

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

*Technical Report No. 32-840*

# *Outgassing Rates in Polymeric Foams*

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## *Outgassing Rates in Polymeric Foams*

*E. F. Cuddihy*

*J. Moacanin*

A handwritten signature in cursive script, reading "Robert F. Landel". The signature is written in dark ink and is positioned above a horizontal line.

Robert F. Landel, Manager  
Polymer Research Section

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## ABSTRACT

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Diffusion rates for carbon dioxide were determined on closed-cell polyurethane foams of varying densities by monitoring, for two to three weeks, the loss of weight from specimens suspended in a vacuum of  $10^{-7}$  mm Hg. The experimental data were used to calculate diffusion coefficients for these materials, which were found to be of the order of  $10^{-6}$  to  $10^{-5}$  cm<sup>2</sup>/sec between 22 and 81°C.

The solution of the diffusion equation for an idealized model for a foam yielded the following expression for the diffusion coefficient:

$$D = P_e \left( \frac{RT}{M} \right) \left( \frac{\rho_0}{\rho} \right) \left[ \frac{1}{(1 - \rho/\rho_0)^{1/3}} + 1 + (1 - \rho/\rho_0)^{1/3} \right]$$

which relates the diffusion coefficient  $D$  to the foam density  $\rho$  and to the permeation constant  $P_e$  and the density  $\rho_0$  of the bulk polymer;  $R$  is the gas constant,  $T$  the temperature, and  $M$  the molecular weight of the gas.

Using this equation and experimentally obtained values of  $D$ , a  $P_e$  of  $5.1 \times 10^{-9}$  (cc STP) mm/sec/cm<sup>2</sup>/cm Hg was calculated for the polyurethane material comprising the foam, which agrees within a factor of 2 for reported  $P_e$  constants for polyurethane.

Author

## I. INTRODUCTION

Currently, there is considerable interest in the possibility of using polymeric foams as lightweight encapsulants for electronic components on spacecraft. Very little is known, however, on the electrical breakdown behavior in foams, where an important parameter is the pressure of the blowing gas within the foam cells; in particular, in the ionization region for the gas. Therefore, a study was undertaken of the diffusion of the blowing gas from foams when placed in high vacuum. The fundamental aspects of this process are of importance to the

general problem of transport properties of inhomogeneous synthetic or natural polymeric systems.

The purpose of this Report is to present: (1) a relationship that was developed to relate the diffusion constant for a foam to its density and the permeation constant of the bulk polymer, (2) a description of the experimental techniques used for this study, and (3) experimental results obtained on closed-cell polyurethane foams.

## II. DIFFUSION EQUATIONS

Diffusion equations for polymeric foams were developed using as a simple, but physically reasonable model, a three-dimensional array of cubical cells having walls of uniform thickness and permeable to gases. Here, only one-dimensional diffusion is considered, although extension to the three-dimensional case is straightforward.

The general relation for the flux  $J$  at which a gas permeates through a membrane is

$$J = \frac{dw}{dt} = \frac{P_c A}{L} \Delta P \quad (1)$$

where

$w$  = weight of gas

$P_c$  = permeation constant

$A$  = area

$L$  = thickness of membrane

$\Delta P$  = pressure difference across the membrane

$t$  = time

The net flux for the  $n$ th layer of cells is given by

$$\frac{dw_n}{dt} = J_{n-1} - J_n \quad (2)$$

which, upon substituting for  $J$ , yields

$$\frac{L}{P_c A} \frac{dw_n}{dt} = P_{n-1} - 2P_n + P_{n+1} \quad (3)$$

From the perfect gas law,

$$w_n = P_n \frac{VM}{RT} \quad (4)$$

which can be substituted into Eq. (3) to yield the following differential equation:

$$\frac{LVM}{P_c ART} \frac{dP_n}{dt} = P_{n-1} - 2P_n + P_{n+1} \quad (5)$$

for the pressure  $P_n$  in the  $n$ th layer of cells.

Thus for a system of  $N$  layers, we have a set of  $N$  linear homogeneous equations. For the boundary condition that the external pressure is always zero, along with the initial condition that for zero time the pressure  $P_0$

in all layers is uniform, the following relationship is obtained:

$$\frac{P_n(t)}{P_0} = \sum_{k=1}^N \alpha_k \left[ \sin \frac{\pi n (2k-1)}{2N+1} \right] \times \exp \left\{ - \left( \frac{P_c ART}{LVM} \right) \left[ 2 - 2 \cos \frac{\pi (2k-1)}{2N+1} \right] t \right\} \quad (6)$$

For the limiting case of  $N \rightarrow \infty$ , the coefficients  $\alpha_k$ 's can be readily evaluated, and the solution becomes

$$\frac{P_n(t)}{P_0} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)} \sin \left[ \frac{\pi (2k-1) n}{2N} \right] \times \exp \left\{ - \left( \frac{P_c ART}{LVM} \right) \left[ \frac{\pi (2k-1)}{2N} \right]^2 t \right\} \quad (7)$$

If  $N > 20$ , values of  $\alpha_k$ 's for the limiting case of  $N \rightarrow \infty$  can be used without introducing a significant error. Inasmuch as for a 1-in.-thick foam,  $N$  is of the order of a few hundred, Eq. (7) is applicable for all cases of interest. Now, if formally we consider the gas as a diffusion process in a medium characterized by a diffusion constant  $D$ , the following well-known equation is appropriate (Ref. 1):

$$\frac{P_x}{P_0} = \frac{C_x}{C_0} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)} \sin \left[ \frac{\pi x (2k-1)}{2a} \right] \times \exp \left\{ - \left[ \frac{(2k-1) \pi}{2a} \right]^2 Dt \right\} \quad (8)$$

where

$C_x$  = concentration of gas

$C_0$  = initial concentration

$a$  = thickness of solid

$x$  = distance in from exposed surface

$D$  = diffusion constant

This equation is identical to Eq. (7) only at the limit  $N \rightarrow \infty$ . But, again it will be a close enough approximation for large  $N$ . Noting that since  $n/N = x/a$ , the coefficients in both equations are identical and hence the arguments of the exponential for Eq. (7) and (8) must be equal; thus

$$\frac{D}{a^2} = \frac{P_c ART}{LVMN^2} \quad (9)$$

As  $V/A$  is the length of the side of a cell  $d$ , we substitute and rearrange Eq. (9) to get

$$D = P_e \left( \frac{RT}{M} \right) \frac{a^2}{(NL)(Nd)} \quad (10)$$

As  $a$  is the thickness of the foam and  $NL$  and  $Nd$  are the thickness of the membranes and the cells respectively, it follows that  $a = NL + Nd$ . The ratio  $a^2/\{(NL) \times (Nd)\}$  can be readily expressed in terms of the densities of the foam  $\rho$  and the bulk polymer  $\rho_0$ . For a cube of unit dimensions, i.e.,  $c = 1$ , which contains  $N^3$  cells, the total volume of cells is  $(Nd)^3$ . This volume represents the volume fraction of voids and is therefore equal to  $(1 - \rho/\rho_0)$ . Thus  $(Nd)$  is equal to  $(1 - \rho/\rho_0)^{1/3}$  and since  $(Nd) + (NL) = 1$ ,  $(NL)$  is equal to  $1 - (1 - \rho/\rho_0)^{1/3}$ . Substituting for  $(NL)$  and  $(Nd)$  in Eq. (10) and factoring out  $\rho_0/\rho$ , the following expression is obtained:

$$D = P_e \left( \frac{RT}{M} \right) \left( \frac{\rho_0}{\rho} \right) \left[ \frac{1}{(1 - \rho/\rho_0)^{1/3}} + 1 + (1 - \rho/\rho_0)^{1/3} \right] \quad (11)$$

where

$\rho$  = density of foam

$\rho_0$  = density of membrane material

Equation (11) relates the diffusion constant of a polymer foam to the permeation constant and foam density. The expression

$$\left[ \frac{1}{(1 - \rho/\rho_0)^{1/3}} + 1 + (1 - \rho/\rho_0)^{1/3} \right]$$

varies slowly between 3 and 3.05 as  $\rho/\rho_0$  varies between 0 and 0.5. Since most polymer foams are of low density, the variation in this term can be neglected. Thus for a given family of foams, Eq. (11) predicts that the diffusion constant is inversely proportional to the foam density and can be simply represented as

$$D = K/\rho \quad (12)$$

The experimental data are obtained by measuring the weight loss of gas  $Q$ , from polymer foams in vacuum. The value of  $D$  is then calculated by use of the integrated form of Eq. (8) (Ref. 1):

$$Q = Q_\infty - \frac{8Q_\infty}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{(2k-1)^2} \exp \left\{ - \left[ \frac{(2k-1)\pi}{2a} \right]^2 Dt \right\} \quad (13)$$

where  $Q_\infty$  is the initial weight of gas in the foam. For sufficiently long enough times, all the exponential terms except the first ( $k = 1$ ) can be neglected. Thus a plot of  $\ln(Q_\infty - Q)$  vs time will eventually become linear with a slope of  $[\pi/2a]^2 D$ .

### III. EXPERIMENTAL

To obtain weight-loss data, foams of 3-in. diameter and 1-in. deep were bonded into aluminum containers, leaving the top surface exposed. The bonding agent was Eccobond 55\*, a room-temperature curing epoxy.

Weight-loss data at room temperature,  $22 \pm 1^\circ\text{C}$ , were obtained with an Ainsworth vacuum balance unit. The balance and details of sample suspension are shown in Fig. 1 and 2.

For elevated temperatures, weight loss was measured with a Cahn RH Electrobalance, which was situated inside a vacuum unit manufactured by the Consolidated Vacuum Corporation. The sample was heated by means of a variac-controlled 250-w bulb. A temperature differential of less than one degree was maintained across the sample by means of a reflecting aluminum shroud (Fig. 3 and 4).

The following polymer foams were investigated:

1. Eccosil 5000\*, a syntactic silicone foam of nominal sp. gr. 0.48, prepared by mixing together hollow silicone spheres and a silicone resin.
2. Eccofoam SH\*, a nominal 8-lb/ft<sup>3</sup> polyurethane foam filled with CO<sub>2</sub> gas. This material is purchased already blown in 1-in.-thick sheet stock. Actual measured density of the sample was 7.6 lb/ft<sup>3</sup>.
3. Stycast 1090\*, a syntactic epoxy foam prepared by mixing together hollow glass spheres and an epoxy

resin. System cures hard with a nominal sp. gr. of 0.78.

4. Eccofoam FPH/12/2H\*, a nominal 2-lb/ft<sup>3</sup> polyurethane foam filled with CO<sub>2</sub> gas. Material prepared prior to test by mixing a resin-catalyst system and allowing the combination to foam and cure. Density of sample was 2.1 lb/ft<sup>3</sup>.
5. Eccofoam FPH/12/6H\*, a nominal 6-lb/ft<sup>3</sup> polyurethane foam filled with CO<sub>2</sub> gas. Material prepared prior to test by mixing a resin-catalyst system together and pouring into a mold 2 in. deep and 3 in. in diameter. Using an appropriate weight schedule, the foaming reaction would result in about half of the cured material extending above the top of the mold. Samples prepared from the top and bottom halves were found to be 4.5 and 6.4 lb/ft<sup>3</sup>, respectively.

The family of rigid, closed-cell polyurethane foams known as Eccofoams FPH are asserted by the manufacturer to be capable of withstanding indefinite exposure to a temperature of 300°C, and even to higher temperatures for short periods of time. These materials are available in the density range from approximately 2 to 10 lb/ft<sup>3</sup>.

The initial weights of CO<sub>2</sub> gas ( $Q_\infty$ , mg) in all foams were calculated using the perfect gas law and 1 atm of pressure.

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\*All foams and the bonding agent were supplied by Emerson and Cuming, Inc.



