

Interaction of Gases with Ablative Composites.

I. Ar, CO₂, and N₂*

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Synopsis

The sorption of argon, carbon dioxide, and nitrogen on two heat shield composites SLA-561 and SLA-561V and the SLA components was measured over the pressure range of 10⁻³ to 760 torr and in the temperature range of 30° to 50°C. The sorption of the gases by both the composites and the components varied directly with pressure. The sorption of CO₂ by the phenolic spheres and the silicone elastomer and of Ar by the silicone elastomer varied inversely with temperature. The mechanism involved in the gas sorption was primarily absorption.

INTRODUCTION

The interaction of gases and vapors with composites may affect the composites' properties and hence the sorption of gases by composite materials including ablators is an area of fundamental interest. Mugler et al.¹ reported a 15% vacuum-induced decrease in the thermal conductivity of an ablator; reexposure of the ablator to the atmosphere for 24 hr caused the thermal conductivity to revert to substantially its preexposure value. Similarly, Keshock² has shown that the thermal conductivity of several ablators was a function of gas pressure. These results suggest that gas sorption-desorption, which is known to be pressure dependent,³ may at least be partially responsible for the observed changes in thermal conductivity. On the other hand, it is also known that the thermal conductivity of gas-filled porous solids decreases below a characteristic pressure related to the pore size of the material. This decrease occurs even in the case where there is no interaction between the gas and the solid. Ward and Evans⁴ have postulated that the viscoelastic behavior of polymeric-based materials was affected by water sorption-desorption.

The NASA Viking Project involved in part the selection of an ablative material to be used for entry into the Martian atmosphere. One proposed model of the Martian atmosphere includes argon, carbon dioxide, and nitrogen. The objective of this work was to study the sorption of argon,

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carbon dioxide, and nitrogen on two ablative composites and their components as a function of pressure and temperature.

EXPERIMENTAL

Materials

The following gases were used in this study: argon (prepurified), carbon dioxide (Coleman instrument grade), and nitrogen (prepurified).

Two ablative composites designated SLA-561 and SLA-561V were supplied by the Martin-Marietta Company. The SLA samples were placed in a desiccator at 30% relative humidity (saturated aqueous sodium chloride solution) on receipt. Both SLA composites consisted of a silicone elastomer matrix filled with phenolic spheres, glass spheres, and Armstrong ground cork (20/40 prime milled). The difference between the two composites was that SLA-561 contained a mixture of carbon fibers (Special Products, Inc.) and glass fibers (Haveg Industries), whereas SLA-561V contained only glass fibers. The GE silicone resin was RTV-651A. The particle size of the phenolic spheres (phenolic microballoons, Union Carbide) and the glass spheres (eccospheres, Emerson-Cuming) ranged from 5 to 125 μ and 30 to 125 μ , respectively. The above components were also supplied by the Martin-Marietta Company.

Apparatus and Procedure

The medium-pressure (10 to 150 torr) sorption runs were carried out in a constant-volume mercury manometer system shown schematically in Figure 1. The weighed sample ($1 \times 1 \times 11$ cm) was placed in the sample

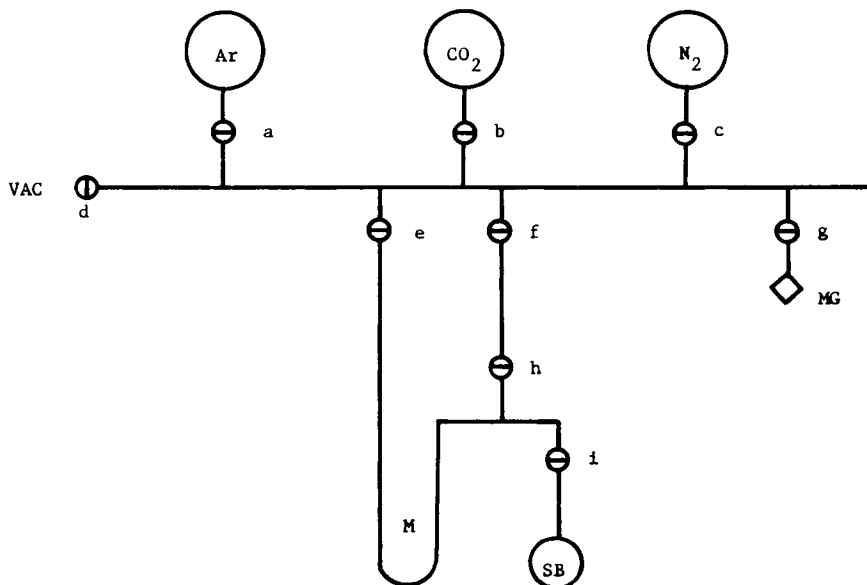


Fig. 1. Schematic diagram of sorption apparatus.

bulb (SB) and evacuated to an ultimate pressure typically $<1 \times 10^{-5}$ torr. The base pressure was read on a McLeod gauge (MG) with stopcocks d, e, f, g, h, and i open while stopcocks a, b, and c were closed. The entire system was pumped by a mechanical pump backed by a liquid-nitrogen trapped custom diffusion pump which had a rated pumping speed of 5 l./sec at 10^{-4} torr. Stopcocks d, e, g, and i were closed, and a known pressure of gas (argon, carbon dioxide, or nitrogen) was admitted through either a, b, or c from the respective storage bulbs. Stopcock h was closed and the pressure in the dose volume was read on a mercury manometer (M) with a cathetometer. The right side of this manometer was always positioned at the same height for each pressure reading thus maintaining a constant system volume at all times. Stopcock i was opened, and the pressure drop due to uptake of gas by the solid sample was followed as a function of time. The run was considered complete when there was no observable pressure change for at least 60 min.

