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Interaction of Water Vapor With Pristine E-Glass Fiber

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ABSTRACT

The surface of the E-glass fiber is subject to subtle chemical changes, as are all glass surfaces. To start with an unmodified surface, pristine E-glass fiber was prepared directly from a melt of E-glass marbles. The experimental conditions were selected to measure adsorption on partially covered surfaces where the influence of surface groups can best be seen. The sample of E-glass fiber was selected so that the surface area was very much larger than the walls of the Pyrex container. The volumetric adsorption procedure employed for krypton was adapted for use with water vapor.

Knowing the length, weight, and density of the pristine E-glass fiber, an independent value was determined for the cross-sectional area of adsorbed krypton at -195°C. The adsorption and desorption of water vapor was followed between 90° and 150°C, and simple Elovich kinetics were observed for times up to 2000 min. Adsorption isotherms for water vapor were calculated after the fractional decrease in pressure ($\delta p/p$) became $\leq$ 0.01. The heat of adsorption for an estimated surface coverage of 0.4 was 7900 cal/mole; the corresponding heat of vaporization of water was 8000 cal/mole. The behavior of pristine E-glass fiber was compared with the behavior after treatments with liquid water. The complexity of a glass surface is obviously compounded after aqueous treatments, and the influence of this on gas adsorption is pronounced.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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INTERACTION OF WATER VAPOR WITH PRISTINE E-GLASS FIBER

INTRODUCTION

The surface of a glass fiber at the gas/glass interface can gain or lose water molecules by (a) an adsorption or desorption process from the gas phase and (b) the migration from and to the bulk glass by some solid diffusion mechanism. At sufficiently high temperatures and partial pressures of water vapor, both processes can contribute and the overall gain and loss may be written as

$$H_2O(g) + S_{glass} \rightleftharpoons S_{glass} \cdot (H_2O)_x \rightleftharpoons V_{glass} \cdot (H_2O)_y,$$

where S_{glass} and V_{glass} represent the surface and volume, respectively. Although these overall reactions can be reversed, it has been very difficult to establish the extent to which a steady state might have been approached.

At ambient temperatures, the water-vapor flux into the glass surface appears to be dominated by a gas-adsorption process; the amount of adsorbed water that is initially present and the nature of the surface bonds are the important parameters. Preliminary outgassing at temperatures above 300°C, followed by cooling to room temperature in a good pumping system, generally leaves a glass surface with a rather low coverage of the residual gases. Hobson and Armstrong (1) were able to obtain a pressure of 2×10^{-10} torr in a Pyrex container after a bakeout at 500°C, followed by an intensive evacuation. When such a procedure is prefaced by some "cleaning" technique of the glass container, the inner boundary is surely subjected to chemical decomposition and it is most probable that the adsorbing surface studied by Hobson and Armstrong had one of many heterogeneous porous structures derivable from Pyrex glass. This is shown by the different behavior in the physical adsorption of the noble gases on Pyrex observed by other investigators (2,3) at very low pressures. In numerous other published studies (4-8) including glass and quartz powders, the sample preparation has sought to "clean" the specimen by washing with aqueous solutions (acids, bases, etc.). All of these procedures, combined with subsequent heat treatments, have most probably modified the boundary surface of the glasses to varying extents; thus, the considerable variations in the reported gas-adsorption isotherms must be attributed to both the obvious differences in source and the more subtle differences in sample preparation.

This report is concerned with the interaction of water vapor with the surface of pristine E glass, directly after being drawn from the melt. This boundary surface was never in contact with any "cleaning" medium. The chemical composition of an E-glass-fiber surface varies, of course, with bulk formulations*, but additional variations are possible due to selective adsorption of the components into the boundary surface as the melt solidifies. While the glass fiber is being drawn, and before it has rapidly cooled, surface tension directs the complex molecular networks found in the glass structure (9,10) to locate preferentially in or near the boundary surface. The actual three-dimensional networks of silica, alumina, or boria have been described in

*Approximate bulk composition of E glass is 52% SiO_2, 14% Al_2O_3, 11% B_2O_3, 18% CaO, 4% MgO, 1% Na_2O, and 1% K_2O.

terms of low coordination polyhedra linked flexibly through the oxygen linkages, thus yielding structures not completely in disorder and yet far from being completely ordered. The alumina and boria are trivalent network formers and probably mix with the silica. Thus, on an atomic scale the adsorbing surface of an E-glass fiber is one of great chemical complexity, and the many possible sites for water-vapor adsorption will be discussed in the section "Reaction Mechanism."

