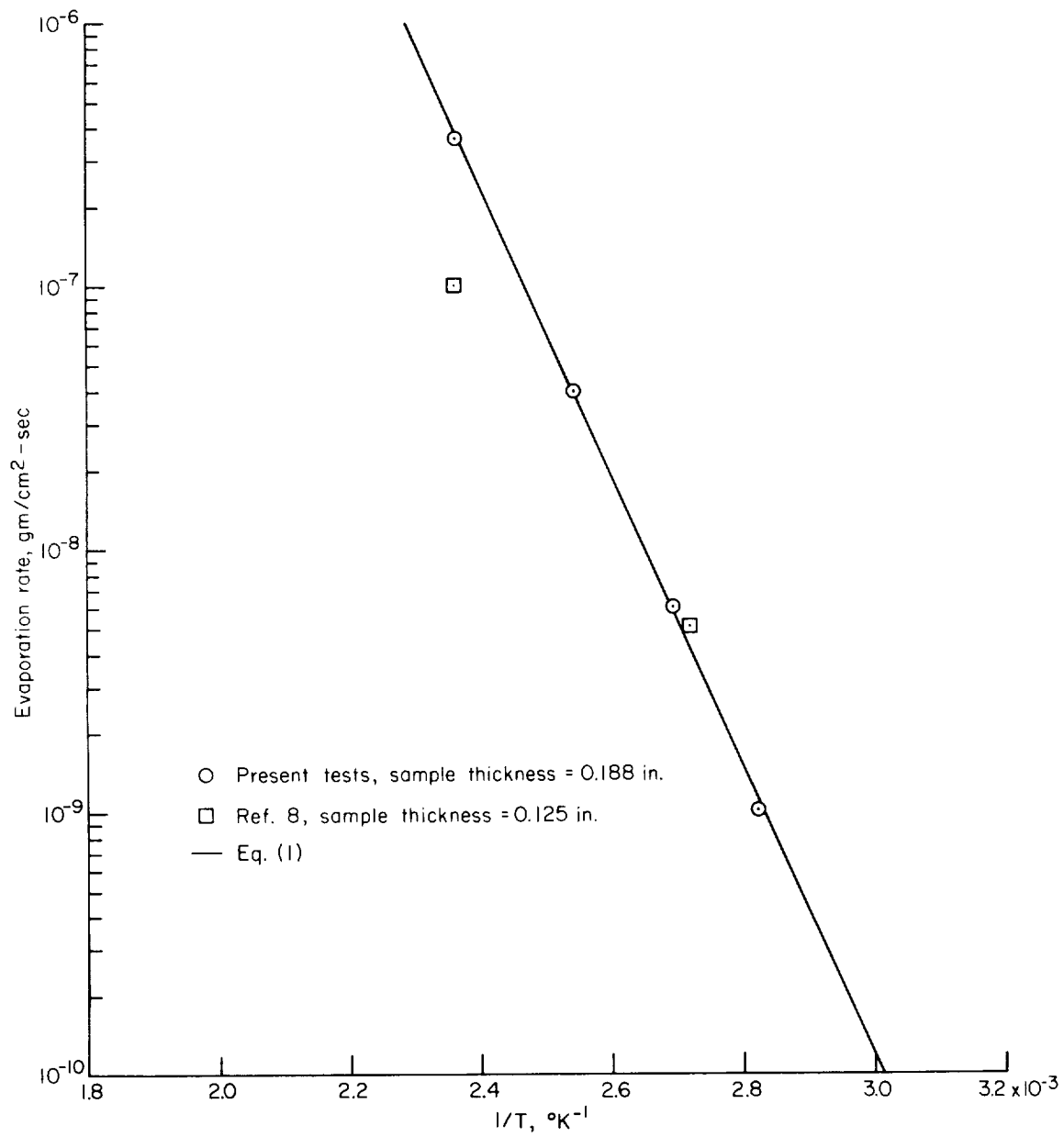


Figure 4.- Evaporation rates for cadmium.