The same procedure was used for a blank run in which carbon dioxide was expanded into an empty sample bulb. Likewise the same procedure was used to study the effects of varying the length of time (2 and 14 days) of pretreatment at 30% relative humidity of the SLA-561V composite on gas uptake. Again, the same procedure was used to study the effect of sample size on gas uptake. Sorption runs were made at 30°, 40°, and 50°C by immersion of the sample bulb in a constant temperature water bath. Room temperature was monitored in all sorption runs. The dose volume needed in subsequent calculations was determined by expansion of argon from a calibrated volume into the sample system. The volume of the calibrated bulb which replaced the sample bulb (SB) was determined by weighing with and without mercury.

The high-pressure (150 to 760 torr) runs were carried out in a similar manner, except that a larger dose volume was added between stopcocks f and h so as to obtain higher equilibrium pressures. The low-pressure (10^{-3} to 10 torr) studies were carried out in a similar apparatus as above, using calibrated thermocouple gauges to monitor the pressure instead of the mercury manometer.

Data Reduction

The number of moles of gas sorbed per gram of solid (N^{σ}) was calculated by eq. (1):

$$N^{\sigma} = \frac{1}{(82.054)(760)(W)} \left[\frac{P_1 V_1}{T_1} - \frac{P_2 V_1}{T_1} - \frac{P_2 V_2}{T_1} - \frac{P_2 V_3}{T_2} \right] \quad (1)$$

where volumes (cc) V_1 , V_2 , and V_3 are the dose volume, volume above constant temperature bath, and volume below bath, respectively; P_1 and P_2 are the pressures (torr) in the dose volume before expansion and the final pressure in the system after expansion and equilibration with the solid, respectively; and T_1 and T_2 are the room and bath temperatures, respectively. The sample weight is W . It was assumed over the pressure range

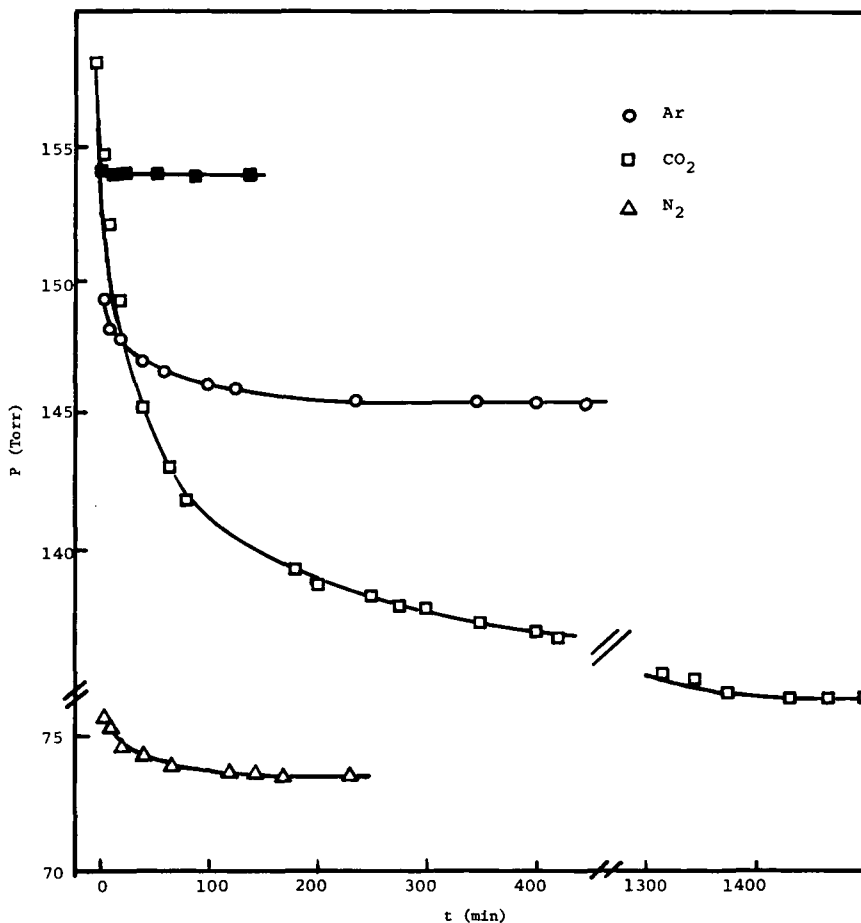


Fig. 2. Typical pressure-time plots on exposure of SLA-561 to argon, carbon dioxide, and nitrogen.

studied that there was a negligible temperature gradient between V_2 and V_3 . Values of P_2 were obtained from typical pressure-time plots shown in Figure 2 for sorption of argon, carbon dioxide, and nitrogen on SLA-561 at room temperature. Calculations were carried out using a FOCAL program written for a Digital Equipment Corp. PDP-8I computer. The results of an error analysis indicate a 14% error in the value of N^* .