The adsorption measurements have been made by a volumetric technique, which requires special attention to wall effects. Water-vapor pressures were between 2 and about 0.05 torr, and the temperatures were between 90° and 150°C. The results for the pristine E-glass fiber are compared with results for the same sample after a limited contact with liquid water. The surface area changes were followed by krypton adsorption at liquid nitrogen temperature. The important factors in the drawing of glass fiber for research studies have been discussed by Thomas (11) and Cameron (12).

EXPERIMENTAL PROCEDURE

Formation of E-Glass Fiber

The facility for glass-fiber drawing at the Naval Ordnance Laboratory, described by Fisher (13), was kindly made available for this work.* A charge of E-glass marbles was brought to a temperature somewhat above the drawing temperature for several hours. It was then cooled to the desired temperature, and the fiber was collected within a groove machined in the outer rim of a stainless-steel rotor (Fig. 1). In operation the speed of the rotor was controlled with a precision of 10 parts in 5000 and monitored frequently with a stroboscope. The running speed could be rapidly reached, and the total length of the unbroken fiber could be estimated from the speed, the diameter of the groove, and the drawing time. The weight of the fiber (≈ 15 g) was determined after the completion of the adsorption measurements.

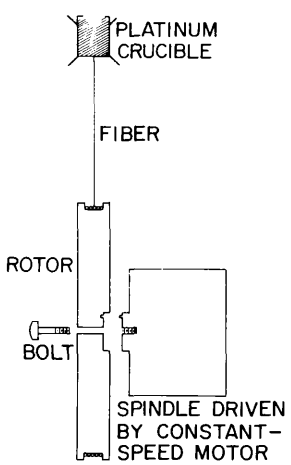


Fig. 1 - Collection of the pristine E-glass fiber

Immediately after the rotor had stopped, the accumulated fiber was cut free with a thin blade inserted in a slot on the rim of the collecting wheel and immediately transferred to the reaction vessel shown in Fig. 2. "Clean-room" gloves were used in these operations. The evacuated tube D was inserted to diminish the dead space, and the closure was quickly made using ConFlat flanges with a copper gasket and with Pyrex tubulations, furnished with a sealoff bubble E. About 30 sec were required for these manipulations. The sample tube was then sealed to the vacuum apparatus after inserting a glassed hammer to break the sealoff bubble for the evacuation of the sample.

Pressure Manometer

A capacitance manometer was used as the pressure tranducer with a recorder readout in the early measurements and digital voltmeter in all succeeding measurements.

*Acknowledgment is made to Mr. F. Robert Barnet, Chief, Nonmetallic Materials Division, for permission to use the glass-fiber drawing equipment and to Mrs. J.R. Fisher for her kind cooperation in demonstrating the procedure for fiber drawing.

The sensing head was thermostated with a precision of ±0.05°C. The calibration was made against a precision McLeod gage. A U-shape cold trap (solid CO_2-alcohol) was placed between the McLeod gage and the system to protect the metal valves from mercury vapor; the trap was made of constant-diameter tubing. To minimize the mercury-vapor error brought about by the flow of vapor into the cold trap, the mercury column just below the cutoff point of the McLeod gage was cooled for a length of about 1 cm to about -40°C; after equilibration, the mercury was quickly raised. Although the conductance between the McLeod gage and the trap was small, the above procedure showed that an error of about 2% would otherwise have been made.

