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PERMEATION IN FUSED SILICA

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ABSTRACT

April 1971

The effect of hydroxyl ion content and fictive temperature on the permeation of helium and hydrogen through fused silica was studied. The permeating membrane consisted of tubing, .018 inches outside diameter with a .0028 in. wall, wound in a 38 turn/in. helix. Specimens were saturated with hydroxyl ions at 1000 and 1100°C in one atmosphere water vapor. The permeation constant K, atoms/cm-sec-atm, of fused silica was determined after each treatment in a series of environmental exposures designed to change independently both the fictive temperature and hydroxyl ion content of the fused silica.

In the temperature range of 14°C to 530°C, the activation energy for the permeation of helium through fused silica did not change significantly as a function of thermal or water treatment. The same was also observed for hydrogen in the range of 200 to 600°C.

It was discovered that a carbon coating on the silica had an effect on the permeation of helium. The coating decreased the permeation at

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room temperature and increased the activation energy for the permeation of helium through fused silica. When the coating was removed by high temperature oxidation, the permeation at room temperature was restored to its original value.

I. INTRODUCTION

The unique physical and chemical properties of fused silica make it an interesting material to study. Fused silica's optical transmittancy and thermal shock resistance due to its low coefficient of thermal expansion enable it to be used as an infrared heater envelope. Fused silica's chemical inertness makes possible its use in chemical ware, corrosion resistant tubing and telescope mirror blanks.

Around the turn of the century it was first noticed by Villard[1] that gases can permeate glass readily at high temperatures. During the first 40 years of the century many publications followed, giving the permeability, diffusivity and solubility of gases in fused silica and other silicate based glasses. As a result, fused silica is widely used in the construction of standard leaks for calibration of mass spectrometers. In recent years several investigations[2-14] have used more sophisticated methods and treatments in their analysis of gas permeation through fused silica.

It is a well known fact that the structure at room temperature of fused silica depends on its fictive temperature. With one exception,[14] the previous studies on helium and hydrogen permeation through fused silica, permeation specimens were not characterized according to the fictive temperature.

Recently it was noted that different fused silicas had different hydroxyl ion contents. Depending upon its method of manufacture, fused silica may contain from 10 to 3000 ppm of hydroxyl ions. Roberts[15-17] has now well established that "water" (OH) can be introduced or removed from silica glass at high temperatures. At the temperatures used in the

fabrication of a permeating membrane it can be calculated that the entry and removal of hydroxyl ions would be fairly rapid. It is possible that if the membrane were made by using an oxy-hydrogen flame, the glass could become saturated with hydroxyl ions. No attempt has been made in the previous investigations to determine the hydroxyl ion content of the permeating membrane. The only evidence that hydroxyl ions may effect permeation was put forth by Lee[12] who stated that the hydroxyl content had no effect on hydrogen permeation in fused silica.

The purpose of this study was to investigate the effects of fictive temperature and hydroxyl ion content on the permeation of helium and hydrogen through fused silica. A monatomic and diatomic gas were used in order to elucidate whether the chemical activity of the permeating gas could allow interaction with hydroxyl ions in the fused silica. Activation energies for the permeation of helium and hydrogen through fused silica were calculated as a function of the two variables, hydroxyl ion content and fictive temperature.

II. EXPERIMENTAL PROCEDURE

(1) Specimens

Permeation specimens were fabricated by drawing down Amersil* fused silica tubing to a size approximately 0.018 in. outside diameter and with a wall thickness of 0.0028 in. The very fine tubing was wound on a mandrel during the drawing process to form a helix one in. in diameter with approximately 38 turns per in. length. This permeation membrane provided a very large surface area to thickness ratio in a small volume

*Clear fused quartz tubing, Amersil Inc., Hillside, N.J.

necessary for permeation studies. A support tube of fused silica which had an outside diameter of 8 mm and a wall of 3-1/2 mm was chosen because its total permeation in the hot zone would be less than 1% that permeating the helix.

One end of the permeation coil was inserted in a fused silica support tube and sealed with a bead of sealing glass. The other end of the coil was sealed by flame fusion, Fig. 1. The permeating gas surrounding the helix would permeate through the coil and exit to the residual gas analyzer (mass spectrometer) via the support tube. A cage of fused silica was built around the helix to protect it during handling.

(2) Permeation Apparatus

A molybdenum wound alumina (Al_2O_3) core was heated electrically in the vacuum furnace, Fig. 2. A fused silica protection tube was located inside the Al_2O_3 core. The permeation assembly was inserted in the protection tube, Fig. 3. This fused silica sample cavity was used to prevent impurities from transporting from the protection tube to the permeation section and causing devitrification at high temperatures. Early experiments using an alumina protection tube resulted in the fused silica permeation specimen devitrifying when the temperature was above 1000°C. The temperature was measured by inserting a Pt-Pt 10% Rh thermocouple near the helix. The temperature of the furnace was controlled to ± 1%.