RESULTS AND DISCUSSION

A scanning electron photomicrograph ($\times 200$) of the SLA-561V composite is shown in Figure 3. The honeycomb-like structure at the upper right is a piece of cork. Broken fragments of the glass spheres and glass fibers are seen. The components are distributed randomly in the composite.

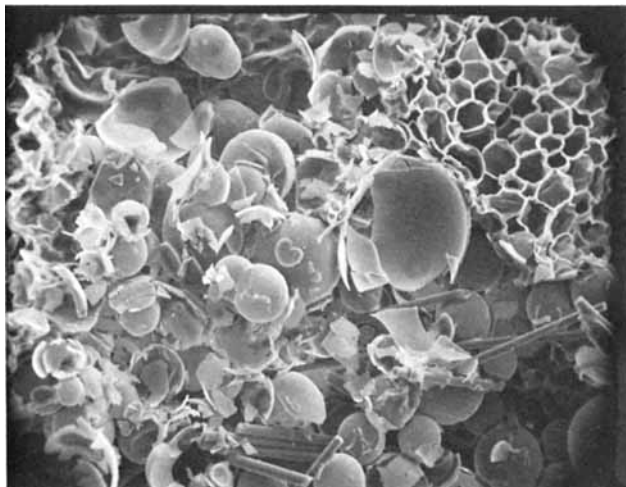


Fig. 3. Scanning electron photomicrograph ($\times 200$) of the SLA-561V composite.

Composite Sorption

A blank run was carried out to see if the drop in pressure which was ascribed to sorption by the materials might be due to a number of other factors, including sorption on the glass walls or a temperature effect due to the cooling of the gas upon expansion. The pressure-time plot for the expansion of carbon dioxide (the most nonideal gas studied) into an empty sample bulb is shown by the closed symbols in Figure 2. Note that after the initial expansion, there is no further drop in pressure as was observed in many of the sorption runs. Thus, it was concluded that the pressure drops observed in many of the runs were due exclusively to sorption by the solids.

It is to be noted from Figure 2 that the times to reach equilibrium on exposure of the gases to SLA-561 were of the order of several hundred minutes. Examining the pressure-time plots for 22 runs on SLA-561 and SLA-461V, sorption times for carbon dioxide were typically 500 min, whereas both argon and nitrogen were typically 100 min. The results of desorption experiments of argon and carbon dioxide on SLA-561V suggest that there is no wide discrepancy between times of sorption and desorption.

The quantity (N^s) of argon, carbon dioxide, and nitrogen sorbed per gram of SLA-561 (open symbols) and SLA-561V (closed symbols) at 30°C as a function of equilibrium pressure (P_2) over the range of 50 to 760 torr is shown in Figure 4. Values of N^s were calculated by eq. (1), and values of P_2 were obtained from the pressure-time plots. Sorption of each gas increases as the equilibrium pressure increases. Carbon dioxide is taken up to a greater extent than argon and nitrogen. The difference in the amounts of argon and nitrogen sorbed is not significant. In comparing the sorption of SLA-561 and SLA-561V, it was found that SLA-561V showed a reduced uptake for all gases studied.

