

## Interaction of Gases with Ablative Composites. II. Water\*

R. H. HONEYCUTT, III, and J. P. WIGHTMAN, *Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

### Synopsis

The sorption of water vapor on two heat shield composites SLA-561 and SLA-561V and the SLA components was measured over the pressure range of  $10^{-3}$  to 10 torr and at 25°, 30°, and 35°C. The sorption of water vapor by both the composites and the components varied directly with pressure and equilibrium was attained typically within 30 min. The sorption of water by SLA-561V, phenolic spheres, and silica fibers varied inversely with temperature. The mechanism proposed for the interaction of water vapor with the SLA composites was a combination of absorption and adsorption.

### INTRODUCTION

A review of the literature reveals little previous work concerning gas and vapor sorption by composite materials. King and Wightman<sup>1</sup> have reported sorption studies of carbon dioxide, nitrogen, and argon on the ablative composites SLA-561 and SLA-561V, silicone-based materials. SLA-561V pretreatment at 30% relative humidity caused no change in the amount of carbon dioxide sorbed. Akers et al.<sup>2</sup> have reported water sorption studies on NASA E4A1, a RTV-602 silicone elastomer filled with silica spheres, phenolic spheres and silica fibers. Type-II water sorption isotherms were obtained at 27°C, and the total water uptake at 10 torr was 150  $\mu\text{mole/g}$ . Water sorption was essentially complete within 10 min. A physisorption mechanism was postulated for the interaction of water with each component.

Water vapor sorption studies by solids typical of the components present in composites have been reported. Long and Thompson<sup>3</sup> reported that increasing relative humidity increased the diffusion coefficient of water in cellulose acetate and cellulose nitrate. Barrie and Platt<sup>4</sup> reported that the diffusion coefficient of water vapor in a poly(dimethylsiloxane) increased from  $7 \times 10^{-5}$  to  $1 \times 10^{-4}$   $\text{cm}^2/\text{sec}$  as the temperature was increased from 35° to 65°C. The water vapor capacity of the polymer increased with temperature, and no desorption hysteresis was observed.

\* Presented in part at the Symposium on the Surface Chemistry of Composite Materials, 163rd National ACS Meeting, Boston, Massachusetts, April 9-14, 1972; based in part on the M.S. Thesis of R. H. Honeycutt, III.

Barrie and Machin<sup>5</sup> reported that a poly(dimethylsiloxane) rubber filled with Aerosil 200B (a powdered silica) had a greater sorptive capacity than the unfilled rubber.<sup>4</sup> Heats of dilution for water in the filled rubber ranged from 2.6 to 3.6 kcal/mole at 0.25 and 0.75 S.T.P. cc/cc, respectively. No desorption hysteresis was observed, although sorption was faster than desorption. Isothermic heats of adsorption for water vapor on quartz particles at different surface coverages were reported by Whalen.<sup>6</sup> As the surface coverage increased from 0.25 to 1.98, the isothermic heats of adsorption decreased from 23.11 to 10.70 kcal/mole.

The objective of this work was to study the sorption of water on two ablative composites and their components as a function of pressure and temperature.

## EXPERIMENTAL

### Materials

The two ablative composites designated SLA-561 and SLA-561V were described in the previous paper.<sup>1</sup>

### Apparatus and Procedure

The water vapor sorption studies were performed in the Pyrex vacuum system diagrammed in Figure 1. Weighed rectangular test samples (0.24–1.16 g) were placed in the sample bulb (SB). The system, with stopcocks a, c, d, e, f, and i opened, was evacuated with a liquid nitrogen-trapped, mercury diffusion pump to  $<1 \times 10^{-3}$  torr, as indicated by the calibrated thermocouple gauge (TG #2: 0 to 1 torr). The sample bulb was surrounded by a constant temperature water bath which was held at 50°C during system evacuation to facilitate outgassing of the test sample. The

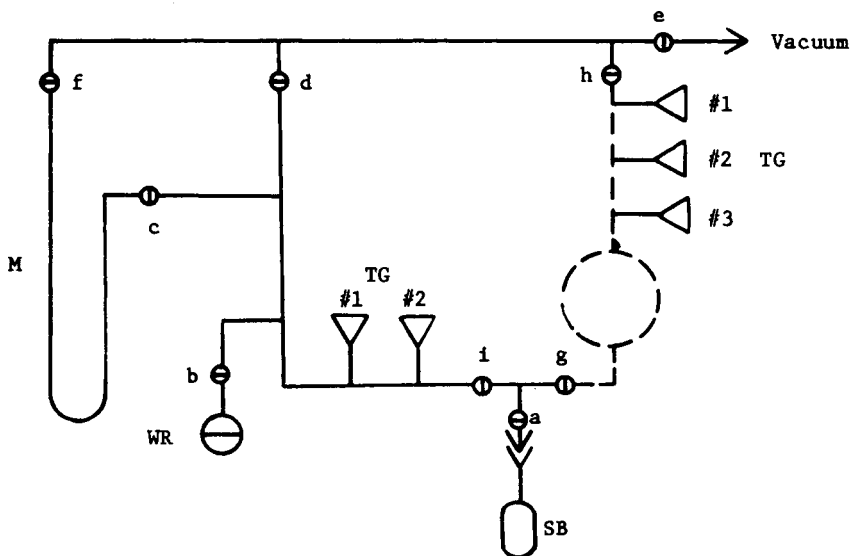


Fig. 1. Water sorption-desorption apparatus.