The inside of the permeation membrane was kept under a vacuum of approximately 1×10^{-6} torr by the turbo molecular pumping system. The pressure on the outside of the sample was varied so that flow rates through the permeation membrane could be measured. The sample cavity

was evacuated to 1×10^{-3} torr and then the permeating gas would be introduced from a surge tank. The pressure of the gas was measured by gages in the line. A vent in the line was opened to exhaust excess gas into the atmosphere so that the gas pressure on the outside of the sample would be at atmospheric pressure. The volume of the surge tank and gas line was large enough to insure a constant pressure gradient during a permeation experiment.

The flow of gas through the fused silica membrane was measured on a Veeco GA-4 Residual Gas Analyzer. The gas analyzer was mounted on a stainless steel tank which was kept at a pressure of 1×10^{-6} torr by the turbo molecular pump.

The analyzer recorded the flow on a 3-decade logarithmic recorder. Flow rates from the sample were converted into absolute values in atoms/sec by calibrating the analyzer with a standard leak.

(3) Saturation and Desaturation Apparatus

Figure 4 illustrates the apparatus used to establish given fictive temperatures and hydroxyl ion contents. The Kanthal wound alumina core furnace was used to keep the permeating specimens at various temperatures. The isothermal bath kept the lower half of the saturation assembly above 100°C so that water would not condense on its walls. The water vapor pressure was controlled by varying the temperature of the hot plate and was monitored on a compound gage. For desaturation the water was removed from the lower finger and the system was run under a vacuum of 1×10^{-3} torr. The oil in the isothermal bath was used to keep the ball joint "O" ring cool in this case.

In order to determine the "water" or hydroxyl content in the sample disks of fused silica from the same source as that used for the permeation specimens and approximately the same thickness of the permeation section were made. Two disks were included with the permeation specimen in the treatment apparatus. One of these disks was analyzed on a double beam Beckman IR-4 infrared spectrometer at 2.7 microns after each treatment. Hetherington and Jack's[18] technique was used in calculation of the "water" content. In order to correlate the density versus fictive temperature and OH content of the glass sample, a piece of the other disk was broken off after each treatment. The density of these pieces was then measured using a density gradient column which contained a mixture of carbon tetrachloride and bromoform. The density column was standardized by using a set of calibration floats provided by the manufacturer.

(4) Test Procedure

After the vacuum furnace was pumped to a pressure of 1×10^{-5} torr it was back-filled with argon to provide better heat transfer. All runs began at the lowest temperature. The permeation helix, support tube and stainless steel tank were evacuated to approximately 1×10^{-6} torr. A solenoid safety valve was placed between the sample and the tank containing the gas analyzer in order to protect the gas analyzer in the case of failure of the permeation section. This valve was set such that, if the pressure on the inside of the permeation coil rose above 1×10^{-3} torr, the gas analyzer would shut off and the valve would close. The sample cavity was pumped down to about 1×10^{-3} torr by a roughing pump.

When the temperature was stable, one atmosphere of helium or hydrogen was introduced into the cavity. The sigmoidal increase in the flow rate was monitored on the recorder of the residual gas analyzer. When the flow reached a steady state value it was recorded and used in the calculation of the permeation constant. In the case of helium the sample cavity was then evacuated and the temperature was increased to a new stable value. This process was repeated seven times between room temperature and 530°C. For hydrogen the gas pressure was maintained in the sample cavity while the temperature was raised. This was done because of the longer times to reach equilibrium. The flow rate was measured at seven intervals between approximately 200 and 600°C. A liquid nitrogen cold finger, which was inserted in the gas analyzer tank, was used to freeze condensable gases. Without the cold finger there was an unreasonably high hydrogen background which made measurements impossible.

In order to obtain absolute values, calibration of the residual gas analyzer was done before and after every flow rate determination by shutting off the sample from the tank and introducing the standard leak.

The output of the gas analyzer could be recorded in two different ways. The residual gas analyzer could be set on the helium or hydrogen peak maximum, mass to charge ratio equal to 4 or 2 respectively, or the peak could be scanned by sweeping back and forth over it. It was found that the scanning technique was preferable for two reasons. First, it is possible that the gas analyzer could drift off the peak after long periods of time and secondly, by scanning, changes in the background could be monitored. The scanning was accomplished by impressing a ramp

function on the accelerating voltage of the gas analyzer.