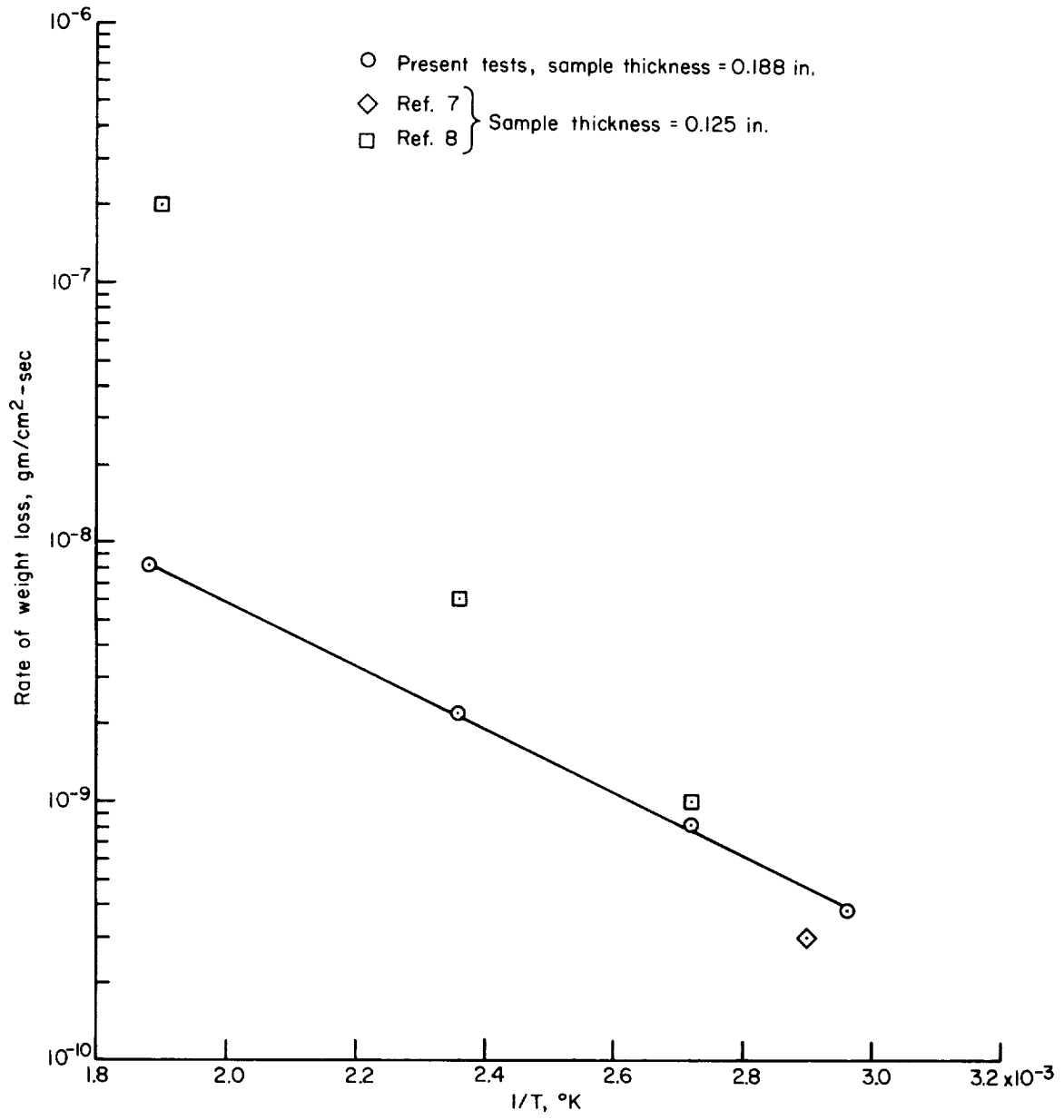


Figure 5.- Initial rates of weight loss for Teflon.