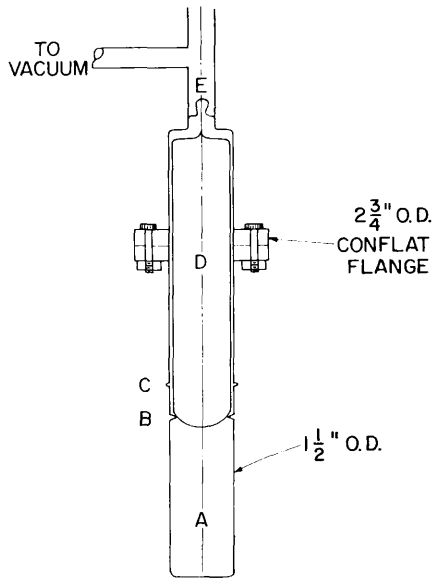


Fig. 2 - Adsorption vessel for the sample of the E-glass fiber

The capacitance manometer readings C and the pressures P were correlated through the relationship

$$P = \frac{C}{k_1 + k_2C + k_3C^2},$$

The constants k_1, k_2, and k_3 were determined using 34 calibration points. The details of the calibration and an analysis of the fundamental behavior of the capacitance manometer will be given at another time (14).

Sample Pretreatment

During the formation and collection of the E-glass fiber and its transfer to the closed adsorption vessel, the sample was exposed to ambient conditions which, of course, included water vapor. On evacuation there was a pronounced degassing, a quantitative estimate of which is not available at present. The temperature of the sample was steadily raised and was then maintained at 300°C. At regular intervals the sample was isolated from the pumps and the pressure buildup during 30 to 60 min was measured. Within a day's evacuation, the outgassing rate of the pristine fiber was less than 3 nanomoles/hr-m^2 at 300°C. In general, the time required to reach this level varied with the previous exposure of the sample to water vapor. The use of 300°C as the outgassing temperature is a compromise of several factors and experience alone will justify its choice. At higher temperatures a greater fraction of the evolved gas comes from the bulk phase, and this makes it uncertain as to whether the surface boundary itself is being cleaned by the pyrolysis reactions. On evacuation between about 200° and 300°C it has been reported that the infrared absorption bands associated with close neighbors of Si-OH bonds (on silica and leached glasses) are decreased to very low levels. Since the onset of physically adsorbed water is now considered to be defined by the process of hydrogen bonding to neighboring Si-OH groups (15), it is likely that an adequate evacuation at 300°C eliminates this type of water-adsorption site.

The same outgassing procedure at 300°C was followed before each group of adsorption experiments with either krypton or water vapor. Figure 3 is a graphical representation of the final values determined just before cooling to the temperature of the adsorption measurements. Combining the results with the surface-area measurements, these evolved quantities correspond to an estimated surface coverage of less than 0.0001.

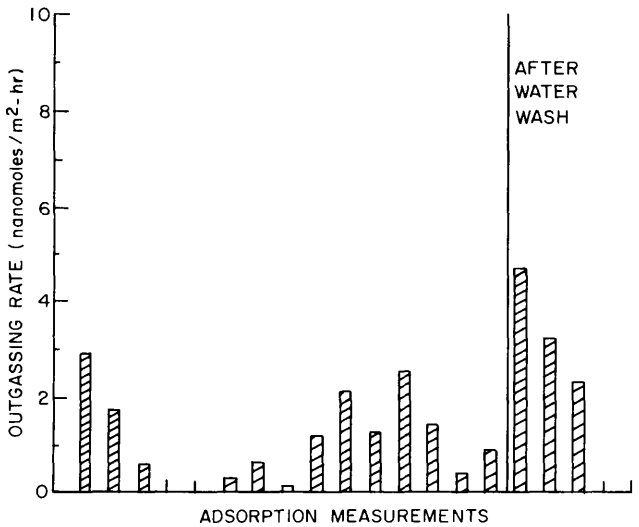


Fig. 3 - Rates of outgassing of E glass at 300°C observed before each of the adsorption measurements

Krypton Measurements

Mass-spectrometer-grade krypton was used in which the detectable impurities were no more than 10 ppm. After this source of krypton had been used for a number of measurements, the vapor pressure of the sublimate in boiling liquid nitrogen was determined and the results were found to agree closely with those of Fisher and McMillan (16).