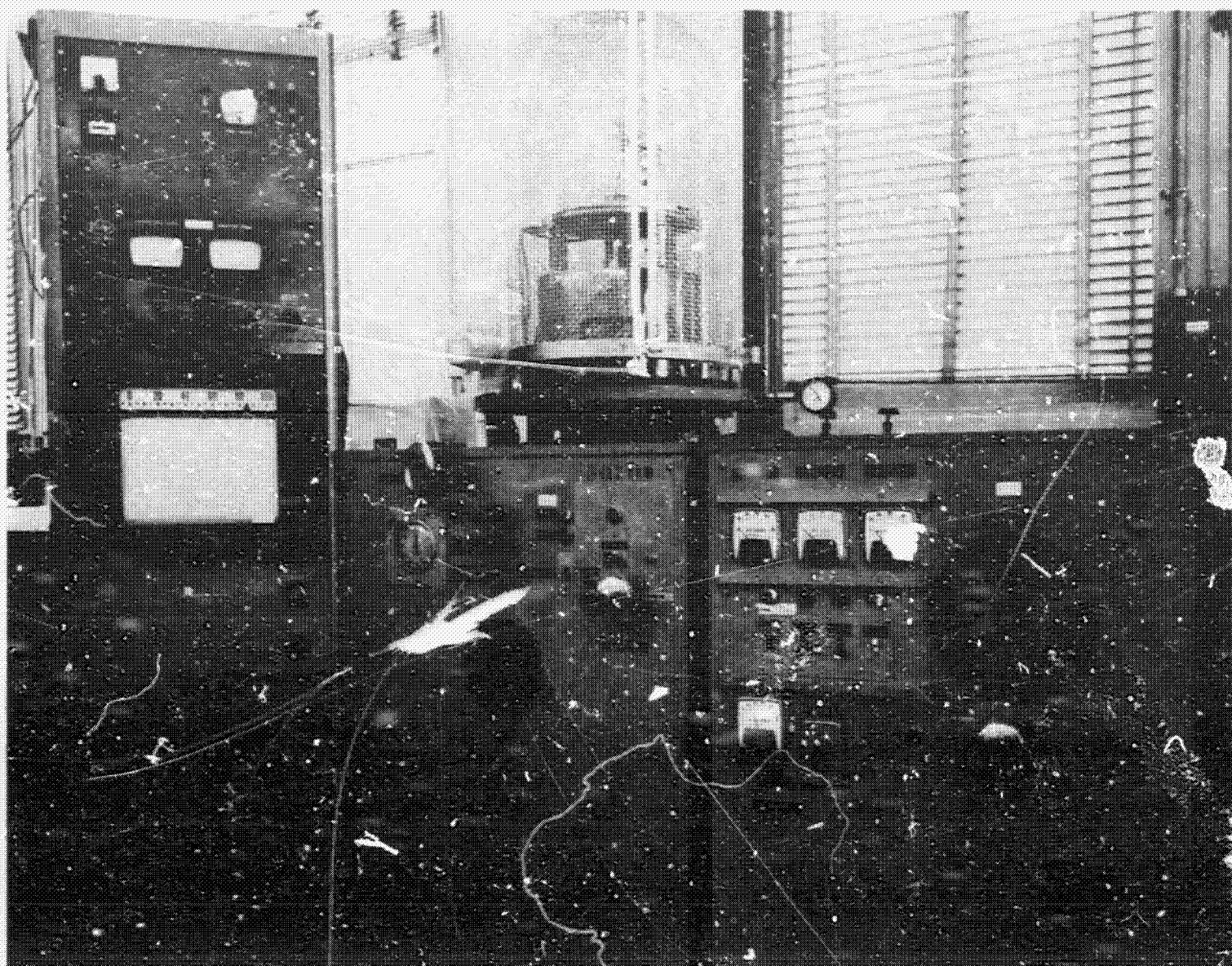


Fig. 1. Ainsworth vacuum balance

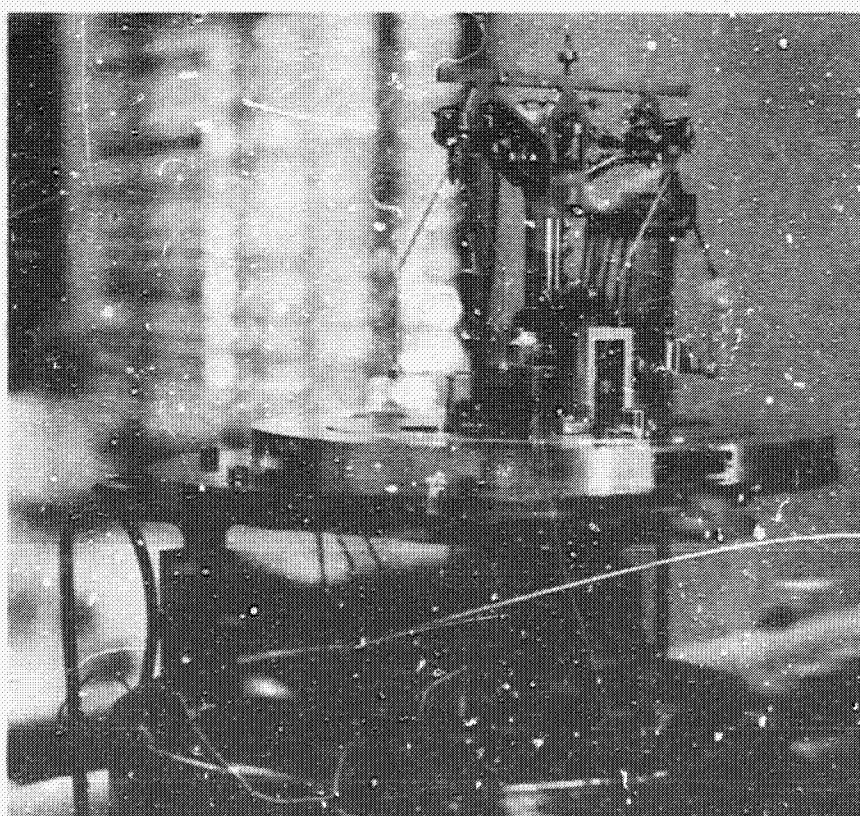
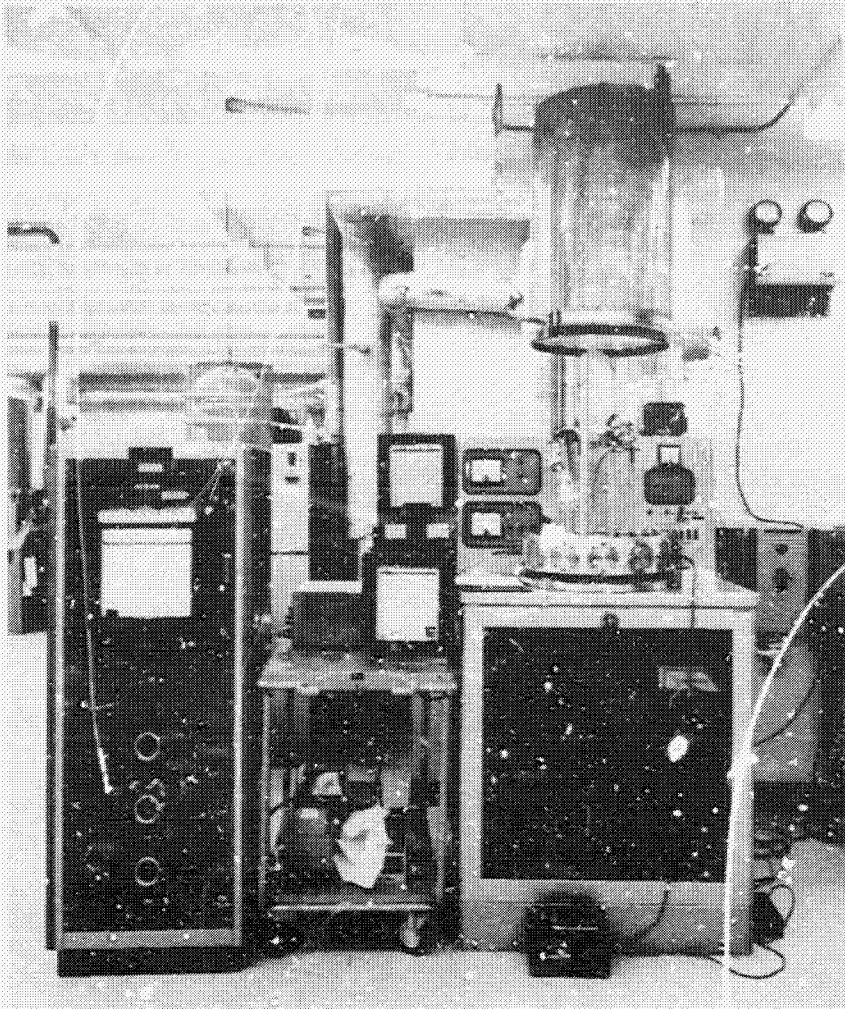
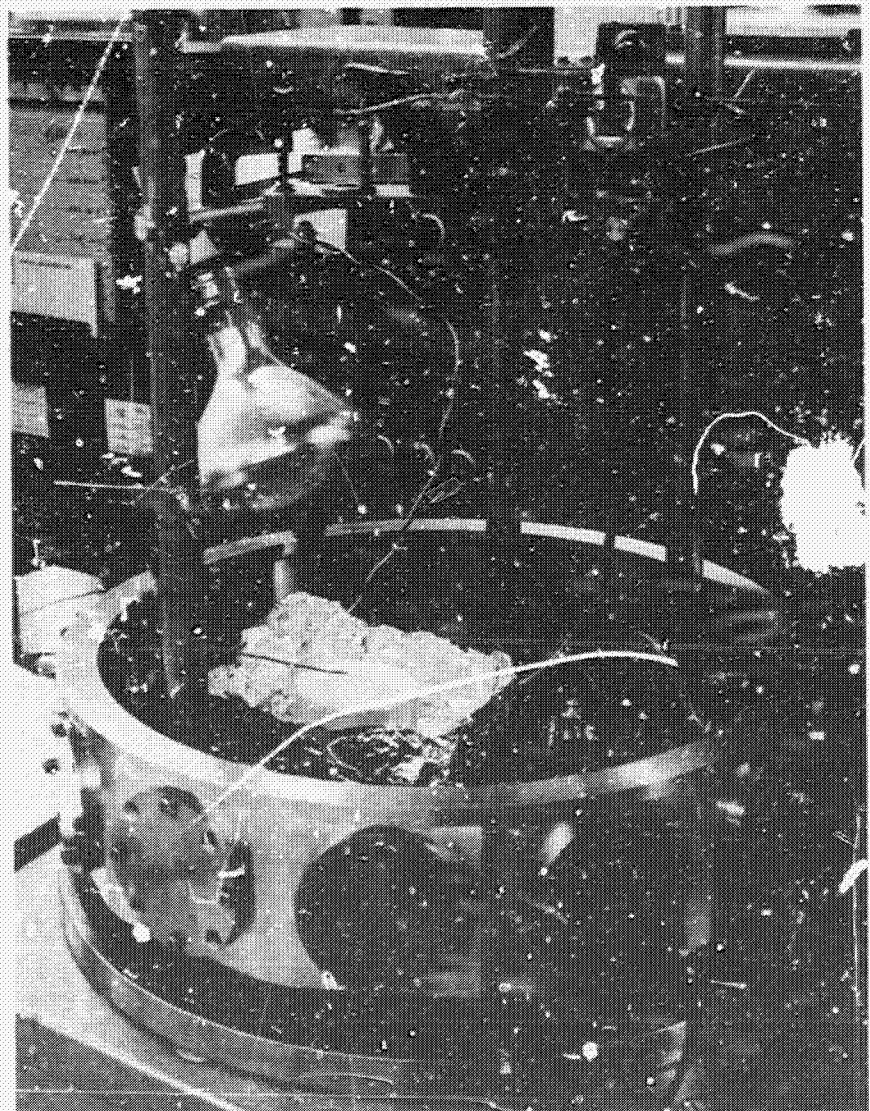