test samples were evacuated for a minimum of 3 hr. After adjustment of the bath temperature to 30°C, stopcocks a and d were closed and the equilibrium level of the oil manometer (M) was read using a cathetometer. Stopcock b was momentarily opened to admit water vapor into the system from the water reservoir (WR). The water had been evacuated previously several times to remove dissolved gases. The pressure was indicated by the two calibrated thermocouple gauges (TG #1: 0 to 20 torr) and TG #2 and the oil manometer. Stopcock a was then opened to expose the test sample to the water vapor.

The system pressure was monitored as a function of elapsed time using the thermocouple gauges and the oil manometer. After the change in system pressure had decreased to  $<6 \times 10^{-3}$  torr/min over a 15-min period, a final system pressure was recorded using the oil manometer. Stopcocks a and d were then opened and the entire system evacuated as before to  $<1 \times 10^{-3}$  torr, typically in 3–4 hr. The above procedure was repeated at different initial water pressures to obtain a sorption isotherm. Several runs were made using an empty sample bulb in order to determine the uptake of water vapor by the Pyrex walls of the sample bulb.

The effect of temperature on the sorption of water vapor was studied using the SLA-561V composite, the phenolic spheres, and the silica fibers. Runs were made at 25°C and 35°C for these three test samples using the sorption procedures described above.

The sorption apparatus was modified as indicated by the dashed line in Figure 1 to study desorption of water vapor from the SLA-561V composite. The test sample was placed in the sample bulb (SB) and the system, with stopcocks a, c, d, e, f, g, h, and i opened, was evacuated to  $<1 \times 10^{-3}$  torr, as indicated by the calibrated thermocouple gauge (TG #3: 0 to 0.1 torr). TG #1 and TG #2 were described above. The water bath surrounding the sample bulb was maintained at 50°C to facilitate sample outgassing during evacuation. Stopcocks d, f, g, and h were then closed and the water bath adjusted to 30°C. Stopcock b was momentarily opened to admit water vapor into the system and expose the test sample.

After the change in system pressure became  $<6 \times 10^{-3}$  torr/min over a 15-min period, the system pressure was read using the oil manometer (M). Stopcock i was then closed and stopcock g was opened. The system pressure, as indicated by the thermocouple gauges, was recorded as a function of elapsed time. After the change in the system pressure became  $<6 \times 10^{-3}$  torr/min over a 15-min period, the final pressure was recorded. Stopcocks d, f, g, h, and i were opened and the entire system evacuated to  $<1 \times 10^{-3}$  torr, as indicated by TG #3.

### Data Reduction

The number of moles of water vapor taken up per unit weight of test sample,  $N^\sigma$ , was calculated using eq. (1):

$$N^\sigma = \frac{1}{62360 W} \left[ \frac{P_1 V_1}{T_1} - \frac{P_2 V_1}{T_2} - \frac{P_2 V_2}{T_2} \right] \quad (1)$$

where  $W$  is the sample weight,  $P_1$  is the initial pressure (torr) of the system before stopcock a is opened,  $V_1$  is the system volume (cc),  $T_1$  is the ambient temperature,  $P_2$  is the final pressure of the system after stopcock a was opened and sorption equilibrium was attained,  $T_2$  is the bath temperature, and  $V_2$  is the sample bulb volume less the sample volume. Calculations were carried out on a Digital Equipment Corporation PDP-8/I computer using a FOCAL program. The results of an error analysis indicated an 8% deviation in the value of  $N^\sigma$ .

The following mass balance equation was set up for the closed desorption apparatus previously described:

$$N^\sigma = N^G + N^R - N^{SB} \quad (2)$$

where  $N^\sigma$  is the number of moles of  $H_2O$  sorbed by the sample as determined from the sorption data at 30°C for any given starting pressure,  $N^G$  is the number of moles of water vapor present as determined by the final system pressure (or amount desorbed) and total volume,  $N^R$  is the number of moles of  $H_2O$  sorbed by the sample at the final equilibrium pressure as determined from the sorption data, and  $N^{SB}$  is the number of moles of water vapor in the sample bulb before stopcock g is opened, as determined from the pressure and volume of the sample bulb.

## RESULTS AND DISCUSSION

### Sorption by the Composites

A blank water sorption run was carried out to determine if the drop in system pressure, hereafter ascribed to sorption by the test materials, might be due to adsorption of water on the glass walls of the sample bulb. The uptake of water on the sample bulb walls was found to be negligible over the pressure range of 0.4 to 15 torr.