III. EXPERIMENTAL RESULTS

(1) Helium Permeation

The permeation constants as a function of temperature were calculated by using Darcy's law

$$F = \frac{K\Delta PA}{\ell} \qquad (1)$$

where F = flow rate, in atoms/sec

K = permeation constant, in atoms/cm-sec-atm

ΔP = pressure differential across membrane, in atmospheres

A = effective permeating area of membrane, in cm^2

ℓ = thickness of membrane, in cm

A computer program was used to determine the semilog plots of the log permeation constant, K, versus $1/T^{o}K$, Fig. 5. The line of best fit for the points was calculated by using a least squares fit with a confidence level of 95%. The activation energy was then determined from the slope of this line (Arrhenius plot). A comparison of the permeation constants at approximately room temperature with thermal treatment is given in Table I.

The permeabilities and activation energies for the different thermal treatments lie within a narrow range. Therefore, helium permeation through fused silica is not significantly affected by hydroxyl content or fictive temperature in the range studied. Investigations currently under way using a different furnace arrangement have given approximately the same results, Table II.

It was discovered that if the permeation specimen was coated with carbon, the permeation at room temperature decreased with increasing carbon coating, Table III. The coating was developed by heating the sample in the permeation apparatus to 950°C and holding in vacuum. This produced a uniform coating probably due to thermal cracking of hydrocarbons on the silica. The coating thickness increased with time at temperature. The actual thickness was not measured, Fig. 6. In order to remove the coating the sample was heated in air to 950°C.

(2) Hydrogen Permeation

The method used in calculating the permeation constant was the same method as for helium. Table IV shows the comparison of permeation constants with thermal treatment.

The permeability and activation energy for permeation of hydrogen through fused silica are apparently less effected by thermal treatment than those of helium. Hydrogen permeation in fused silica is not significantly affected by hydroxyl content or fictive temperature in the range studied.

IV. DISCUSSION

The permeation constants for helium determined in this study agree fairly well with those reported in the literature. The actual values determined in this study at room temperature are about 2/3 those obtained by Swets et al.[7] Swets et al. reported an activation energy for permeation of 4900 calories while that obtained in this work was approximately 5100. The differences in the low temperature permeation constants would explain the higher ΔH values obtained from this study. The earlier literature data[2-4] report activation energies for permeation

of helium in the range of 5600 calories. These larger values of activation energy for permeation may be the result of different experimental techniques of the flow rate determination. The values in this study agreed more closely with those obtained in other mass spectrometric studies as would be expected.

Because of the experimental difficulties observed in the hydrogen permeation studies more confidence is placed on the results obtained with helium. Although no significant changes in the permeation constant, K, of helium or in activation energy for permeation were observed, there is a definite trend indicated in the permeation constant. As shown in Fig. 7, if the permeation constant for helium at 14 to 15°C as given in Table I is plotted against the room temperature density, there appears to be a direct relationship of decreasing helium permeation with decreasing density. This would indicate that either the fictive temperature or hydroxyl ion content which both affect the density of fused silica[19] are related to the permeation characteristics. It is apparent, however, that much more precise measurements of the permeation constant are necessary to fully substantiate this observation. The same trend is indicated in the activation energy in that the highest activation energy was observed on the lowest denstiy fused silica tested. This is consistent with the observation of Srivastova.[14]

In the range studied, the permeation constant of hydrogen as H_2 through fused silica was in good agreement with the data reported by Lee et al.[11-12] The activation energies for hydrogen permeation obtained in this study were significantly lower than those determined in Lee's mass spectrometric studies. Lee's work included the temperature

range of 300 to 1000°C, while in this study the permeability was recorded in the 200 to 600°C range. Recent work by Weaver et al.[20] shows that there is a break in the temperature versus diffusivity curve at approximately 800°C. In the case of gases which do not react with glass, the permeability is equal to the diffusivity times the solubility. Therefore, a change in diffusivity should proportionally affect permeability. Weaver shows that the activation energy for hydrogen diffusion is about five times greater above 800°C than below. Since Lee's data covered the entire range of 300 to 1000°C, this could explain why his activation energy of about 9000 calories is 10% higher than the 8200 obtained in this study. No change in permeability with hydroxyl content or fictive temperature was observed in this hydrogen permeation study in agreement with Lee's observations.

V. SUMMARY AND CONCLUSION

The effect of hydroxyl content and fictive temperature on the permeation of helium and hydrogen through fused silica was studied. Permeation membranes of fused silica were both saturated and desaturated with "water" at 1000° and 1100°C. It was observed that the permeation of helium and hydrogen is virtually independent of hydroxyl content and fictive temperature.