Fig. 2. Details of balance and sample suspension





**Fig. 3. Vacuum-balance facility for elevated temperature operations**



**Fig. 4. Details of heating and balance assembly for elevated temperature operations**

## IV. RESULTS AND DISCUSSION

Weight-loss curves for Eccosil 5000, Eccofoam SH, and Stycast 1090 are shown in Fig. 5. The outgassing rates of these materials parallel the relative order of their respective gas-permeability constants (Ref. 2). Eccosil 5000 lost 130 mg of weight in 225 hr, approximately 90 mg more than the calculated  $\text{CO}_2$  content of 90 to 100 mg ( $Q_\infty$ ). The additional weight loss presumably results from volatile impurities or volatile components that were not consumed in the curing reaction.

The rate of weight loss for Stycast 1090 is extremely low, as only 3.5 mg out of a possible 70 mg of gas were removed under vacuum in approximately 130 hr. This is to be expected because the  $\text{CO}_2$  gas is contained inside glass spheres of low permeability. In addition, the high density of this material results in the formation of very thick membranes between the glass spheres.

For the Eccofoam SH, the plot of  $\log(Q_\infty - Q)$  vs time shown in Fig. 6 was constructed from the weight loss data (Fig. 5) and  $Q_\infty = 184$  mg. Using Eq. (13) and the slope of the linear portion of the curve ( $t > 120$  hr), a diffusion coefficient of  $2.40 \times 10^{-6} \text{ cm}^2/\text{sec}$  at  $22^\circ\text{C}$  was calculated.

Weight loss curves at  $22^\circ\text{C}$  for three Eccofoam FPH systems of densities 2.1, 4.5, and 6.4  $\text{lb}/\text{ft}^3$  are shown in

Fig. 7. Using these data, plots of  $\log(Q_\infty - Q)$  vs time were obtained (Fig. 8), and the diffusion coefficients were found to be  $6.2 \times 10^{-7} \text{ cm}^2/\text{sec}$  for the 2.1- $\text{lb}/\text{ft}^3$  foam,  $1.76 \times 10^{-6} \text{ cm}^2/\text{sec}$  for the 4.5- $\text{lb}/\text{ft}^3$  foam, and