The level of liquid nitrogen was maintained at ±0.3 mm by an automatic syphon system using a thermistor sensor. A sleeve heater surrounded the adsorption tube above the refrigerant leaving no more than 1 cm between the surface of the liquid nitrogen and the heater; the heater current was manually controlled to maintain this section at room temperature. In its absence, considerable frosting would have occurred on the tubing above the liquid nitrogen during measurements over long periods. This arrangement made it possible to follow pressure changes for periods of more than a day.

Water-Vapor Measurements

The small water reservoir was isolated from the dosing space of the adsorption apparatus by a Type C, Granville-Phillips vacuum valve. The liquid water (about 2 ml) was alternately frozen and thawed, the reservoir being evacuated during freezing. After about 20 such cycles, the reading of the capacitance manometer remained constant. Thereafter, the pressure was periodically measured with an ice bath surrounding the water reservoir. The agreement with the vapor pressure of water at 0°C is given in Table 1. The procedure employed in the measurements is given in the section under "Results."

The temperature gradient between the sample space and room temperature is located in the annular region defined by two concentric cylinders. The corrections for thermal transpiration (17,18) have not previously been calculated for this geometry, and it has been necessary to make the required measurements. This was readily done with the empty container using helium and krypton under the conditions of the adsorption measurements. The correction is expected to vary with the gas, and it is necessary to make these measurements for each adsorbate species at the temperature of the experiment.

Table 1

Capacitance Manometer Reading at the Vapor Pressure of Water* at 0°C

Run	P_0 (torr)
4	4.59
5	4.61
6	4.57
9	4.56
10	4.56
13	4.56
Av	4.58

*Vapor pressure at 0°C = 4.58 torr.

RESULTS

Surface-Area Changes

The krypton surface area was determined at various stages in the experimentation. The results for the first krypton series are summarized in Table 2 with notations as to the immediate pretreatment; all are concerned with one original sample of bare

Table 2
BET Surface Area with Krypton

Experiment	Pretreatment	Monolayer Coverage, N (μ mole Kr)	Area (m^2)
1	Evacuated at 300°C	33.1	3.89
2	Water vapor at 22.5°C, cooled to 77°K	31.4	3.69
3	Evacuated at 300°C	33.0	3.88
4	4 hr in water vapor at 120°C, evacuated at 300°C	32.2	3.78
5	4 hr in water vapor at 300°C, evacuated at 300°C	30.0	3.52
11	After five exposures at 93 to 150°C, each evacuated at 300°C	26.6	3.12
12	Exposure to ambient temperature and subsequent evacuation at 150°C	28.7	3.37
13	After water-vapor treatment at 150°C	28.7	3.37
16	Washed with 1 liter of water at 90°C (5 portions) and evacuated at 300°C	45.9	5.4
Surface area calculated from length, density, and weight (15.88 g)			3.96

fiber. Good linear plots were found for the BET monolayer coverage, and the areas given in Table 2 were calculated using 19.5 $Å^2$ for the cross-sectional area of adsorbed krypton.

One point to make is the close agreement of the krypton area when first observed (3.89 m^2 per 15.88-g sample) with the calculated geometrical area S. The length ℓ, weight W, and density ρ of the fiber are used to calculate S:

$$S = 2\pi\sqrt{\frac{W\ell}{\pi\rho}}.$$

W is 15.885 ± 0.005 g; ρ is 2.57 ± 0.01; ℓ is $\pi D \times \alpha \times t$, where the rotor diameter D is 12.70 ± 0.02 cm, α is 5825 ± 5 r.p.m., and the time of fiber collection t is 87 ± 0.5 min. Therefore,

$$\frac{\delta S}{S} = \sqrt{\frac{\delta W}{W} + \frac{\delta D}{D} + \frac{\delta \alpha}{\alpha} + \frac{\delta t}{t} - \frac{\delta \rho}{\rho}}.$$

Hence, S = 3.96 ± 0.06 m^2. The corresponding fiber diameter was 6.28 μ.