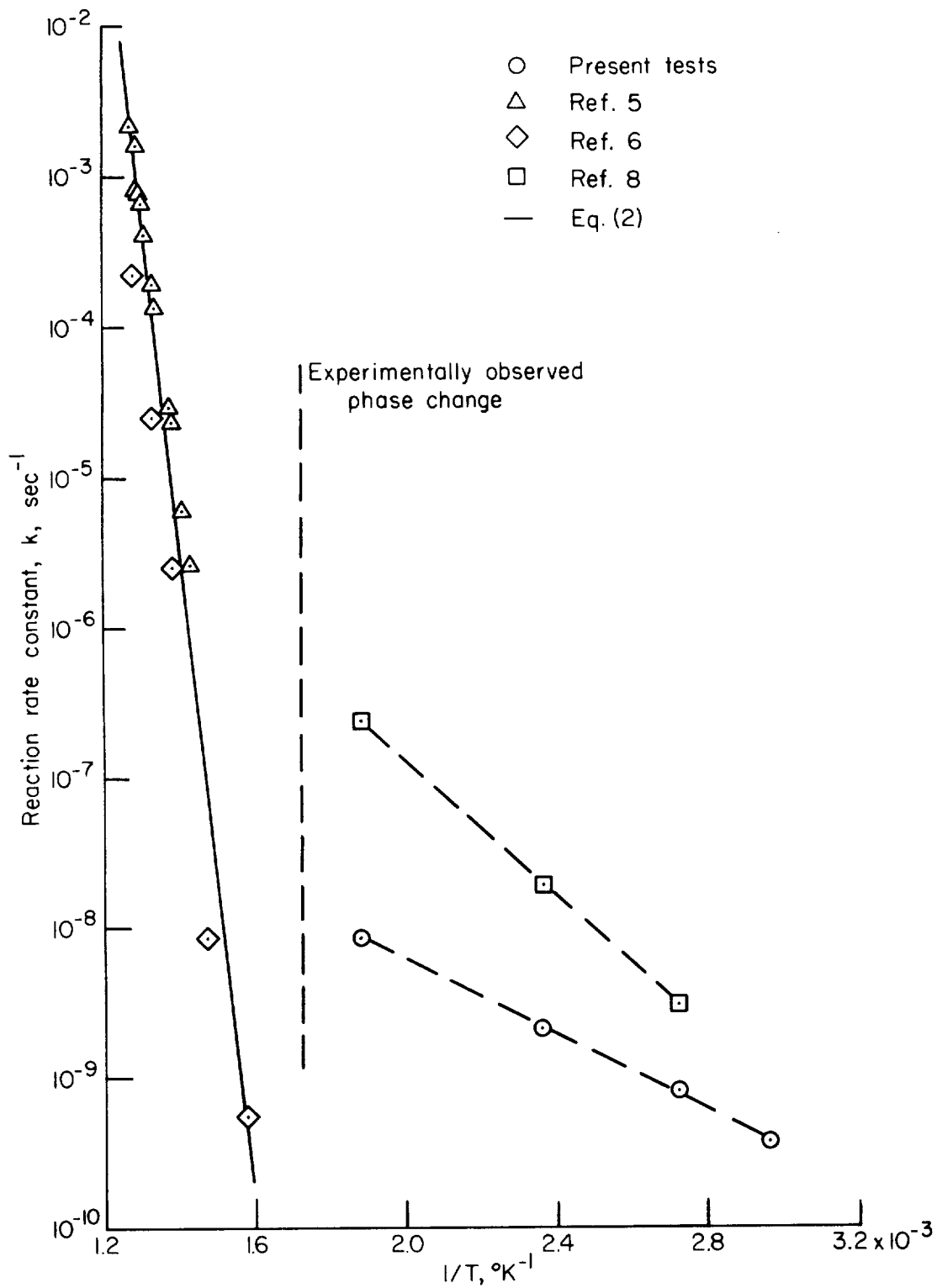


Figure 6.- Arrhenius plot of Teflon rates of weight loss.