The quantities  $N^\sigma$  of water vapor sorbed by the composites SLA-561 and SLA-561V at 30°C were calculated using eq. (1) and are shown in the semi-log plot in Figure 2 as a function of equilibrium pressure ( $P_2$ ) over the range of  $5 \times 10^{-3}$  to 10 torr. For each composite, the amount of water sorbed increased as the equilibrium pressure increased. At 7.6 torr, the water sorbed by SLA-561V was 370  $\mu\text{mole/g}$  or  $6.7 \times 10^{-3}$  g  $H_2O/g$ , which represents a weight increase of 0.67%. Comparison of the water sorption isotherms at 30°C for SLA-561 and SLA-561V at equal final pressures indicates that over the pressure range of 0.1 to 10 torr, SLA-561V sorbs about 18% less water than SLA-561.

The point labeled A in Figure 2 corresponds to the amount of  $CO_2$  sorbed by SLA-561V at a final pressure of 10 torr.<sup>1</sup> At this pressure, the sorption of water by SLA-561V is two orders of magnitude greater than the sorption of  $CO_2$ . These quantitative water vapor sorption results are significant since there have been repeated references to the role of sorbed water in the properties of these composites but no reported data of actual water uptake. For example, Ward and Evans<sup>7</sup> have ascribed observed changes in storage

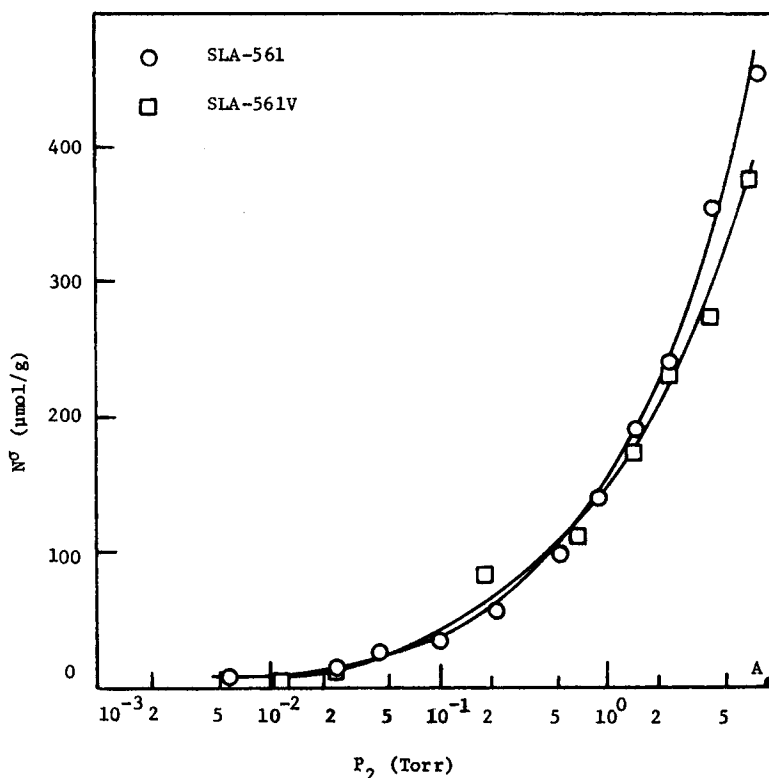


Fig. 2. Sorption of water by SLA-561 and SLA-561V at 30°C.

modulus and log decrement of SLA-561 to a changing water concentration in the composite. The amount of water taken up as measured in this work could account for the observed property changes.

A typical plot of pressure as a function of elapsed time is shown in Figure 3 for SLA-561V. The sorption of the water by SLA-561V as shown in Figure 3 is 92% complete within 5 min. All sorption runs were terminated within 60 min, since the condition that the change in system pressure be  $< 6 \times 10^{-3}$  torr/min over a 15-min period was always satisfied within 60 min. In contrast, the time needed for completion of water sorption is two to three times faster than for completion of argon, carbon dioxide and nitrogen sorption on SLA-561 and SLA-561V.<sup>1</sup>

### Sorption by the Components

The quantities  $N^s$  of water sorbed by the SLA-561 and SLA-561V components at 30°C were calculated using eq. (1) and are shown in Figures 4 and 5 as a function of pressure over the range of 0.1 to 12 torr. The quantity of water sorbed by the components increased with increasing pressure.