The activation energy of 5100 calories/mole for helium permeation was in close agreement with current literature values. The hydrogen permeation activation energy of 8200 calories/mole is approximately 10% lower than that of 9000 calories/mole, recently reported in the literature. The high literature value can be accounted for because it is extended through a transition point where the activation energy for

diffusion is increased five fold.

It was discovered that a thin carbon coating on the permeation membrane could reduce the helium permeation by a factor of two at room temperature. The carbon coating increased the activation energy for helium permeation from 5100 to 5400 calories/mole.

It is concluded that the method of manufacture of fused silica does not significantly affect its permeation characteristics above room temperature for hydrogen or helium.

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Table I. Permeation of He

Treatment	T°C	Permeation Constant $\frac{\text{Atoms}}{\text{cm-sec-atm}}$	Activation Energy ΔH $\frac{\text{calories}}{\text{mole}}$	wt % OH	Density $\frac{\text{grams}}{\text{cc}}$ ± .0002
As received	14	8.25×10^9	5115.0 ± 33.5	.0097	2.2049
Desaturated 1100°C	14	8.20×10^9	5095.6 ± 58.6	.0105	2.2029
Saturated 1100°C	14	6.95×10^9	5120.4 ± 53.3	.186	2.2011
Desaturated 1000°C	15	7.35×10^9	5107.5 ± 34.1	.0193	2.2013
Saturated 1000°C	15	6.30×10^9	5215.5 ± 69.5	.106	2.2006

Table II. Permeation of He

Treatment	T°C	Permeation constant	ΔH
As received	16°C	7.43×10^9	5100.8 ± 88.31
Desaturated 1200°C	16°C	6.48×10^9	4984.8 ± 47.43
Saturated 1000°C	16°C	6.31×10^9	5187.1 ± 55.20

Table III. Effect of Carbon on Silica

T°C	Permeation constant K $\left(\frac{\text{atoms}}{\text{cm-sec-atm}}\right)$	Activation energy $\Delta H \left(\frac{\text{calories}}{\text{mole}}\right)$	Total time under vacuum at 950°C
14	7.80×10^9	5030.4 ± 90.4	0 hours
16	3.83×10^9	5420.4 ± 100.7	36 hours
21	3.35×10^9	5470.1 ± 137.3	75 hours
18	7.40×10^9	5133.6 ± 69.1	Air for 1 hr.

Table IV. Permeation of H_2

Treatment	T°C	K $\frac{\text{atoms}}{\text{cm-sec-atm}}$	Activation Energy ΔH $\frac{\text{calories}}{\text{mole}}$	wt % OH	Density $\frac{\text{grams}}{\text{cc}}$ ± .0002
As received	188	3.45×10^9	8264.1 ± 92.8	.0097	2.2049
Desaturated 1100°C	196	3.57×10^9	8234.4 ± 73.5	.0105	2.2029
Saturated 1100°C	196	3.65×10^9	8214.5 ± 131.8	.186	2.2011
Saturated 1000°C	194	3.57×10^9	8282.3 ± 151.0	.106	2.2006
Desaturated 1000°C	195	3.59×10^9	8498.7 ± 200.2	.0193	2.2013

FIGURE CAPTIONS

Figure 1. Fused silica permeation assembly.

Figure 2. Permeation apparatus.

Figure 3. Sample cavity.

Figure 4. Saturation and desaturation apparatus.

Figure 5. Helium permeation through fused silica.

Figure 6. Helium permeation through fused silica.

Figure 7. Change in helium permeation through fused silica with density at 14 to 15°C.