Gutfreund, Weber, and Brown (19) reported that the BET nitrogen surface area for a multistrand, heat-cleaned, E-glass fiber, previously degassed by evacuation for 4 hr at 150°C, was 0.193 m^2/g. They compared this with the value of 0.173 m^2/g calculated from the total length, weight, and density, but their uncertainty in length appears to be large. One can expect that a heat-cleaned fiber would have a larger BET area than the geometrical value because of surface roughness; however, the precision in the geometrical estimate is not sufficiently accurate to make this point from their data.

The present data may also be used to realize an independent value for the cross-sectional area σ of an adsorbed krypton atom on E glass. Using 3.96 ± 0.06 m^2 for the measured geometrical area and 33.0 μmoles for the monolayer coverage of adsorbed krypton (BET plot), the value of 19.9 $Å^2$ is obtained for σ. The value of 19.5 ± 0.4 $Å^2$/atom was originally proposed by Beebe, Beckwith, and Honig (20); recently, 20.2 ± 2.6 $Å^2$/atom was proposed by McClellan and Harnsberger (21) in their review of all subsequent literature. In the tightly wound sample there were 0.5×10^6 individual fibers and, thus, the surface of all appear to be available to the krypton adsorption process. Moreover, to obtain the above agreement the individual fibers must be fairly constant in diameter and have a surface roughness on an atomic scale less than the cross-sectional area of adsorbed krypton.

A second point is the steady <u>decrease</u> in surface area after repeated exposures of the pristine fiber to water vapor at temperatures between 93° and 300°C, each followed by evacuation to 300°C. This is shown in Table 2 for experiments 1, 3, 4, 5, and 11; the change from 3.89 to 3.12 m^2 amounted to 20% of the initial area.

In contrast, no change in area was found on heating the E-glass fiber in vacuum at 300°C. Ries (22) showed a number of years ago that the sintering of various cracking catalysts was considerably enhanced at temperatures above 500°C when steam pressures of 1 atm and above were used. The strong influence of water vapor on sintering at pressures of 4 torr and less has been studied for MgO powder (23,24), CaO, and BeO (24); in these cases the temperature was considerably higher than in the present observations with glass fiber. At the low temperatures of the present work, a significant number among the approximately 500,000 fibers that made up the sample must have been sintered together to decrease the krypton BET area by 20%. This is a potential source for a defect in the commercial production where a multistrand fiber assembly is drawn and subsequently treated with the finish.

A third point to make is the *increase* in krypton area of the sample after contact with liquid water. Following the water-vapor experiments (to be described), the container was removed from the system and the fiber washed with a liter of distilled water at about 90°C in five portions without removing the sample from the reaction vessel. The washed sample was dried and evacuated at 300°C, and the krypton adsorption was then measured. The area increased to a value 30% greater than the area of the starting fiber. This increase was doubtlessly caused by the chemical leaching of the surface, since 3 ppm calcium and 1.3 ppm sodium were observed present in the washings. The analyses were done by flame spectroscopy using standard solutions of calcium and sodium chlorides.*

The estimated total cross-sectional area of the leached cations was of the same magnitude as the observed increase in surface area. The leaching of glass with strong reagents like cleaning solution is well known to increase the surface area. Pliskin (25) showed that boiling water leached 85% of the boron out of a thin film of Corning 7050 borosilicate glass. However, the surprising aspect of the present observations is the mildness of the treatment; namely, a brief contact with liquid water alone provides the necessary means to remove reaction products of hydrolysis and roughen the surface to the extent noted above.

Water Adsorption

The primary rate data (see examples in Fig. 4) were pressure decreases in a fixed volume. The dosing space (V_α in Fig. 5) at room temperature was filled with water vapor from the source at 0°C and the pressure P_i followed for about 1 hr. The vapor was then expanded into the reaction vessel containing the E-glass fiber, the volume at room temperature being $V_{\beta 1}$ and the volume at the sample temperature $V_{\beta 2}$. Similar measurements were made with the empty container held at the same temperatures used with the glass-fiber sample. In the pressure range given in this report, the wall adsorption followed a Freundlich behavior and the corrections were made as follows:

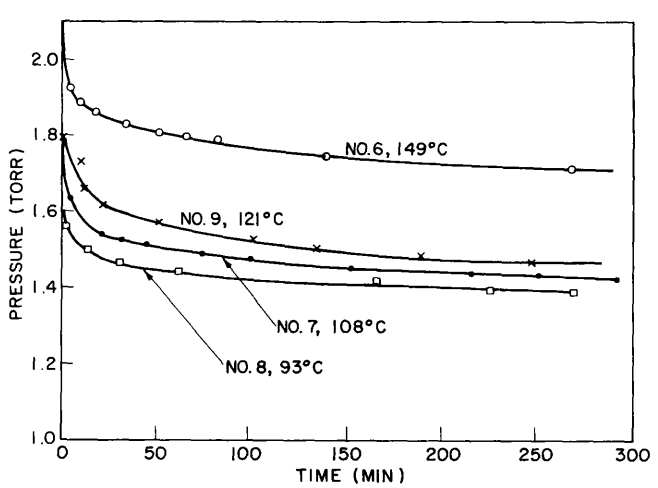


Fig. 4 - Pressure decrements in the adsorption of water vapor by E-glass fiber

*Acknowledgment is made to P. J. Hannan of Ocean Sciences Division for assistance in the measurements.

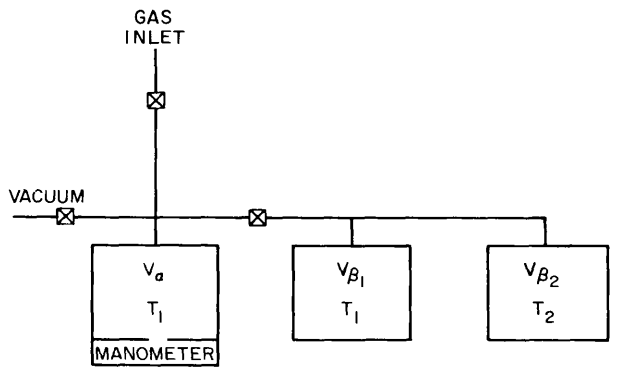


Fig. 5 - Volumetric adsorption apparatus

$$\text{Moles introduced} = \frac{P_i V_\alpha}{RT_R} + a_1 P_i^{\,n}$$

and

$$\text{Moles after expansion} = \frac{PV_\alpha}{RT_R} + a_1 P^n + \frac{PV_{\beta 1}}{RT_R} + a_2 P^n + \frac{PV_{\beta 2}}{RT_R} + a_3 P^n.$$

The constants a and n were determined from measurements with the empty vessel. A test of the procedure is the mass balance in water vapor obtained for the empty vessel using expansion from the α space into the evacuated β space and for subsequent expansions from the β space into the evacuated α space. Table 3 gives some of the results obtained at various times.

The adsorption of water vapor (micromoles per sample) at 93°, 108°, 121°, and 149°C is shown in Fig. 6. The dependence on time was followed for periods up to 48 hr, and the temperature dependence was found to be reproducible after outgassing at 300°C

Table 3
Mass Balance for Water Expansion into an Empty Reaction Vessel

Date	H_2O in V_α (μ moles)	H_2O in $V_\alpha + V_{\beta 1} + V_{\rho 2}$ (μ moles)
Feb. 28, 1968	99.0	99.2
Mar. 15, 1968	53.5	51.2
Nov. 28, 1967	92.1	94.2
		93.9
Mar. 21, 1968	70.4	70.4
Mar. 22, 1968	69.5	68.8
Mar. 20, 1968	68.6	66.9
Mar. 29, 1968	71.5	73.8
Apr. 1, 1968	69.4	70.5