The order of water sorption at 30°C per gram of component at 3 torr is phenolic spheres >cork >carbon-silica fiber mixture>silica spheres. A

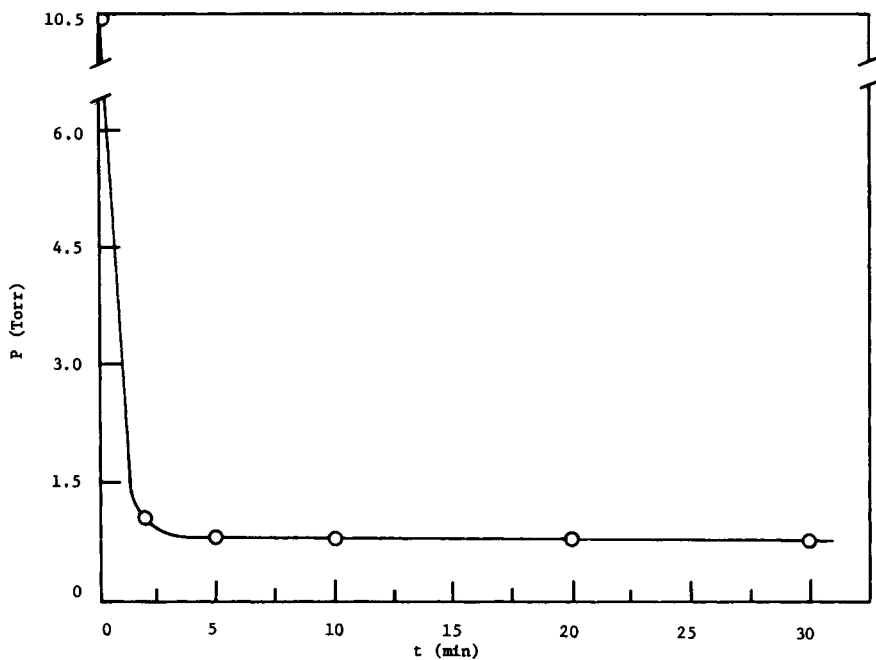


Fig. 3. Pressure-time plot for water on SLA-561V.

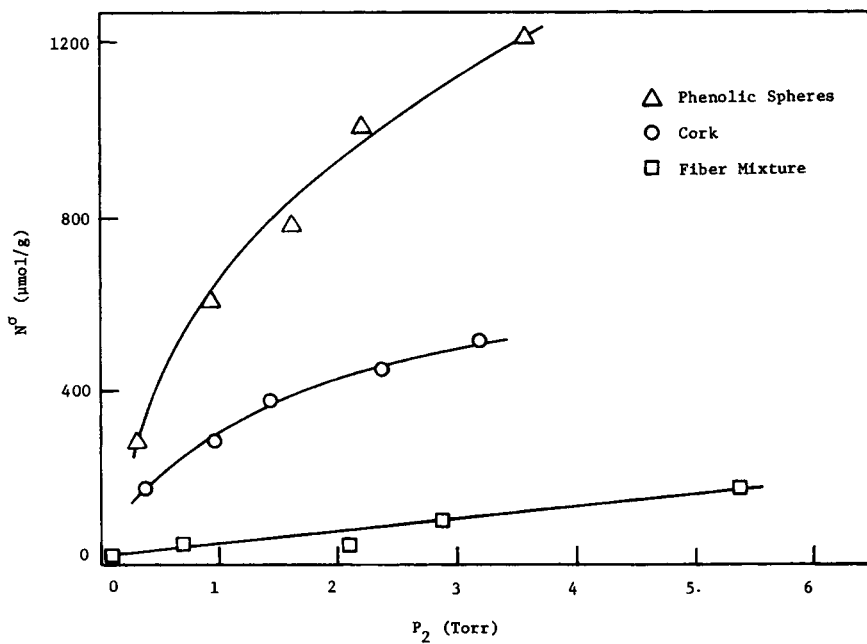


Fig. 4. Sorption of water by the phenolic spheres, cork, and fiber mixture at 30°C.