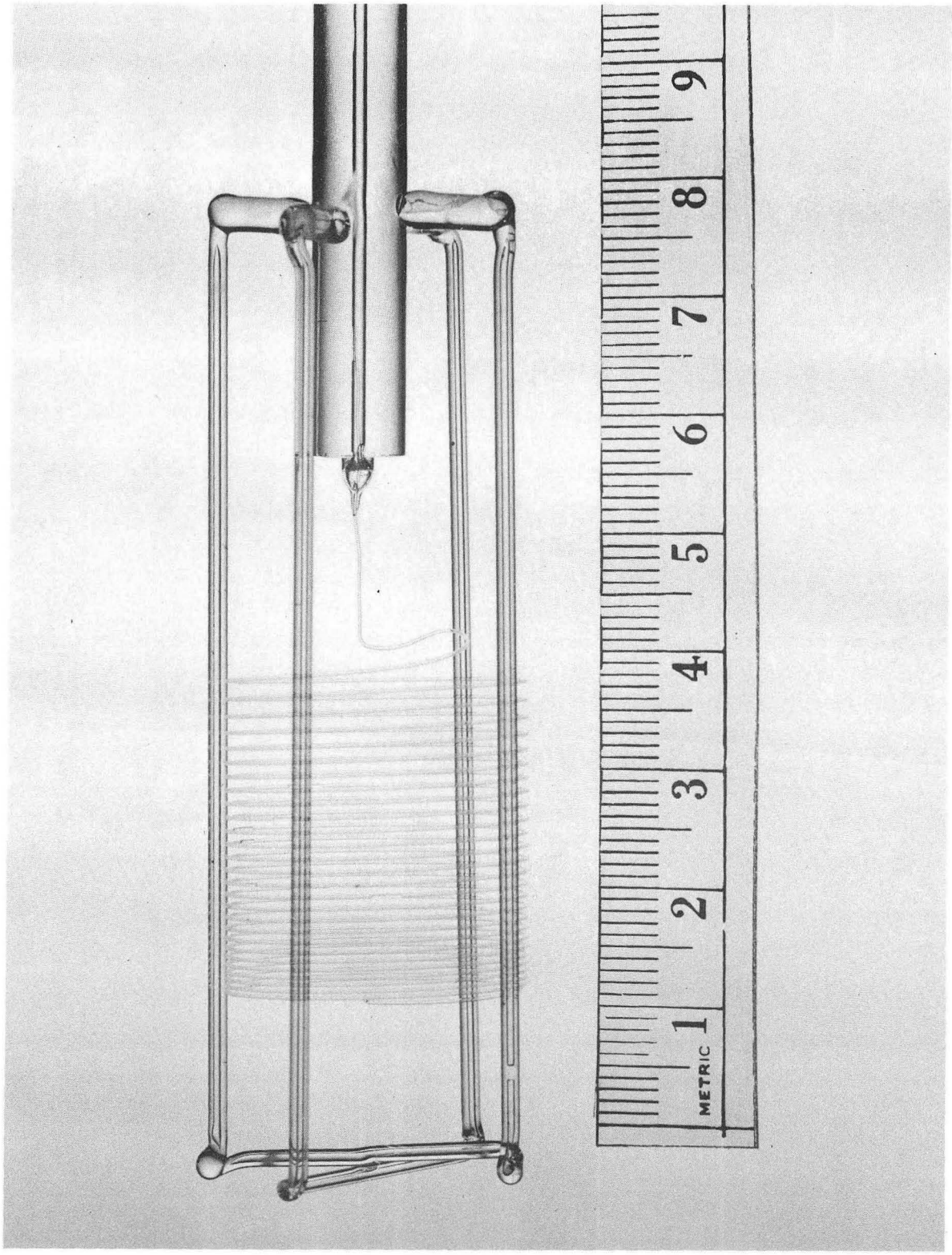

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Fig. 1.