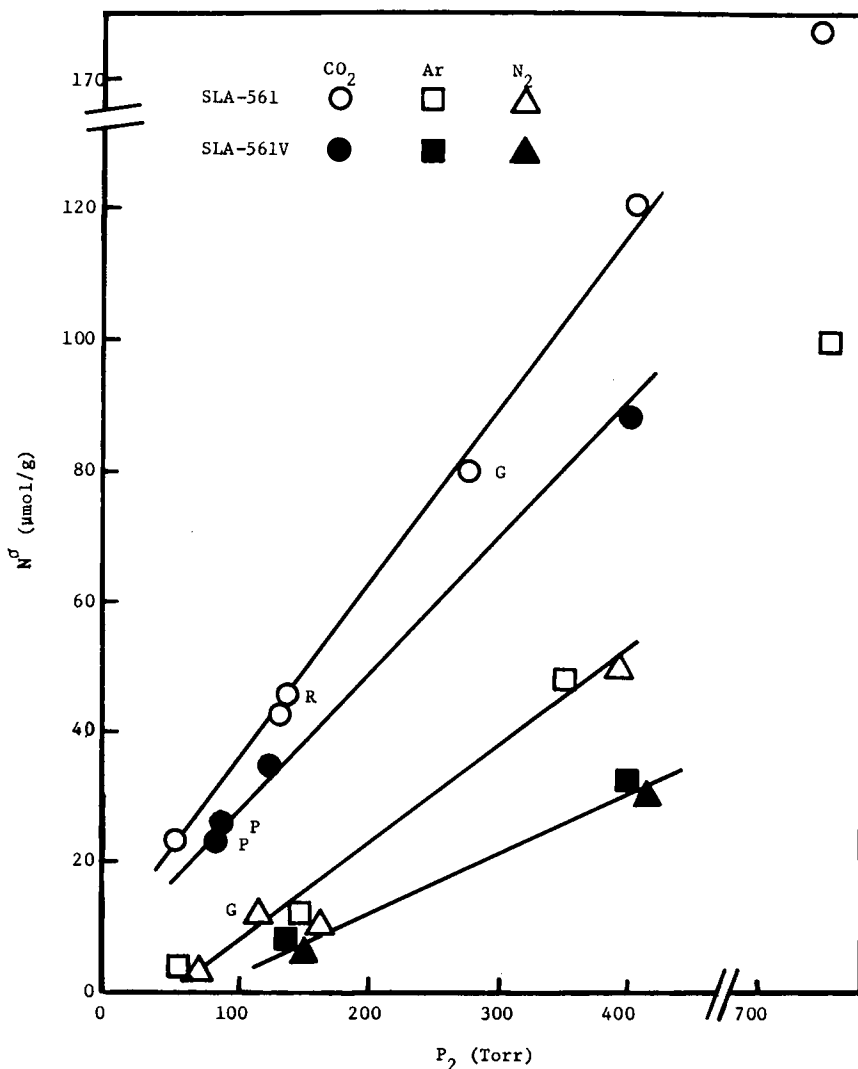


Fig. 4. Sorption of argon, carbon dioxide, and nitrogen on SLA-561 and SLA-561V as a function of pressure at 30°C .

The two points labeled G in Figure 4 are runs showing that varying the size (from $1 \times 1 \times 11$ cm to $1 \times 3.8 \times 12.4$ cm) of the SLA-561 samples does not affect the equilibrium sorption of carbon dioxide or nitrogen. A comparison of the pressure-time plots for these two sample shapes shows that the larger sample takes up gas at a higher initial rate than the smaller sample. The results of the pretreatment studies for the sorption of argon, carbon dioxide, and nitrogen on SLA-561V at about 100 torr are shown by the points labeled P. It is noted that exposure of SLA-561V to 30% relative humidity for 2 or 14 days does not affect significantly the amount of

carbon dioxide sorbed. The point labeled R is a repeat run which shows the reproducibility of carbon dioxide sorption.

Component Sorption

Since the SLA-561 composites consisted of several components, it was of interest to determine how much of each gas was taken up by each component. The quantity (N°) of argon, carbon dioxide, and nitrogen sorbed per gram on the components of SLA-561 and SLA-561V at 30°C as a function of equilibrium pressure over the range of 20 to 280 torr is shown in Figure 5. Again, the quantity of gas taken up by the components in-

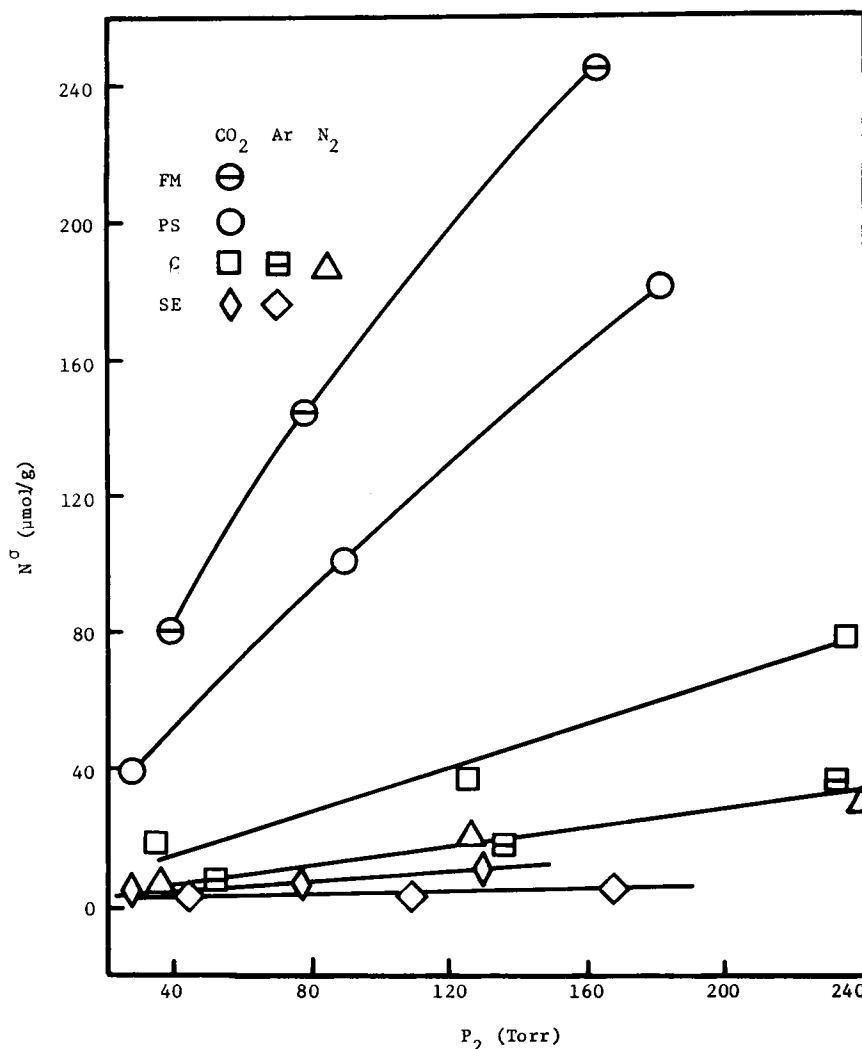


Fig. 5. Sorption of argon, carbon dioxide, and nitrogen by the components of the SLA composites as a function of pressure at 30°C.