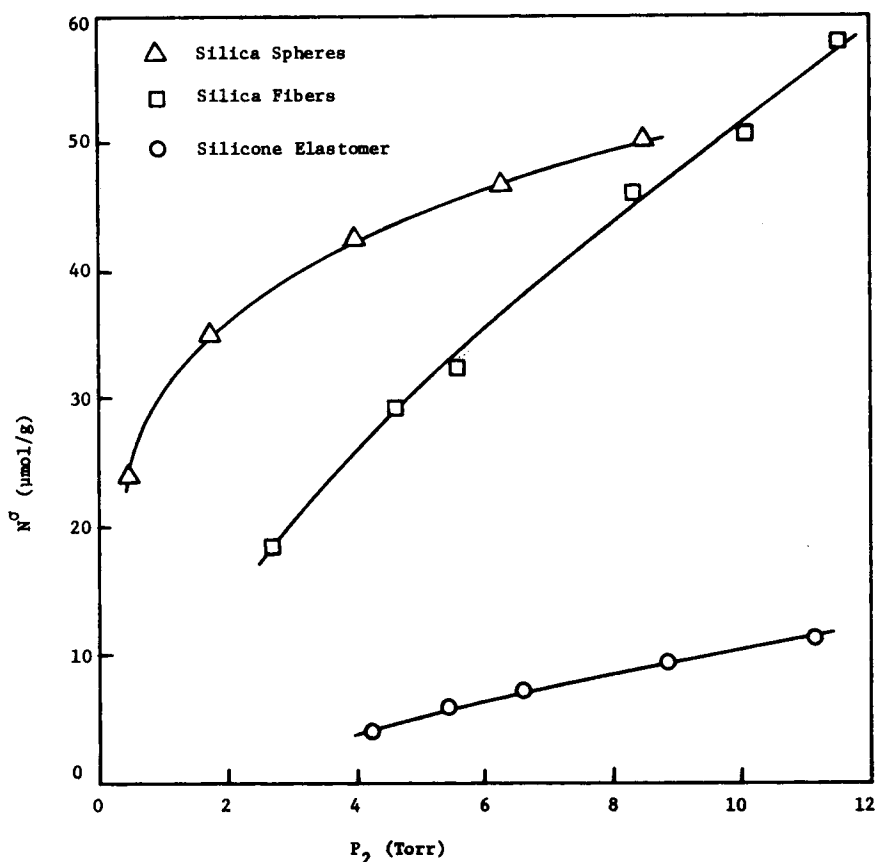


Fig. 5. Sorption of water by the silica spheres, silica fiber, and silicone elastomer at 30°C.

comparison of  $N^\sigma$  values at equal pressures (Figs. 4 and 5) shows that the carbon-silica fiber mixture sorbed about five times more water than the silica fibers. Thus, the smaller uptake of water by SLA-561V is attributed to the replacement of the carbon-silica fiber mixture in SLA-561 by the silica fibers.

The question arises whether sorption by the individual components sums to give the total sorption by the composite. The results of the calculations given in Table I indicate that the total uptake of water by the components is within 10% of the value obtained for the composite. This indicates that the sorption of water by the composites can be treated as a simple sum of the sorption of water by the components. This additivity was not observed for the interaction of argon, nitrogen, or carbon dioxide with the same composite materials.<sup>1</sup> This also indicates that the silicone elastomer, which showed little water sorption (Fig. 5) at 30°C, does not significantly affect the ability of water to interact with the components.

The carbon-silica fiber mixture, the silica fibers, and the silica spheres showed very rapid water sorption at 30°C, and the sorption was virtually

TABLE I  
Comparison of Component and Composite Uptake of Water at 30°C

System	Total Uptake, <sup>a</sup> μmole/g	% Deviation
Phenolic spheres	70.2	
Cork	183.5	
Carbon-glass fiber mixture	7.3	
Glass spheres	11.1	
Silicone elastomer	1.0	
	Σ = 273.1	
SLA 561	303	9.9
Phenolic spheres	70.2	
Cork	183.5	
Silica fibers	1.4	
Glass spheres	11.1	
Silicone elastomer	1.0	
	Σ = 267.2	
SLA 561V	243.	10.0

<sup>a</sup> At 3 torr.

TABLE II  
BET Surface Areas

Material	Surface area, m <sup>2</sup> /g
Phenolic spheres	110.
Silica spheres	2.45
Silica fibers	2.97

complete after 30 min. The phenolic spheres and cork showed significant water sorption at 30°C after 30 min, but sorption was completed only after 60 min. After the first 5 min, water uptake on the silicone elastomer is about 94% complete. However, all water sorption runs on the silicone elastomer were extended to 3 hr to meet the conditions previously stated for determining the equilibrium pressure. One run was extended to 1470 min, with no further significant water uptake after 180 min. Thus, the slow rate of sorption could be attributed to the low diffusion coefficient previously noted (4) for water in polydimethylsiloxane.

BET surface areas were determined for the phenolic spheres, silica spheres and silica fibers based on the water sorption isotherms. The surface areas were calculated using an assigned cross-sectional area of 10.4 Å<sup>2</sup> for an adsorbed water molecule. The results are shown in Table II. The similar surface areas of the silica spheres and the silica fibers indicate that the two materials are very similar in their interaction with water vapor. The phenolic spheres and the silica spheres should have similar surface areas based on particle size data. The very high surface area of the phenolic



spheres compared to the glass spheres indicates that the two materials have very different interactions with water.

**Temperature Studies on Sorption of Water**

Water sorption isotherms at 25°, 30°, and 35°C are presented in Figures 6, 7, and 8 for SLA-561V, phenolic spheres, and silica fibers, respectively. Except for the phenolic spheres, the amount of water sorbed decreased as the temperature increased. The uptake of water by the phenolic spheres is seen in Figure 7 to be greater at 30°C than at 25°C.