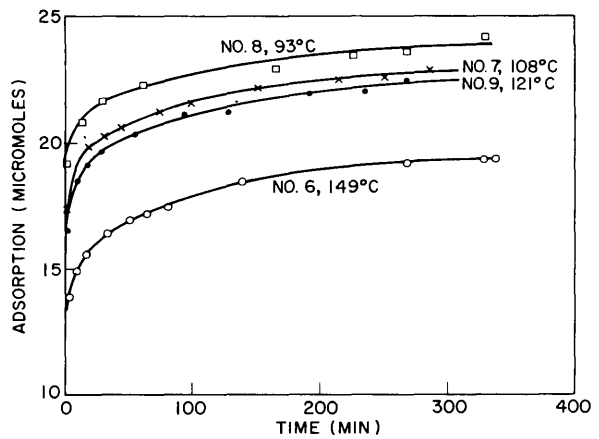


Fig. 6 - Adsorption of water vapor as a function of time for the same fiber outgassed at 300°C before each series of measurements

before each adsorption. The rate of water-vapor adsorption $\Delta n_a/\Delta t$ decreased continuously with time and after 24 hr had reached a magnitude of 0.076 nanomoles/day-cm^2 at 150°C and 0.056 at 93°C. These values are considerably lower than published data for two other systems measured at ambient temperatures (Table 4).

Table 4
Rates of Water-Vapor Adsorption

Surface	dn_a/dt (nanomoles/day-cm^2)	Temperature (°C)	Water Pressure (torr)
Alumina-silicate glass (26)	3 6 8	25 25 25	21 21 21
Vitreous silica (27)	0.6	30	10
E-glass fiber, pristine (this report) E-glass fiber, after liquid water contact	0.056 0.076 0.154 0.166	93 150 100 119	1 to 1.5 1 to 1.5 1 to 1.5 1 to 1.5

Experiments are in progress in which the E-glass fiber is further treated with 3N hydrochloric acid. A further alteration of the boundary surface as well as the overall composition can be expected (28).

The rates of water vapor adsorption were found to obey the Elovich relationship over the complete periods of observation (29). If n_a denotes the molecules adsorbed (micromoles) and t the time (minutes), then the integrated Elovich equation is

$$n_a = \frac{1}{b} \ln \frac{t + t_0}{t_0} ,$$

where $t_0 = 1/ab$, these being the constants in the rate equation

$$\frac{dn_a}{dt} = ae^{-bn_a} .$$

Figure 7 shows good linear behavior over the period 2 to 1200 min for the water adsorption at 100°C (Run 17) using a value of $t_0 < 1$ min. This permits a ready extrapolation of the adsorption to any desired time.

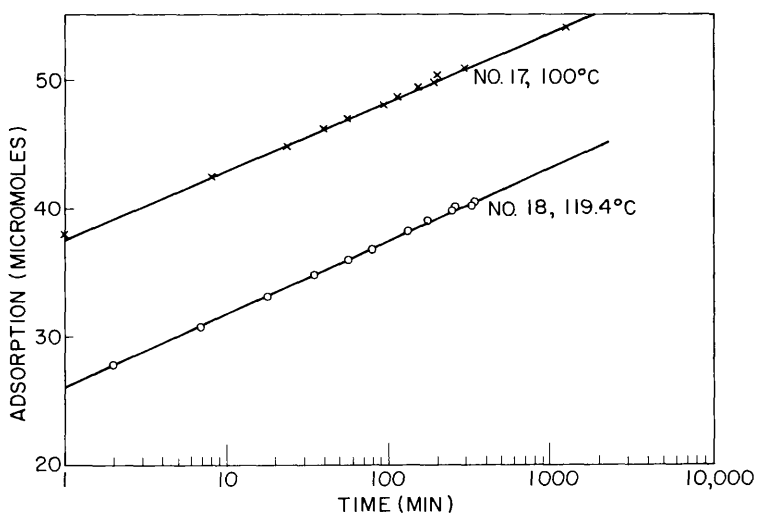


Fig. 7 - Adsorption vs $\log_{10}$ time showing simple Elovich kinetics in the interaction of water vapor with E-glass fiber

When the rate data are viewed on a dn/dt versus t plot, as in Fig. 8, the pronounced fall in the rate within the first few minutes is quite evident. The values of b were determined from the relationship

$$n_{a(nt)} - n_{a(mt)} = \frac{2.3}{b} \log_{10} \frac{n}{m}$$

for the amounts adsorbed between times nt and mt. A constant difference provides a sensitive test for the applicability of the Elovich equation (30).