TABLE I
Relative Per Cent Uptake of Ar, CO₂, and N₂ on the Components
of the SLA Composites*

Component	SLA-561			SLA-561V		
	Ar, %	CO ₂ , %	N ₂ , %	Ar, %	CO ₂ , %	N ₂ , %
SS	0	0	0	0	0	0
PS	0	35	0	0	76	0
C	60	10	100	60	21	100
SE	40	2	—	40	3	—
FM	0	53	0	X	X	X
GF	X	X	X	0	0	0

* All values based on 100 torr from Fig. 5. Silica spheres (SS), phenolic spheres (PS), cork (C), silicone elastomer (SE), fiber mixture (FM), glass fibers (GF). (—) not determined; (X) component not present.

creased with increasing equilibrium pressure. The relative extent of interaction for such gas-component combination is shown in Table I. Clearly, the fact that CO₂ is sorbed by both SLA composites to a greater extent than argon and nitrogen is due to its greater interaction with the components, particularly the fiber mixture and the phenolic spheres. The substitution of the glass fibers for the fiber mixture accounts for the smaller uptake of CO₂ by SLA-561V compared to SLA-561 as noted in Figure 4.

Solubility coefficients for argon and carbon dioxide in silicone elastomer were determined to be 0.05 and 0.24 NTP cc/cc, respectively, at 100 torr. Van Amerongen⁵ reported values of 0.081 and 0.43 NTP cc/cc silicone rubber for nitrogen and carbon dioxide, respectively, at 1 atm. Although the polymers are not the same, it is of interest to note that the values are of the same order of magnitude with CO₂ showing the greater solubility in both cases.

The question arises whether sorption by the individual components sums to give the total sorption by the composites. The results of calculations given in Table II indicate that the uptake of gases by the component is somewhat less in every case than the composite. The fact that additivity accounts for a majority of the sorption by the composite is an interesting and significant result. Akers et al.⁶ have shown previously the additivity of component uptake on a different composite system.

Temperature Effect on Component Sorption

The temperature effect on gas uptake by the components was studied to support possible gas sorption mechanisms. The quantity (N°) of carbon dioxide sorbed per gram of phenolic spheres at 30°, 40°, and 50°C as a function of equilibrium pressure (P_2) over the range of 40 to 180 torr is shown in Figure 6. Similar results for the sorption of argon and carbon dioxide on silicone elastomer at 30°, 40°, and 50°C are presented in Figure 7. A negative temperature dependence of gas sorption was observed. Since a temperature effect on sorption was observed, it was of interest to

TABLE II
Comparison of Component and Composite Uptake

System ^a	N^σ , $\mu\text{mole/g}$	Total uptake, $\mu\text{mole/g}$	% Completion
CO ₂ /SLA-561	31.0 ^b	31.0	
CO ₂ /C	30.0 ^c	8.67	
CO ₂ /FM	169	8.78	
CO ₂ /PS	106	6.16	
CO ₂ /SE	6.93	1.76	
		sum	25.37
			82
Ar/SLA-561	7.00	7.00	
Ar/C	13.8	3.97	
Ar/SE	1.13	.03	
		sum	4.00
			57
N ₂ /SLA-561	7.0	7.00	
N ₂ /C	13.8	3.97	
N ₂ /SE		(.03) ^d	
		sum	4.00
			57
CO ₂ /SLA-561V	27.5	27.5	
CO ₂ /C	30.0	8.67	
CO ₂ /PS	107	6.16	
CO ₂ /SE	6.93	1.76	
		sum	15.6
			62
Ar/SLA-561V	6.00	6.00	
Ar/C	13.8	3.97	
Ar/SE	1.13	.03	
		sum	4.00
			67
N ₂ /SLA-561V	6.00	6.00	
N ₂ /C	13.8	3.97	
N ₂ /SE		(.03) ^d	
		sum	4.00
			67

^a Component symbols same as in Table I.

^b All N^σ values for composites from Figure 4 at 100 Torr.

^c All N^σ values for components from Figure 5 at 100 Torr.

^d Not available—assume like Ar/SE.

determine heats of interaction for the following systems: (1) carbon dioxide-phenolic spheres, (2) carbon dioxide-silicone elastomer, and (3) argon-silicone elastomer. Heats of interaction ΔH_i were calculated using eq. (2):

$$\Delta H_i/R = -[\partial \ln N^\sigma / \partial (1/T)]_p \quad (2)$$

The temperature dependence of the quantity of gas sorbed for the several systems is shown as a semilog plot in Figure 8. The results of calculations using eq. (2) are shown in Table III. Literature values were not available for the systems studied. However, the heats of interaction are similar to the heats of solution of gases in polymers as discussed by Meares,⁷ who reported a value of -1880 cal/mole for argon in poly(vinyl acetate). The