Heats of interaction  $\Delta H_i$  were determined for water with SLA-561V and the silica fibers based on the van't Hoff equation:

$$\Delta H_i = -R[(d \ln P)/d (1/T)]_{N^\sigma} \tag{3}$$

The results of these calculations are shown in Table III. Values of  $\Delta H_i$  for the silica fibers vary with  $N^\sigma$  as reported in a similar study by Whalen.<sup>6</sup> The isosteric heat of adsorption ( $\Delta H_i$ ) of water on quartz particles was reported by Whalen to decrease from 23.11 to 16.89 kcal/mole as  $N^\sigma$  increased from 27.7 to 55.5  $\mu\text{mole/g}$ ;  $\Delta H_i$  for SLA-561V does not vary significantly with  $N^\sigma$ .

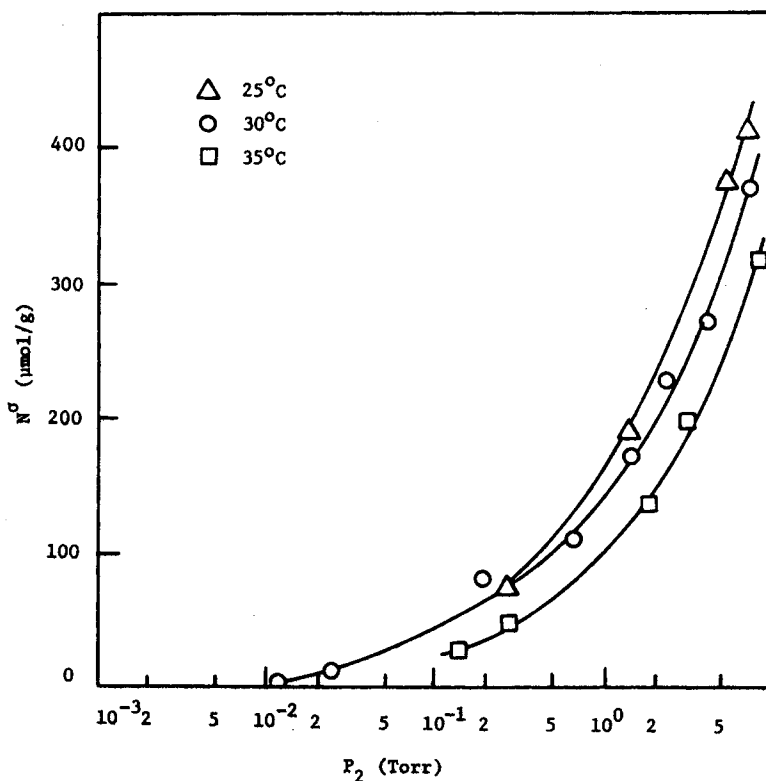


Fig. 6. Sorption isotherms of water on SLA-561V.

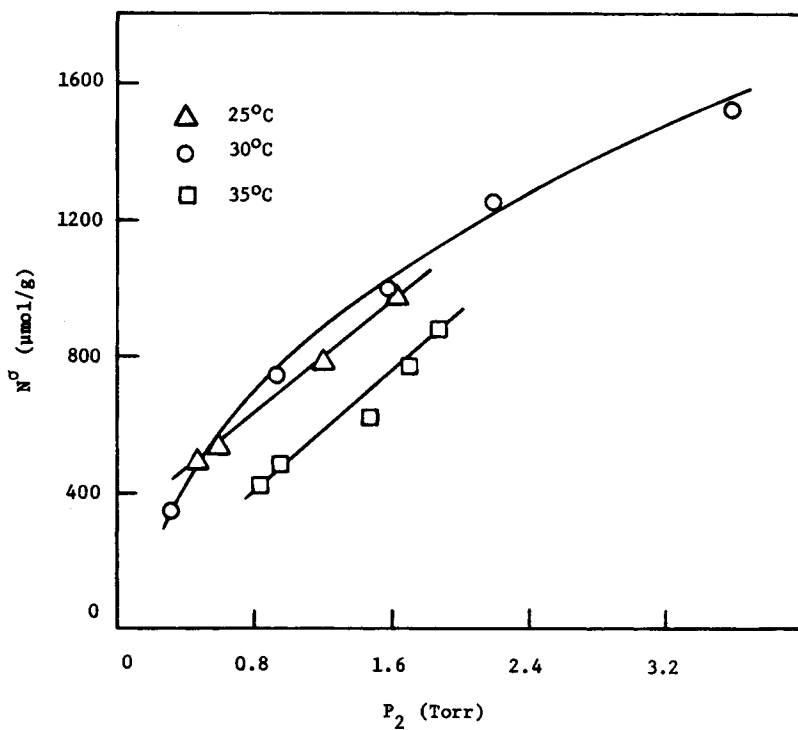


Fig. 7. Sorption isotherms of water on phenolic spheres.