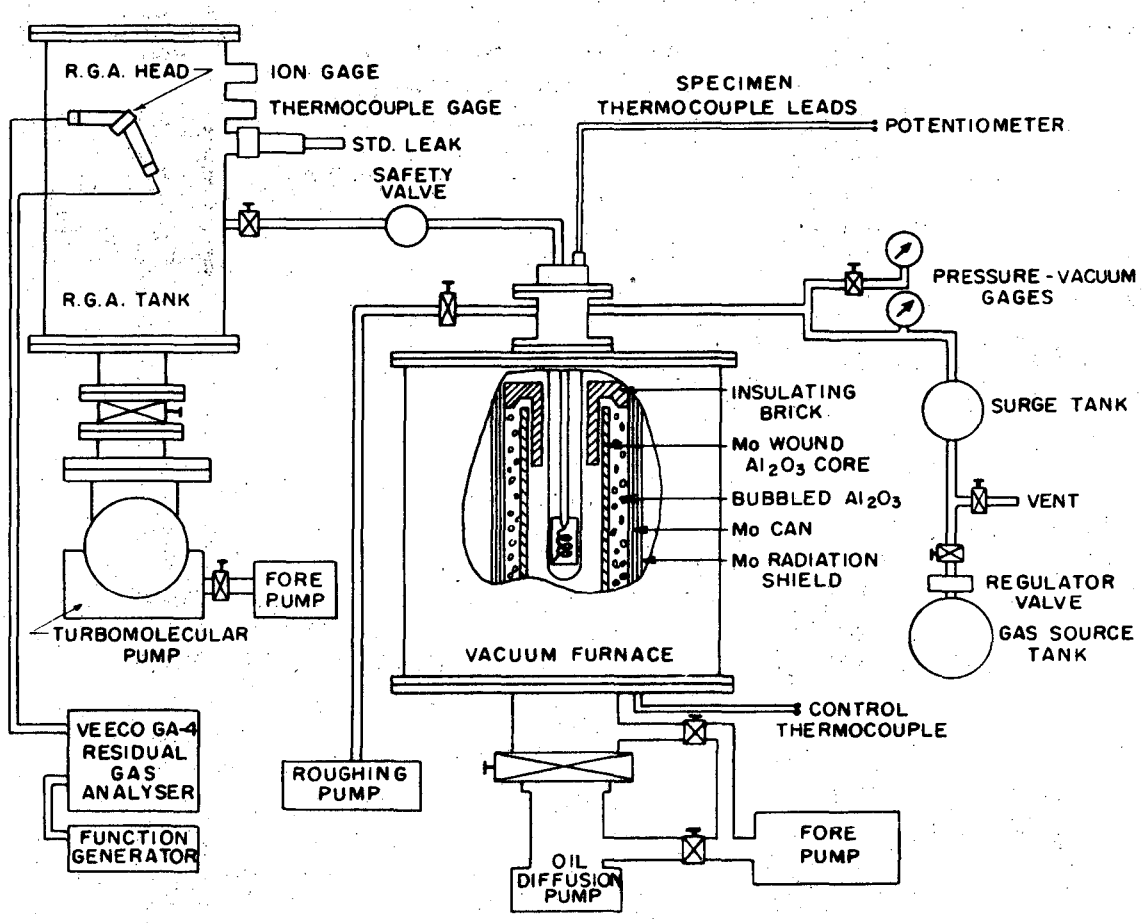

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Fig. 2.