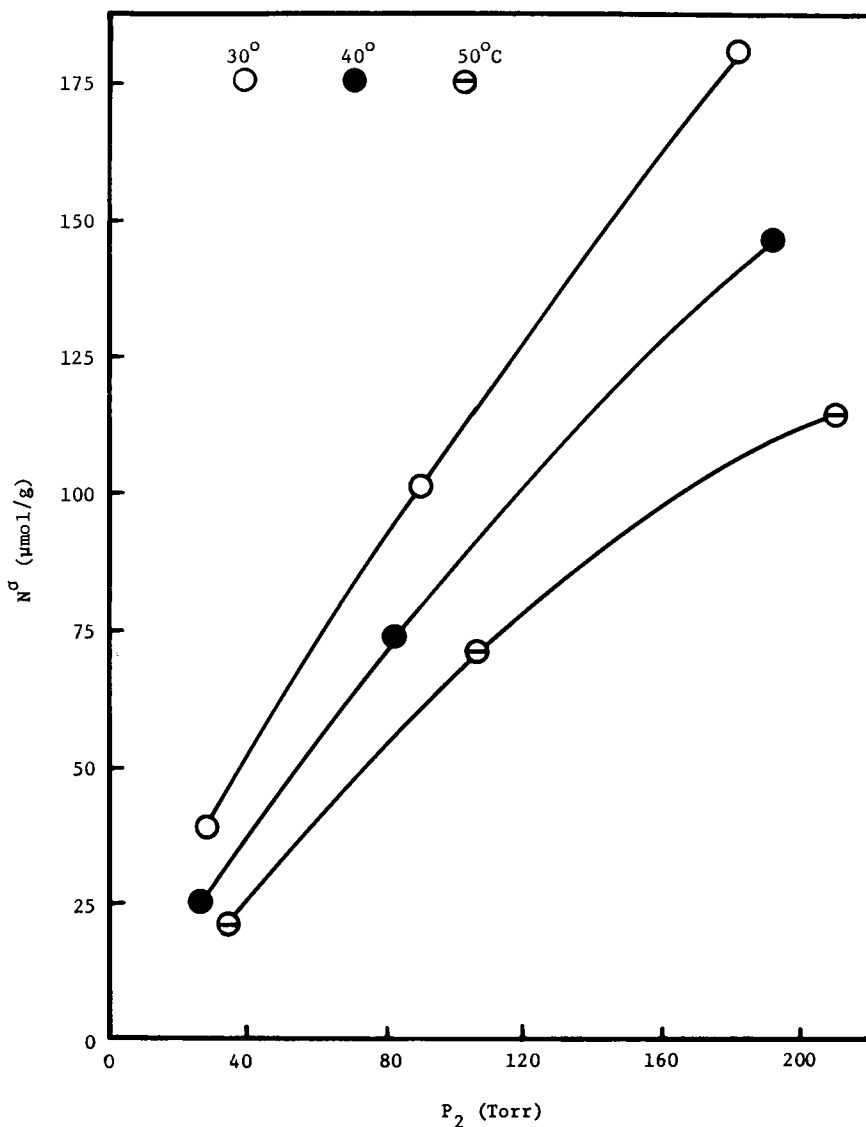


Fig. 6. Sorption of carbon dioxide on phenolic spheres at several temperatures.

larger heat of interaction for carbon dioxide than argon with silicone elastomer may be attributed to additional interactions arising from the quadrupole moment of carbon dioxide. The larger heat of interaction for carbon dioxide with phenolic spheres over silicone elastomer may be attributed to the more polar nature of the phenolic resin. The heat of interaction of argon and carbon dioxide with silicone elastomer is fairly constant over the pressure range studied, whereas a variation is noted in the case of carbon dioxide on phenolic spheres.

TABLE III
Heats of Interaction

System*	P_2 , torr	ΔH_i , kcal/mole
Ar/SE	70	-1.85
	100	-1.90
	160	-1.96
CO ₂ /SE	60	-2.64
	100	-2.51
	120	-2.57
CO ₂ /PS	50	-6.00
	100	-4.71
	150	-4.71

* Component symbols same as in Table I.