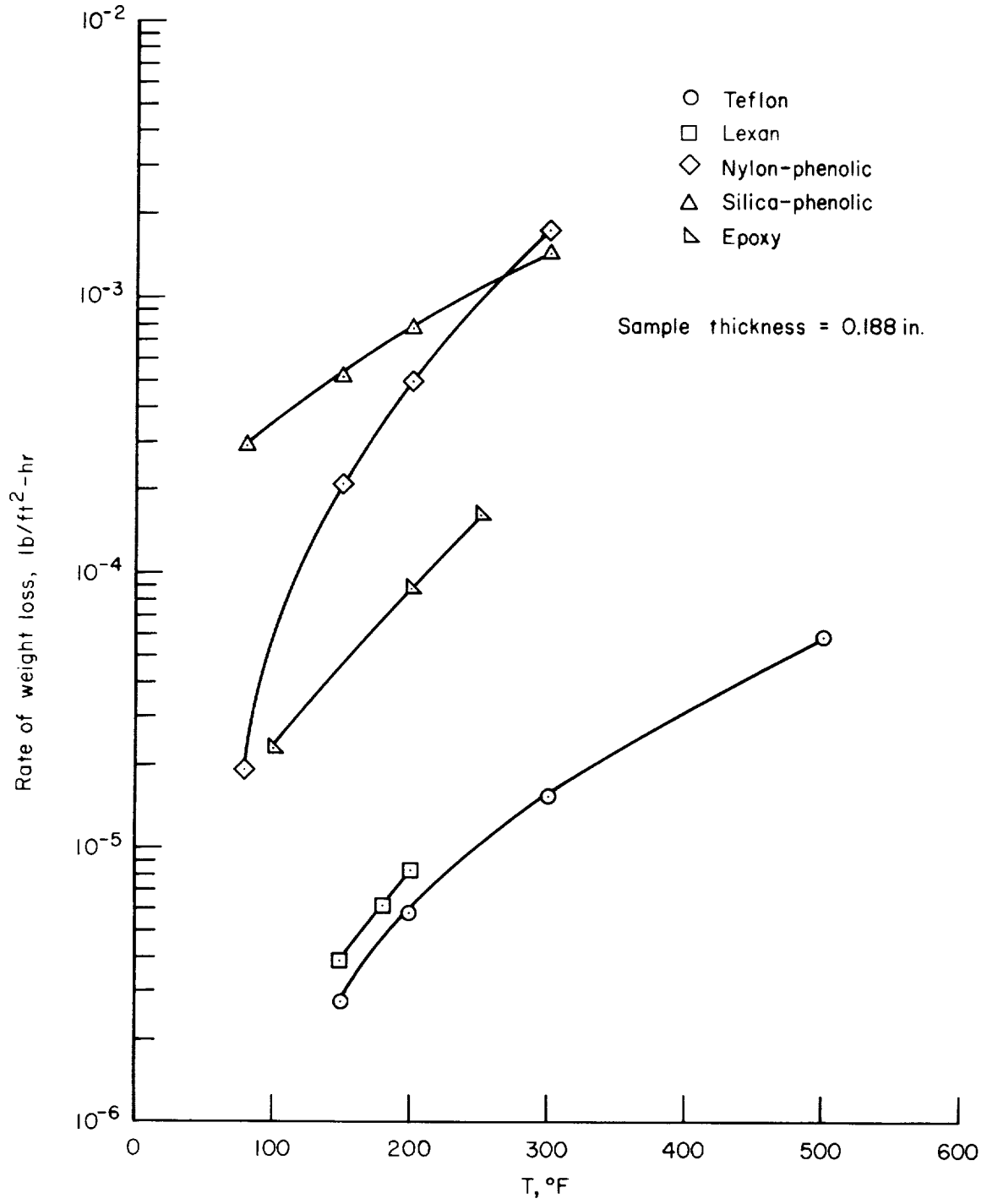


Figure 7.- Initial rates of weight loss for organic materials tested.