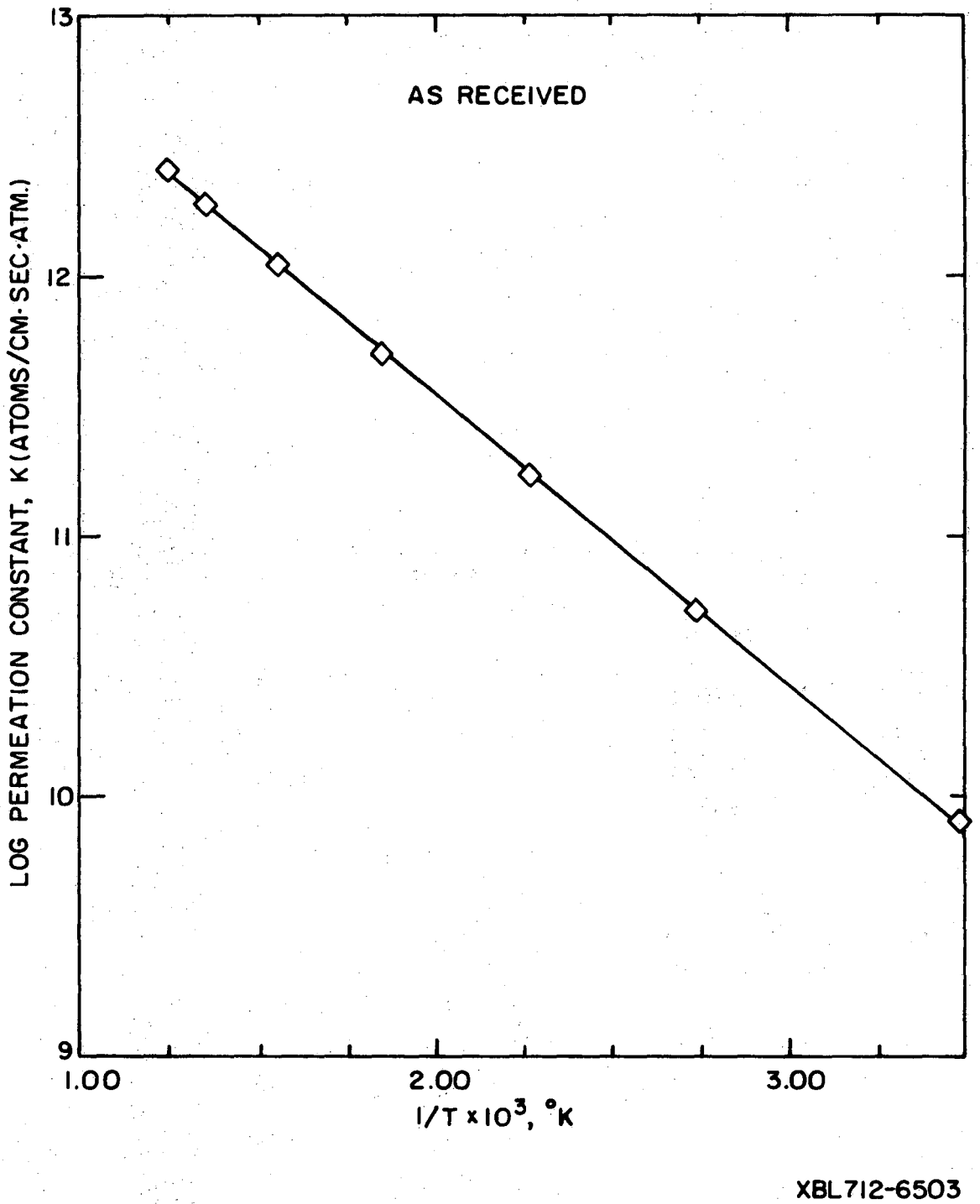
AS RECEIVED
LOG PERMEATION CONSTANT, K (ATOMS/CM·SEC·ATM.)
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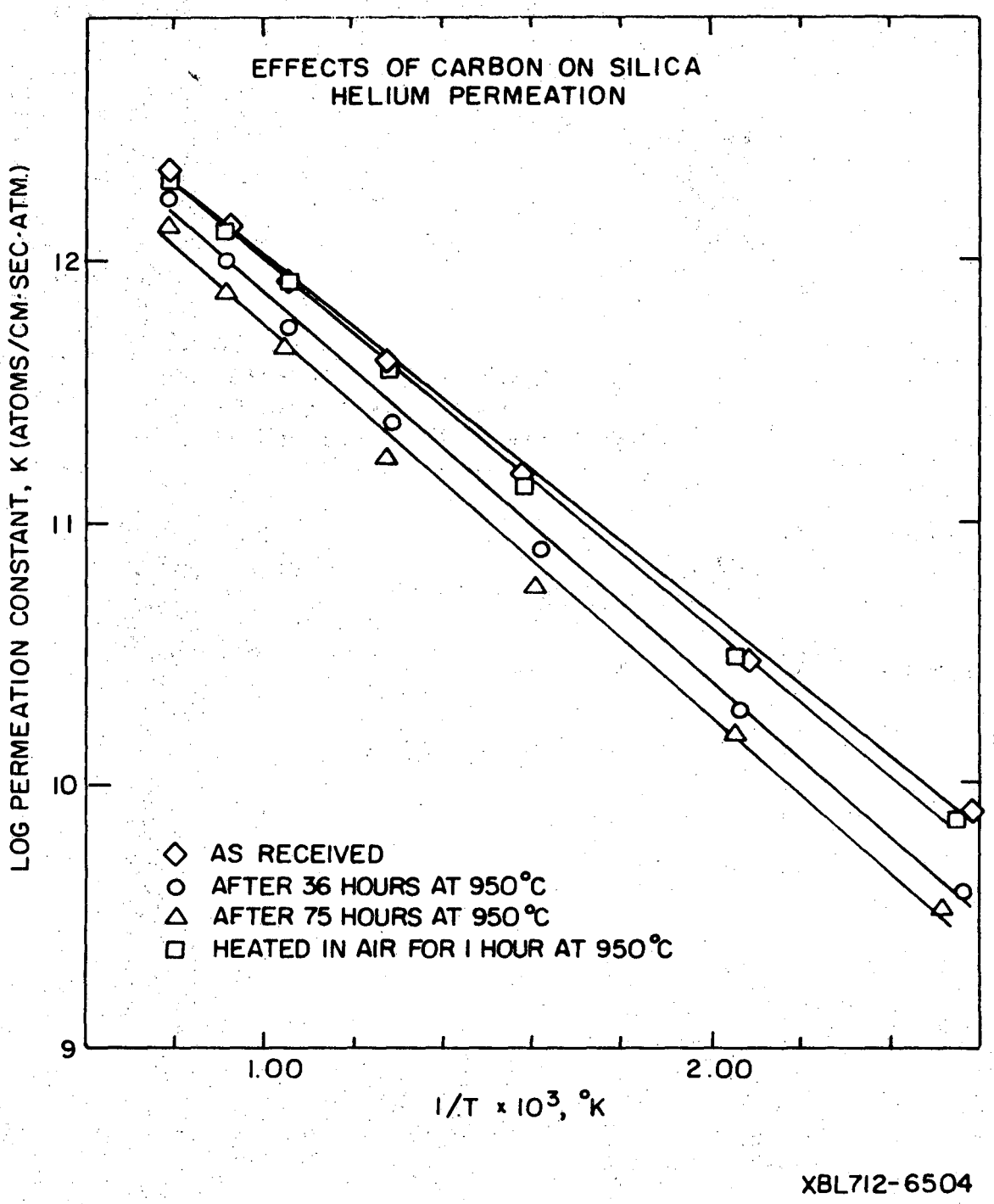
Fig. 5.