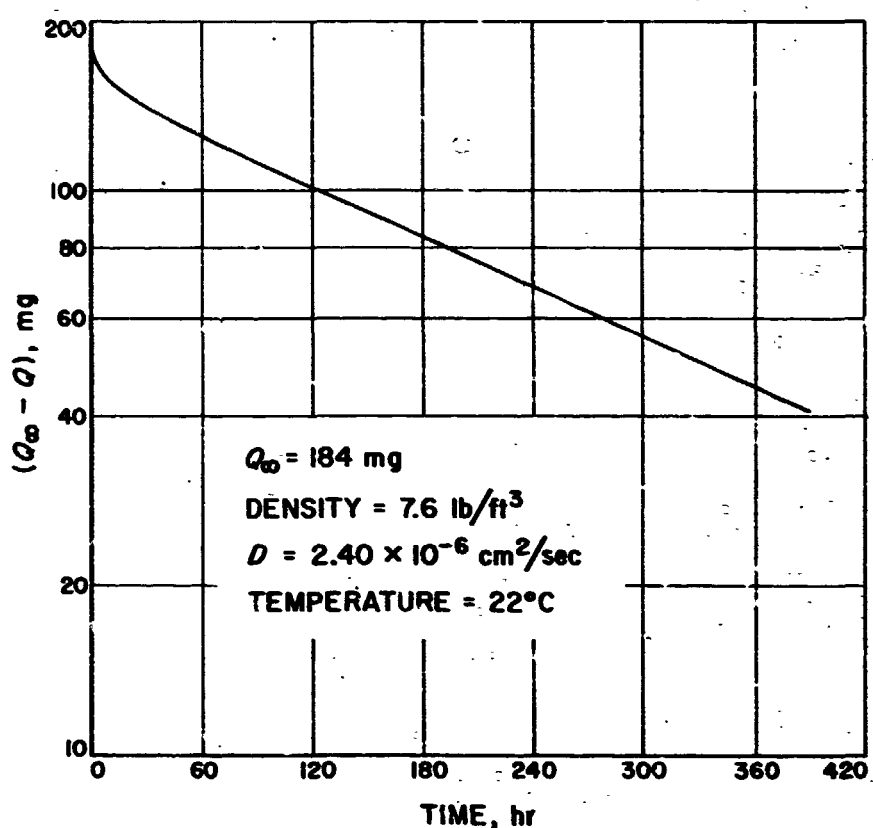


Fig. 6.  $\log(Q_\infty - Q)$  vs time for Eccofoam SH at  $22^\circ\text{C}$

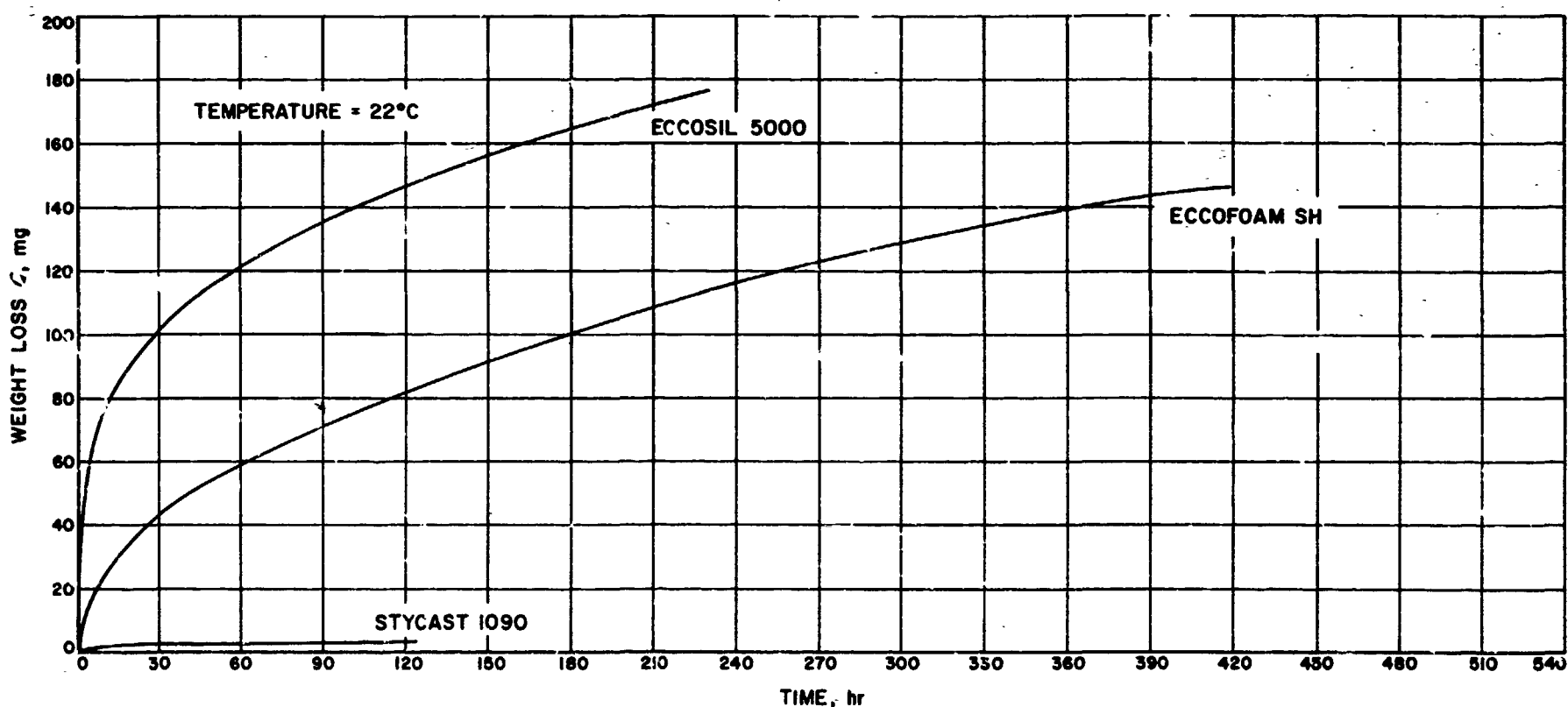


Fig. 5. Weight-loss curves for three polymer foams at  $22^\circ\text{C}$

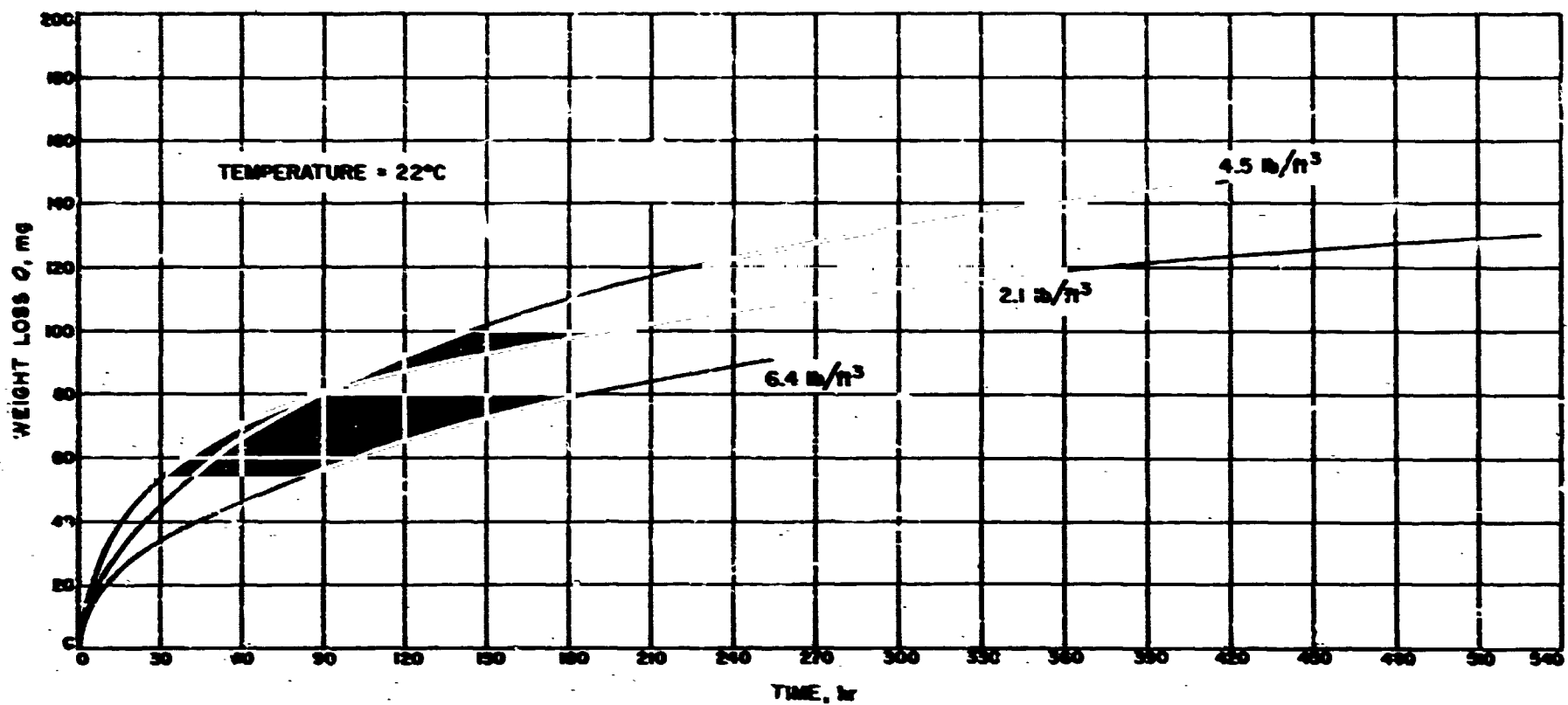


Fig. 7. Weight-loss curves for Eccofoam FPH foams at 22°C

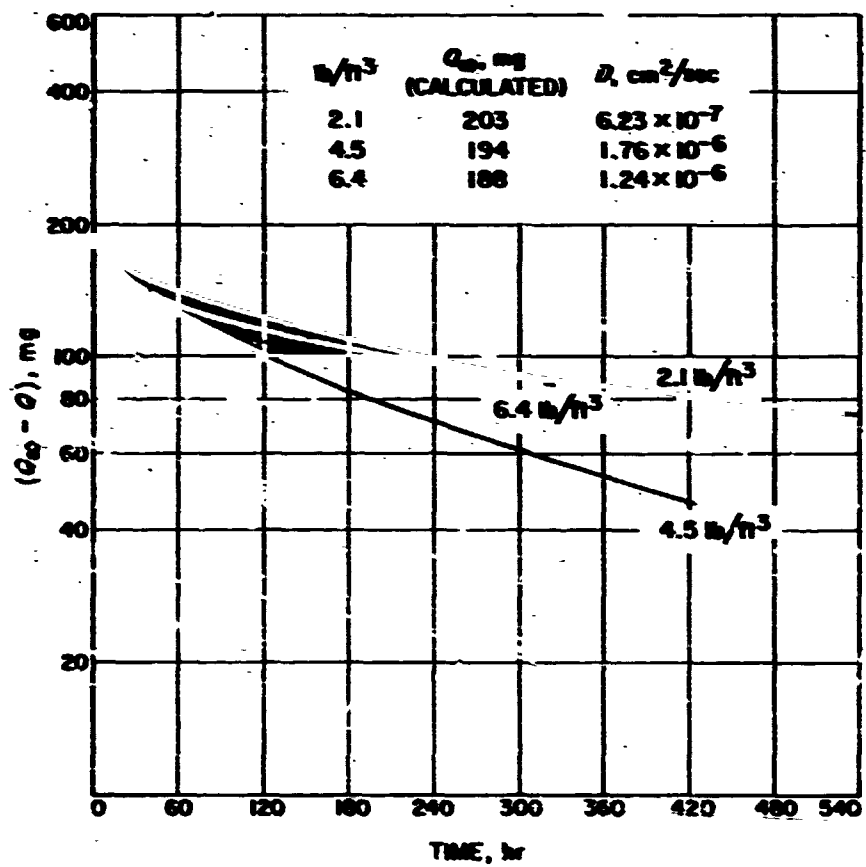


Fig. 8. Log ( $Q_0 - Q$ ) vs time for Eccofoam FPH foams at 22°C

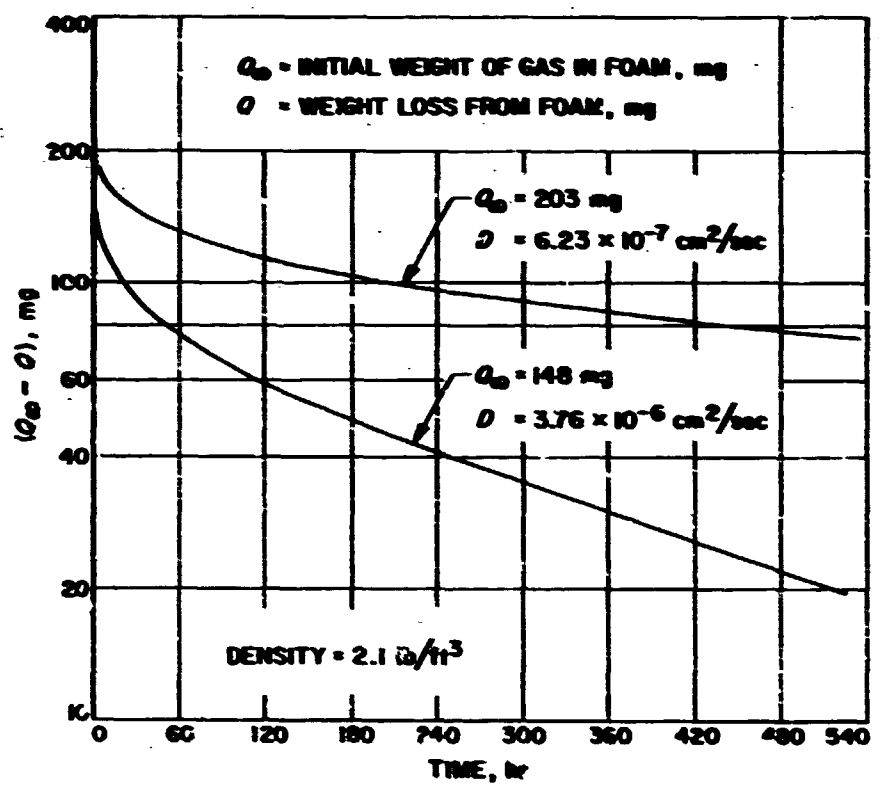


Fig. 9. Log ( $Q_0 - Q$ ) vs time for Eccofoam FPH/12/2H at 22°C

$1.24 \times 10^{-6}$  cm<sup>2</sup>/sec for the 6.4-lb/ft<sup>3</sup> foam. The values used for  $Q_{\infty}$ , which were calculated with an assumed initial gas pressure of 1 atm, were, respectively, 203 mg, 194 mg, and 188 mg of CO<sub>2</sub>.

From Eq. (11), the diffusion coefficient should be inversely proportional to the density. This relationship holds true for the 4.5- and 6.4-lb/ft<sup>3</sup> foams, but not for the 2.1-lb/ft<sup>3</sup> foam, which in fact has the lowest diffusion coefficient of the three. However, this is inconsistent with the faster initial outgassing rate observed for the 2.1-lb/ft<sup>3</sup> foam. This discrepancy can arise from an incorrectly chosen value of  $Q_{\infty}$ . Equation (13) shows that  $D$  is inversely proportional to  $Q_{\infty}$ . Thus a higher value of  $D$  can be obtained from the  $\log (Q_{\infty} - Q)$  plots by using a lower value of  $Q_{\infty}$ . Support for the use of a lower value of  $Q_{\infty}$  can