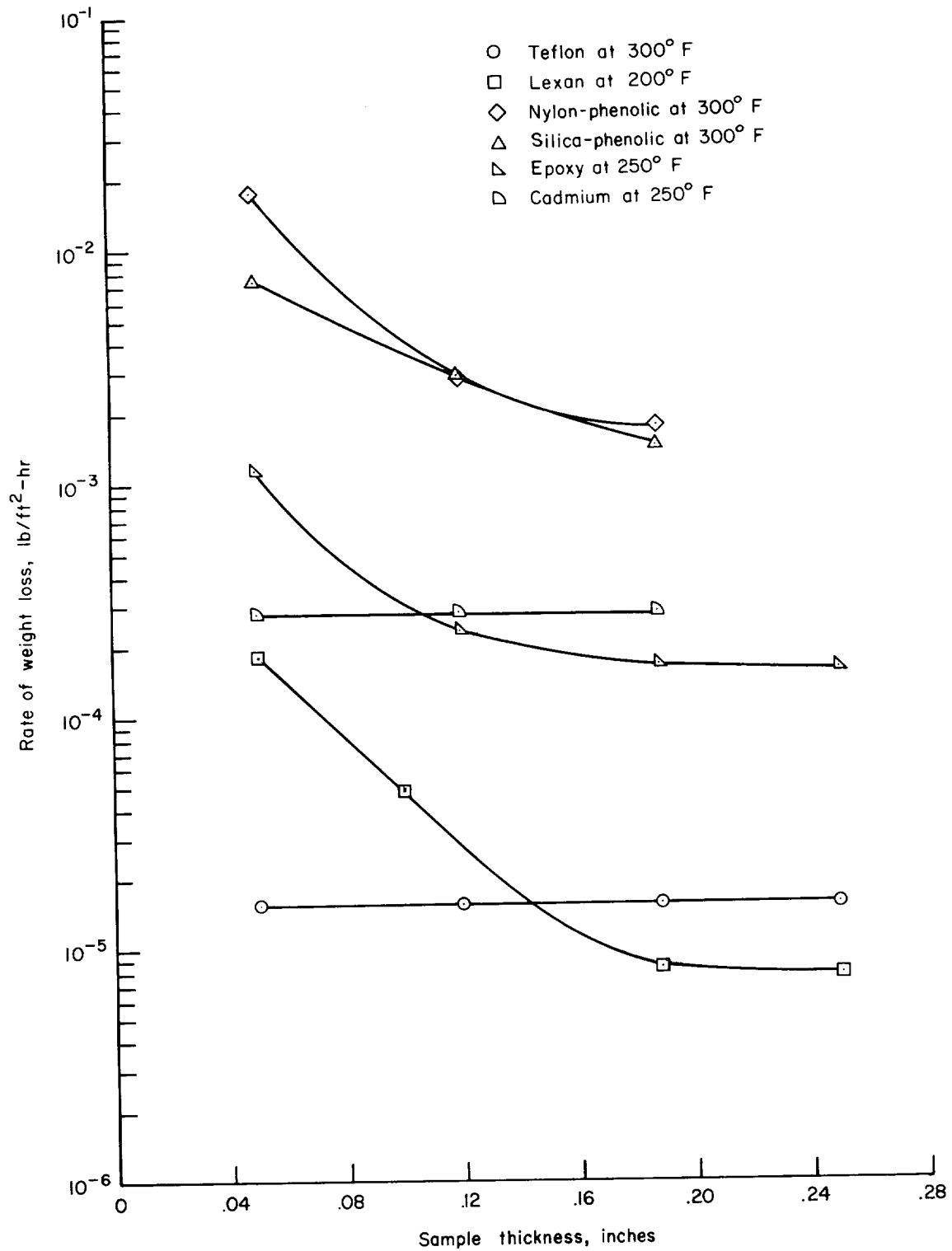


Figure 8.- Effect of sample thickness on initial rates of weight loss.