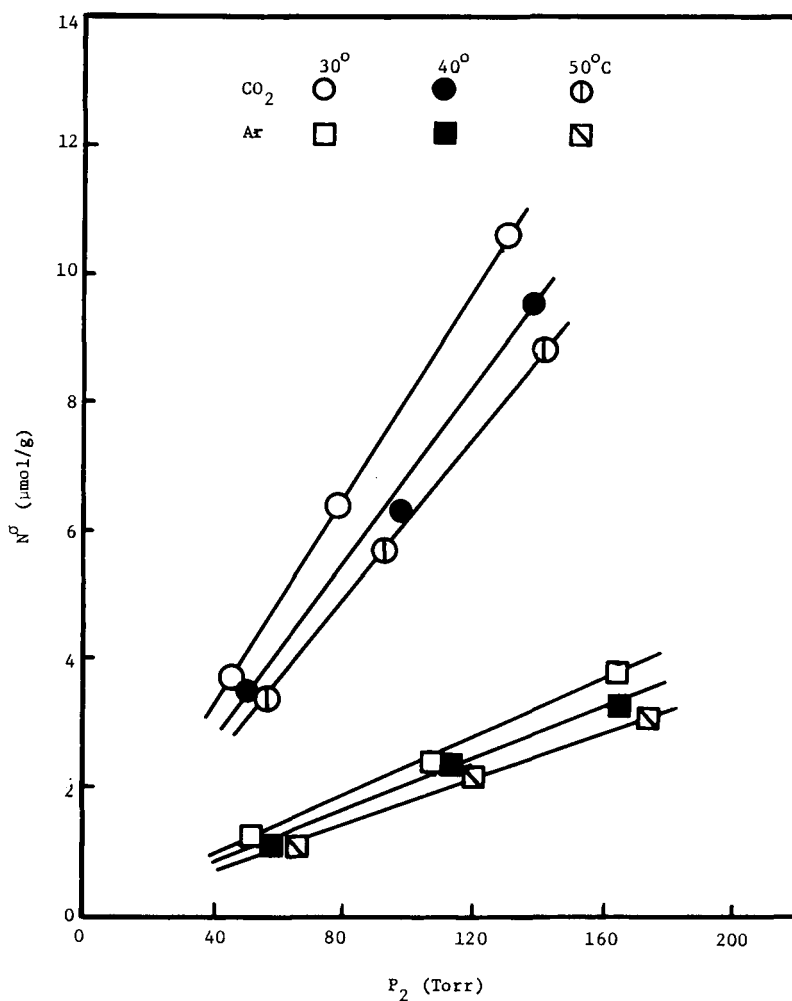


Fig. 7. Sorption of argon and carbon dioxide on silicone elastomer at several temperatures.

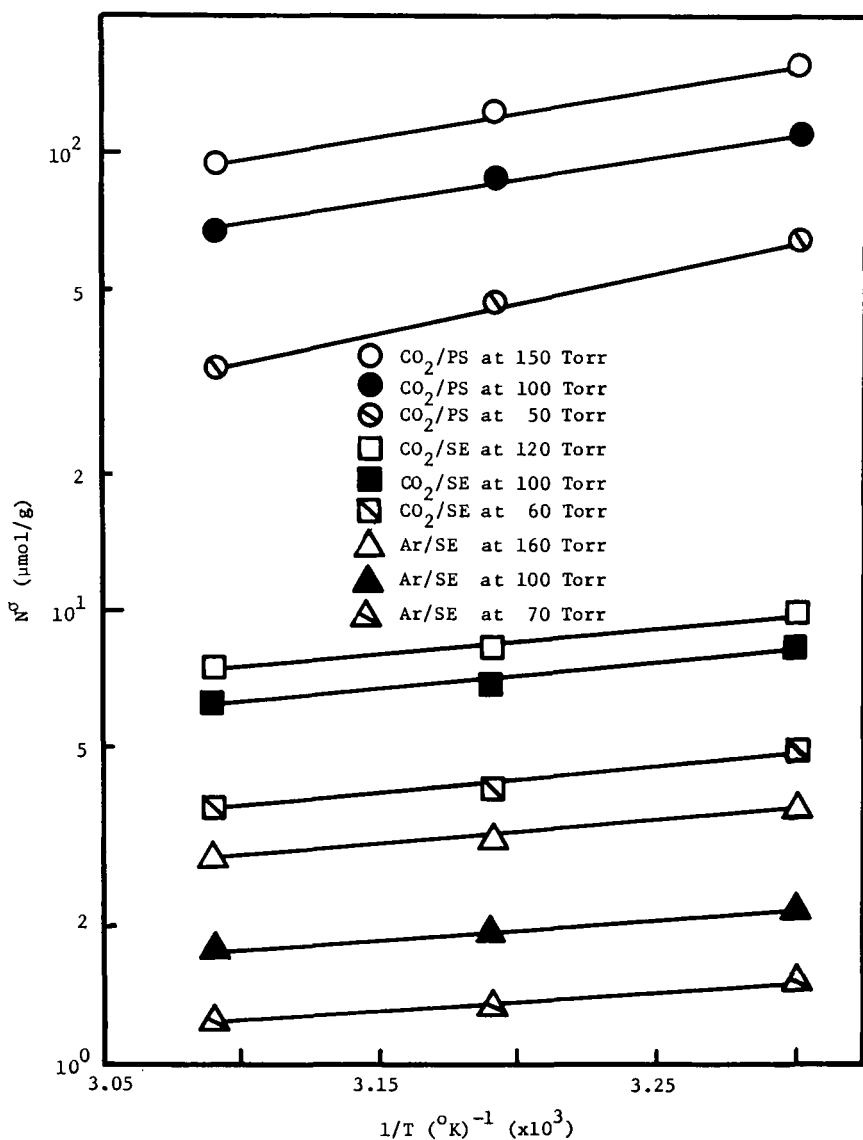


Fig. 8. Van't Hoff plots for carbon dioxide/phenolic spheres, carbon dioxide/silicone elastomer, and argon/silicone elastomer systems.

Low-Pressure Sorption

The quantity (N^σ) of argon, carbon dioxide, and nitrogen sorbed per gram of SLA-561V at 30°C as a function of equilibrium pressure (P_2) over the range of 2×10^{-3} torr is shown in Figure 9. Carbon dioxide was sorbed to the greatest extent, followed by argon and nitrogen, which could not be differentiated as was true at the higher pressures.