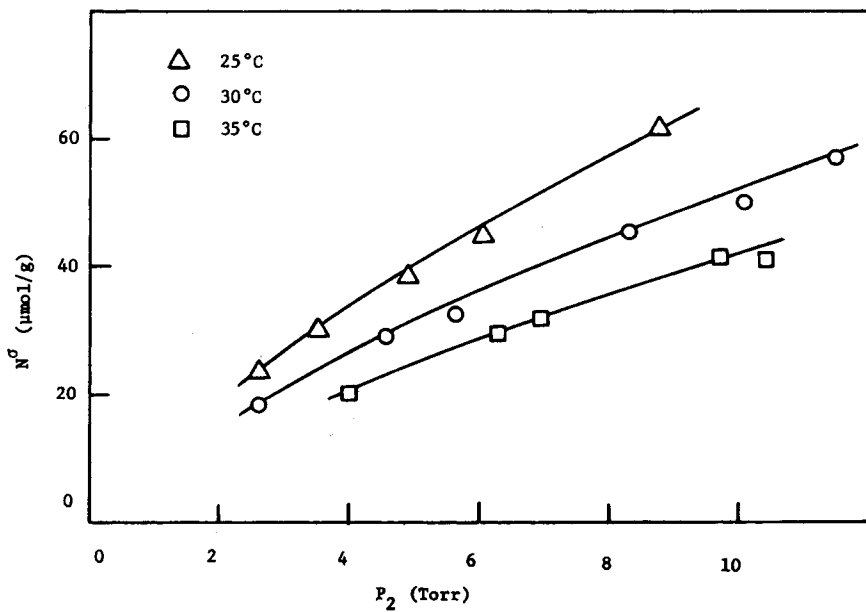


Fig. 8. Sorption isotherms of water on silica fibers.

TABLE III  
Heats of Interaction of Water Vapor

Material	$N^{\sigma}$ , $\mu\text{mole/g}$	$\Delta H_i$ , kcal/mole
Silica fibers	23.7	16.3
	35.6	12.5
	47.5	13.8
SLA-561V	240.	13.4
	300.	13.2
	360.	13.4

### Desorption of Water Vapor

A typical pressure-time plot obtained for the desorption of water from SLA-561V is shown in Figure 9. A comparison of the pressure-time plots for sorption (Fig. 3) and desorption indicates little difference in the times involved for the two processes to occur. The mass balance for the desorption process is shown graphically in Figure 10. The symbols used in Figure 10 were defined in the discussion of eq. (2). The fact that the sum and  $N^{\sigma}$  curves in Figure 10 do not overlap can be attributed to experimental error in the measurements. There is little hysteresis evident in the desorption process. Although desorption from the individual components was not studied, the silicone elastomer has been shown to display no desorption hysteresis.<sup>4</sup>

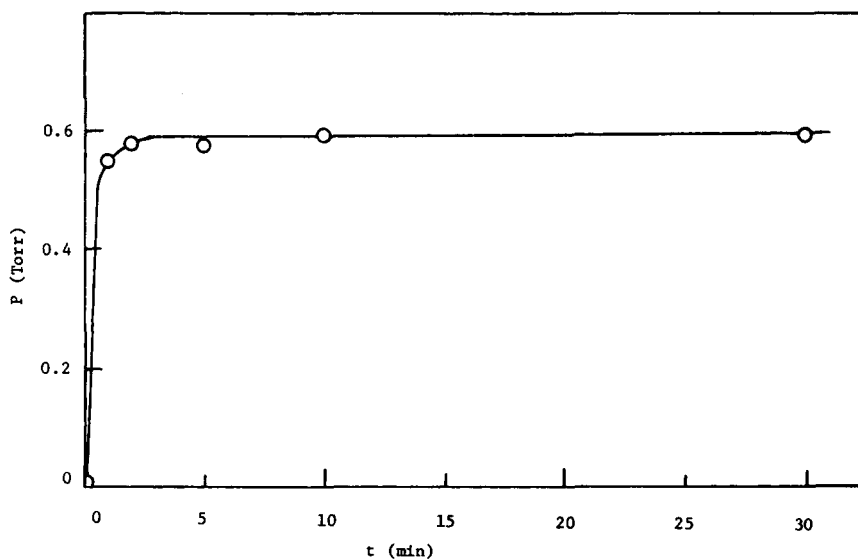


Fig. 9. Pressure-time plot for desorption of water from SLA-561V at 30°C.