be seen from Fig. 7, where the weight loss curve for the 2.1-lb/ft<sup>3</sup> foam is apparently approaching an asymptotic value of  $Q_{\infty}$  that is considerably less than the calculated value of  $Q_{\infty}$ . From Eq. (12) and the diffusion coefficients for the 4.5- and 6.4-lb/ft<sup>3</sup> foam, a value of  $3.76 \times 10^{-6}$  cm<sup>2</sup>/sec is predicted for the 2.1-lb/ft<sup>3</sup> foam. Using the latter value for the diffusion coefficient, and the weight loss data (Fig. 5), a trial-and-error procedure

yielded a value for  $Q_{\infty}$  of 148 mg. Figure 9 is a plot comparing the  $\log (Q_{\infty} - Q)$  plots for  $Q_{\infty}$  values of 203 and 148 mg. Figure 10 is a normalized plot of  $Q/Q_{\infty}$  vs time for all three Eccofoam FPH foams, and it can now be seen that the weight loss curve for the 2.1-lb/ft<sup>3</sup> foam has assumed its expected relationship in relation to the other two foams.

It should be pointed out that extrapolation to zero time of the linear portion of plots of  $\log (Q_{\infty} - Q)$  vs time should intercept at a value of  $\log (8Q_{\infty}/\pi^2)$  (Eq. 13). Thus, if the diffusion coefficient is independent of concentration, the diffusion equations will predict the value of both  $Q_{\infty}$  and  $D$  for a given set of weight loss vs time data. It was found that for the 6.4-lb/ft<sup>3</sup> foam the calculated value of  $Q_{\infty}$  coincided with that obtained by back-extrapolation, justifying the use of the perfect gas law to calculate  $Q_{\infty}$ .