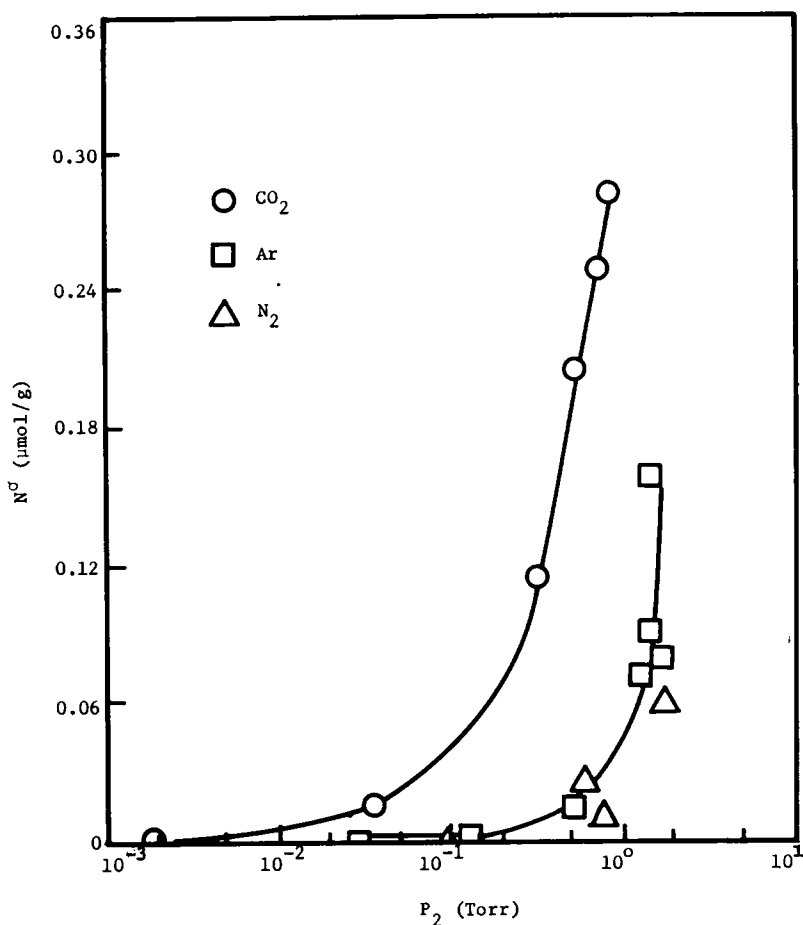


Fig. 9. Low-pressure sorption of argon, carbon dioxide, and nitrogen on SLA-561V as a function of pressure at 30°C.

Mechanisms for Gas Uptake

The establishment of the mechanism(s) by which the gases interact with the composite is of fundamental interest. However, since the composite consisted of several components, it is necessary to establish the mechanism of gas-component interaction. Brunauer³ has delineated two processes which can occur when a gas contacts a solid. Absorption (or solution) occurs when molecules from the gas phase enter the bulk solid. Adsorption occurs when the gas molecules reside on the surface of the solid. It is generally recognized that adsorption can be one of two types, namely, physisorption and chemisorption. The term sorption can imply the simultaneous occurrence of both processes or indicate a process where it is not possible to distinguish between absorption and adsorption. It is recognized that adsorption to a limited extent must precede absorption. Specif-

ically, gases are absorbed by the solid when the rate of diffusion into the solid is appreciable. Absorption processes typically involve longer times than adsorption because of the time required for equilibrium due to gas diffusing into the solid.⁸

The results obtained in the present study support a mechanism for all systems involving the *absorption* of the gases by the components. This absorption mechanism is demonstrated most clearly in the following systems: carbon dioxide in phenolic resin and in silicone elastomer along with argon in silicone elastomer. This conclusion is based on the magnitude of the solubility, the sign and magnitude of the heat of solution, long equilibrium times for sorption and desorption, sorption kinetics for different shaped samples, and finally the reversibility of the sorption process. Similarities in the equilibration times for the other systems suggest that absorption is also the primary mechanism for those systems. Chemisorption as a possible mechanism was ruled out on the basis of equilibration times. Physisorption as a possible mechanism was ruled out on the basis of the long equilibration times and the fact that the temperature range is far above the boiling points of the three gases. Parenthetically, Honeycutt and Wightman⁹ have shown that water is physisorbed on the same components.

CONCLUSIONS

The following conclusions are based on the study of the interaction of Ar, CO₂, and N₂ with SLA-561, SLA-561V, and the SLA components over the pressure range of 10⁻³ to 760 torr and in the temperature range of 30° to 50°C:

1. The equilibrium quantity of argon, carbon dioxide, and nitrogen at 100 torr by SLA-561 and (SLA-561V) was 7.0(6.0), 31.0(27.5) and 7.0(6.0) μ mole/g composite, respectively. Further, gas uptake varied directly with pressure.

2. Pretreatment times of two days and two weeks at 30% relative humidity showed no appreciable effect on the uptake of carbon dioxide by SLA-561V. Varying the geometry of the SLA-561 composite did not affect the amount of either carbon dioxide or nitrogen sorbed by the material.

3. The gas-component systems which showed appreciable uptake (expressed as μ mole/g solid) were as follows: (a) carbon dioxide/fiber mixture = 168.75, (b) carbon dioxide/phenolic spheres = 106.25, (c) carbon dioxide/cork = 30.0, (d) argon and nitrogen/cork = 13.75, (e) carbon dioxide/silicone elastomer = 6.93, (f) argon/silicone elastomer = 1.13. The sum of the individual component uptakes accounts for a majority of the total uptake by the SLA composites.

4. The heats of solution for argon in silicone elastomer, carbon dioxide in silicone elastomer, and carbon dioxide in phenolic resin were -1.90, -2.51, and -4.71 kcal/mole, respectively.

5. The mechanism involved in the uptake of argon, carbon dioxide, and nitrogen by SLA-561 and SLA-561V is primarily an absorption process based on the gas-component studies.

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