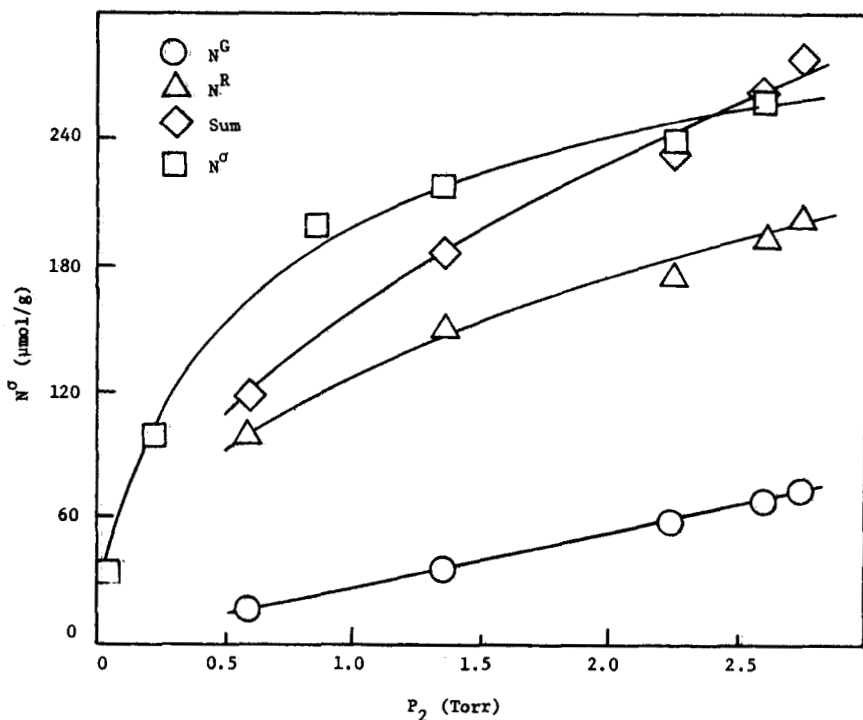


Fig. 10. Mass balance for water desorption from SLA-561V at 30°C.

### Mechanism of Water Sorption

The results of the sorption studies on the components indicate that absorption is the primary mechanism for the interaction of water with the silicone elastomer, the phenolic spheres, and the ground cork. This conclusion is based on the long equilibration time for the silicone elastomer supported by the reported low values of the water diffusion coefficient,<sup>4</sup> the measured high water surface area of the phenolic spheres, and the large uptake of water by the cork analogous to the phenolic spheres. The very small interaction between water and the silicone elastomer may be attributed to the nonpolar character of the polymer. The large interaction of water with the phenolic spheres may be attributed to water being soluble in the highly polar phenol based polymer. Akers et al.<sup>2</sup> erroneously attributed the uptake of water by phenolic spheres to adsorption rather than absorption since the water surface area of the phenolic spheres were not measured. Since cork is an ill-defined material, little can be said about the specific water-cork interaction except to assume that the structure is cellulose, which has been shown to sorb significant amounts of water.<sup>3</sup>

The results of the sorption studies indicate that adsorption is the primary mechanism for the interaction of water with the silica spheres, silica fibers, and the carbon-silica fiber mixture. This conclusion is based on the very

rapid equilibration times, the relatively low uptake of water and the magnitude of the heat of interaction for water and the silica fibers. The absence of desorption hysteresis indicates that water diffusion into any pores present is not significant. Therefore, the interaction of water with the composite materials of this study, SLA-561 and SLA-561V, is a combination of absorption and adsorption.

### CONCLUSIONS

The following conclusions are based on the study of the interaction of water vapor with SLA-561, SLA-561V, and the SLA components over the pressure range of  $10^{-3}$  to 10 torr and the temperature range of 25° to 35°C:

1. The sorption of water vapor by SLA-561, SLA-561V, and the SLA components varied directly with pressure. The order of water uptake by the composites was SLA-561 > SLA-561V. The order of water uptake by the SLA components was phenolic spheres > cork > carbon-silica fibers > silica fibers > silica spheres > silicone elastomer.

2. Equilibrium water sorption times for the composites and the SLA components were typically 30 min, except for the silicone elastomer, which were typically 180 min. Desorption and sorption times for SLA-561V were of the same order of magnitude, and no hysteresis was observed.

3. The sorption of water by SLA-561V, the phenolic spheres and silica fibers varied inversely with temperature.

4. The sum of the individual-component water vapor uptakes accounts for the total uptake by the SLA composites.

5. The mechanism of water vapor interaction with SLA-571 and SLA-561V is a combination of absorption by the phenolic spheres, cork, and the silicone elastomer and adsorption by the carbon-silica fibers, silica fibers, and silica spheres.

Financial support for this work under NASA Grant NGR 47-004-016, including a graduate research assistant for one of us (R.H.H.), is gratefully acknowledged. The authors thank Mr. John P. Mugler, Jr., for examining this manuscript and making helpful suggestions.

### References

1. C. A. King and J. P. Wightman,
2. F. I. Akers, W. H. Griest, R. K. Lengel, and J. P. Wightman, *J. Spacecraft and Rockets*, **7**, 1135 (1970).
3. F. A. Long and L. J. Thompson, *J. Polym. Sci.*, **15**, 413 (1955).
4. J. A. Burrie and B. Platt, *Polymer*, **4**, 3031 (1963).
5. J. A. Barrie and D. Machin, *J. Macromol. Sci.—Phys.*, **B3**, 673 (1969).
6. J. W. Whalen, *J. Phys. Chem.*, **65**, 1676 (1961).
7. T. C. Ward and M. L. Evans, NASA Contractor Report, NASA CR-2074, Washington D.C., 1972.

Received June 26, 1973

Revised August 30, 1973