However, extrapolation of the  $\log (Q_{\infty} - Q)$  plot for the 4.5-lb/ft<sup>3</sup> foam did not yield the calculated value of  $Q_{\infty} = 194$  mg. Inspection of the  $\log (Q_{\infty} - Q)$  plot for this foam shows that there is a greater drop in the initial

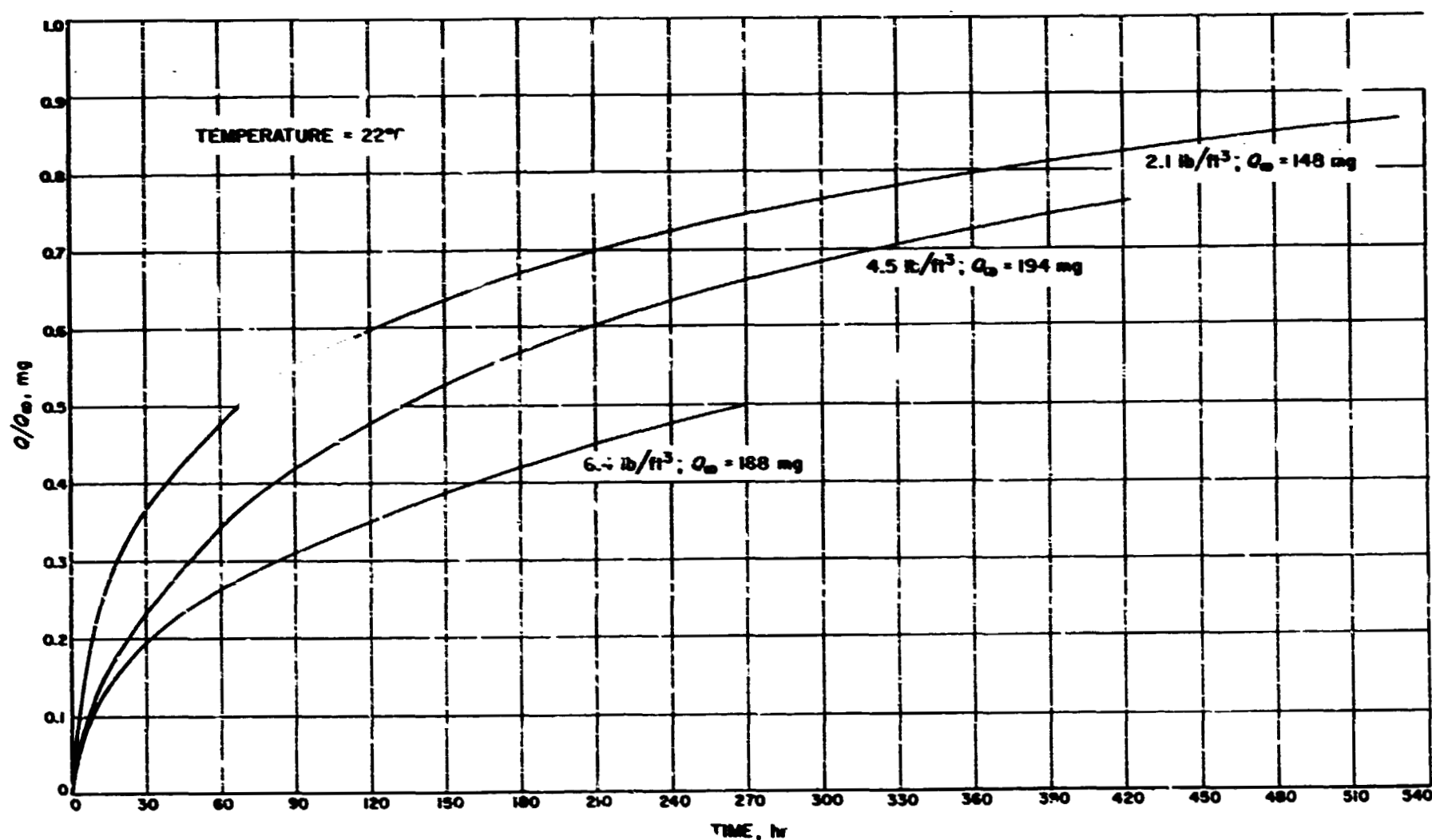


Fig. 10.  $Q/Q_{\infty}$  vs time for Eccofoam FPH foams at 22°C



portion of the curve than that observed for the 6.4-lb/ft<sup>3</sup> foam. For the 2.1-lb/ft<sup>3</sup> foam, which also failed to satisfy the equations, the drop in the initial portion of the log ( $Q_{\infty} - Q$ ) curve is greater yet. This behavior is most readily attributed to a pressure dependence of the diffusion coefficient, which becomes more pronounced with decreasing foam density. If for a polymer foam the initial diffusion coefficients are higher, then the initial portion of the log ( $Q_{\infty} - Q$ ) would drop more rapidly and then after a long time, the asymptotic diffusion coefficient can be obtained from the linear portion. But because of the initial larger drop, back-extrapolation will yield a lower value of log ( $8Q_{\infty}/\tau^2$ ), and this is observed for the 4.5- and 2.1-lb/ft<sup>3</sup> foams.

The foregoing has shown that the initial gas contents of polymer foams of densities greater than 4.5 lb/ft<sup>3</sup> can be determined from the perfect gas law. Also, there seems to be little if any dependence of the diffusion coefficient on pressure for densities greater than 6.4 lb/ft<sup>3</sup> and thus both weight loss and pressure distributions can be predicted employing a single diffusion

equation and the diffusion equations for a homogeneous solid.

Using the diffusion coefficients for the 4.5- and 6.4-lb/ft<sup>3</sup> foams, it was possible to calculate the value of the constant  $K$  in Eq. (12). This equation for the Eccofoam FPH polyurethane foams is

$$D = \frac{7.9 \times 10^{-6}}{\rho}$$

where  $D$  is in units of cm<sup>2</sup>/sec and  $\rho$  in units of lb/ft<sup>3</sup>.

The permeation constant of the bulk polyurethane polymer comprising the foam material can now be calculated from Eq. (11), using the experimentally obtained diffusion coefficients. This procedure yielded a value of  $P_e$  equal to  $5.1 \times 10^{-9}$  (cc STP) mm/sec/cm<sup>2</sup>/cm Hg, which can be compared to a value of  $12 \times 10^{-9}$  reported for rubbery polyurethanes (Ref. 2). However, a lower  $P_e$  value for the rigid foam material would be expected in comparison to the equivalent rubbery material (Ref. 2).

## V. TEMPERATURE DEPENDENCE

Outgassing rates for a 4.5-lb/ft<sup>3</sup> foam were determined at 22, 41, 61, and 81°C. The tests were conducted by first heating the samples in air to the desired temperature and then subjecting them to a vacuum. It was found,

however, that the samples heated in air would lose an amount of CO<sub>2</sub> which increased with increasing temperature. It became a practice therefore to start recording the weight loss in air during heating. When the desired