EFFECTS OF CARBON ON SILICA
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12
11
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9
1.00
2.00
1/T x 10³, °K
AS RECEIVED
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AFTER 75 HOURS AT 950°C
HEATED IN AIR FOR 1 HOUR AT 950°C
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Fig. 6.

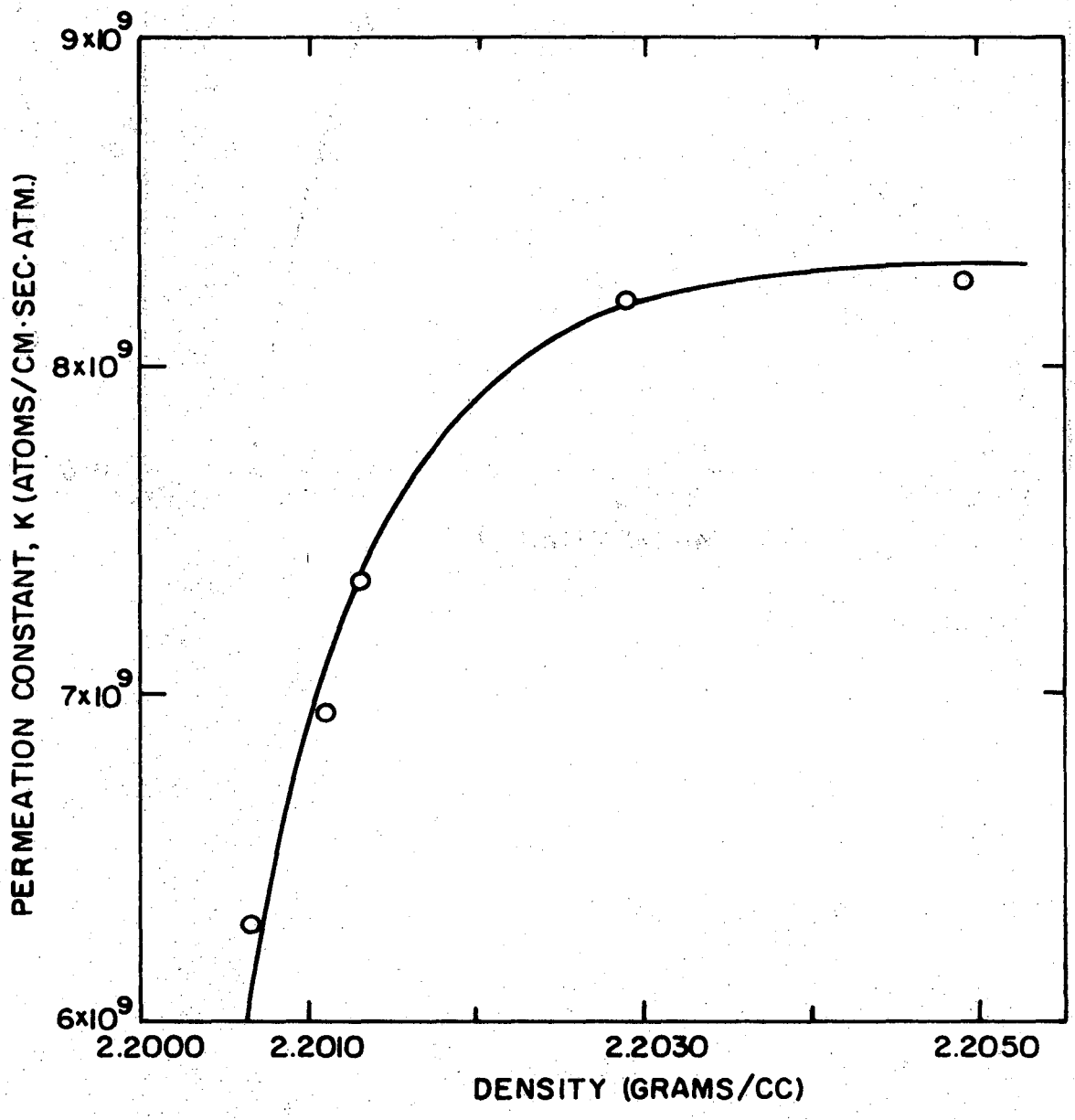

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Fig. 7.

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