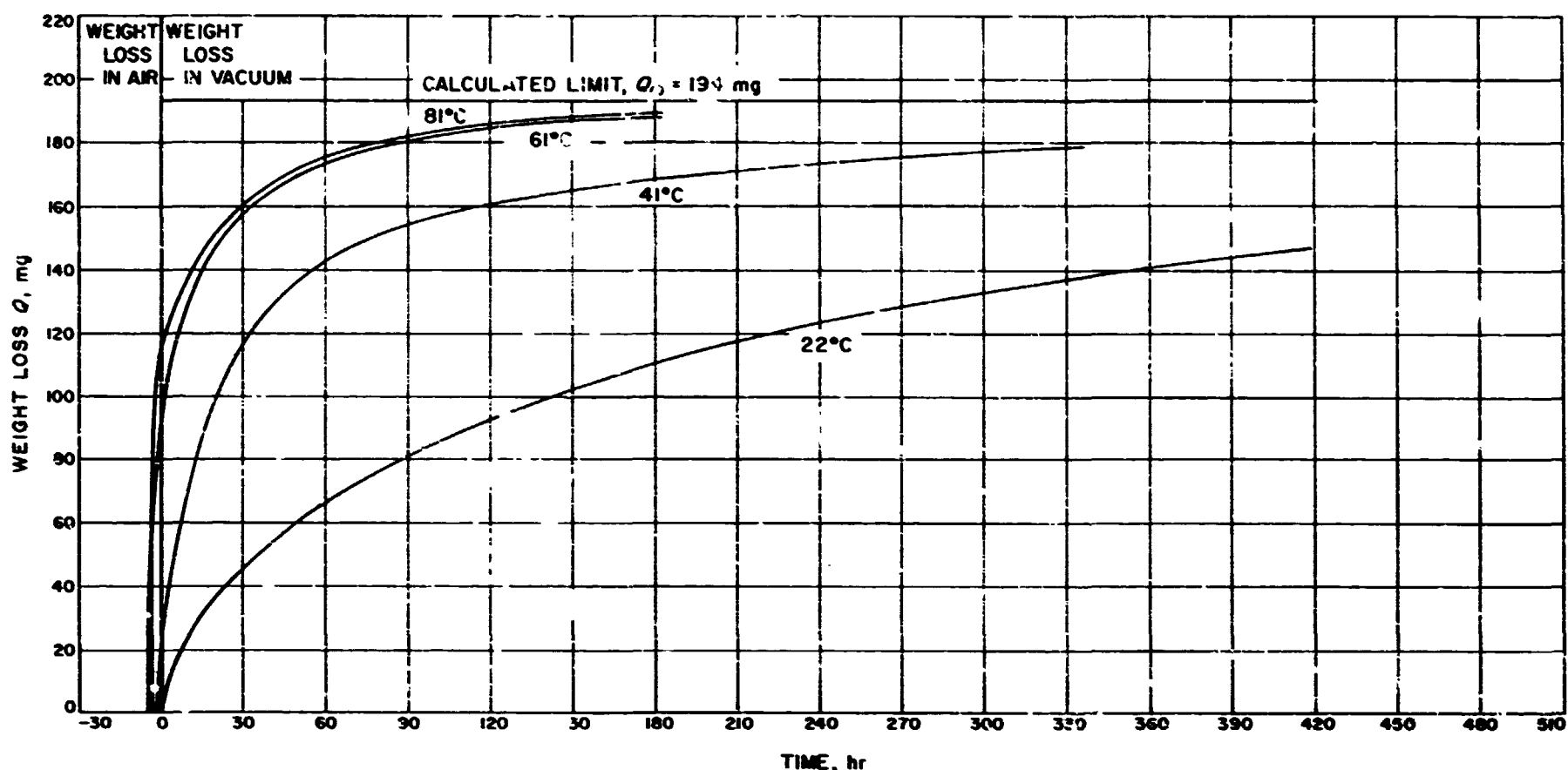


Fig. 11. Temperature dependence of the outgassing rate for an Eccofoam FPH/12/6H foam of density 4.5 lb/ft³

temperature was reached and the weight loss rate slowed significantly, vacuum was applied. The results of the tests are given in Fig. 11, which shows weight loss both in air and in vacuum with zero time taken as the point when vacuum was initiated.

The curves in Fig. 11 show a dramatic increase in the rate of gas removal with increasing temperature. The largest change occurs between 22 and 61°C. Above 61°C the changes are small. It is instructive to observe that at the higher temperatures, the weight loss asymptote appears to be the value of  $Q_{\infty} = 194$  mg, which was calculated from the perfect gas law. This further justifies the use of this value in determining the diffusion coefficients from plots of  $\log (Q_{\infty} - Q)$ . Using the same value of  $Q_{\infty} = 194$  mg, it is seen that this foam has lost approximately 97.5% of its gas content in 180 hr at 61°C and higher, whereas only 57% of the gas content was lost in 180 hr at 22°C.

The diffusion coefficients obtained at the various temperatures are plotted in Fig. 12 as  $\log D$  vs  $1/T$  in °K. The general appearance of this curve is sigmoidal and indicates that the largest changes in the diffusion coefficient occur between 22 and 81°C, above and below which there appears to be only a gradual dependence of  $\log D$  on  $1/T$ .

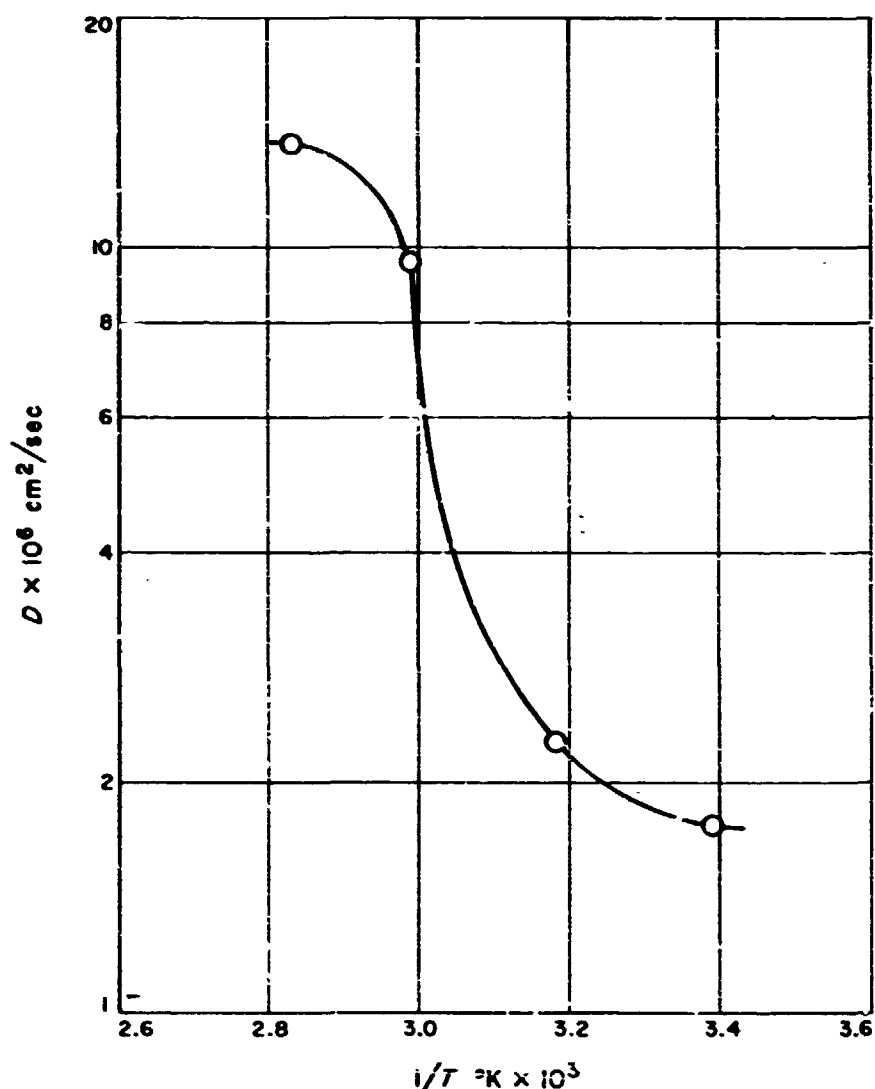


Fig. 12.  $\log D$  vs  $1/T$  °K for an Eccofoam FPH/.2/6H foam of density 4.5 lb/ft³

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