The present data do not include measurements for times less than about 1 min. During this interval, pressure surges followed the transport of gas from the dosing volume plus the manometer space into the reaction vessel, with accompanying back-pressure effects. The influence of the geometry of the apparatus was readily shown by the expansion of helium into an empty reaction vessel; 1 to 2 min were required for steady-state readings. Consequently, a large fraction of the total adsorption was completed before a dependable pressure measurement could be made.

Rand (31) studied the kinetics of water-vapor adsorption on wafers of a porous glass that were obtained from the intermediate material in the manufacture of Vycor from the Corning Glass Works. Apparently, more adsorption was indicated on a weight basis than in the present work; however, the sample had a much larger surface area

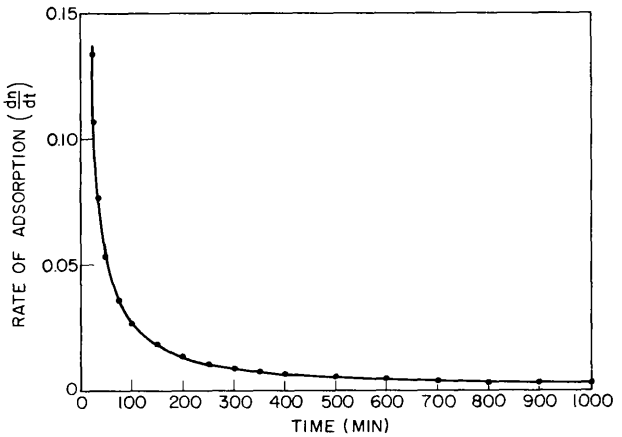


Fig. 8 - Rate of water-vapor adsorption at 150°C on E-glass fiber (pressure drop from 2.3 to 2.0 torr)

(215 m^2/g) compared to the E-glass fiber (0.24 m^2/g). When reported on a per unit area basis, the E glass adsorbed more water vapor than the porous glass sample. This important point will be further examined in the "Discussion."

The present study has demonstrated that the interaction of water vapor with E-glass fiber does not lead to precise steady-state values that are demanded for an application of adsorption thermodynamics. Nevertheless, it is worthwhile to estimate the shape of an isotherm compatible with the data after an initial contact time of 1200 min. Desorption was then followed by expanding the sample volume into the evacuated V_a space for repeated cycles, allowing time in each case for the fractional pressure change $\Delta P/P$ to decrease to less than 0.01. The evacuation of the V_a space also removed the water vapor adsorbed to the walls of this space with about the same precision.

The resulting isotherms at 100° and 150°C given in Fig. 9 are Langmuir in behavior. The strong adsorption at low pressures indicates that extensive evacuation would be necessary to remove the major fraction of the water adsorbed to the E-glass fiber without a temperature increase above 150°C. The indicated monolayer adsorption of water vapor was 27 and 24 μmoles per sample at 100° and 150°C, respectively. An estimate of monolayer surface coverage by water vapor can also be made using 10 $Å^2$ for the cross-sectional area of an adsorbed water molecule and 19.9 $Å^2$ for adsorbed krypton. The result was about twice that indicated by the Langmuir behavior.

After the pretreatment with liquid water (already noted in the results for surface-area changes), the adsorption of water vapor was measured at 100.0° and 119.4°C. In each case the sample was initially evacuated at 300°C to the residual rate of outgassing given in Fig. 3. At a comparable temperature of 100°C, the water-vapor adsorption for the liquid-water-treated sample (curve A of Fig. 10) was 1.5-fold greater than for the pristine E-glass fiber (curve B of Fig. 10). The surface area had increased by a factor of 1.6 relative to the starting material, but the water-vapor adsorption in Fig. 10 is corrected to unit area (micromoles per square meter). The rate of water-vapor adsorption after a 24-hr contact was twice that for the original pristine fiber.

Desorption measurements were made with the liquid-water-treated E-glass fiber, and the isotherms given in Fig. 11 were found Langmuir in behavior. The indicated

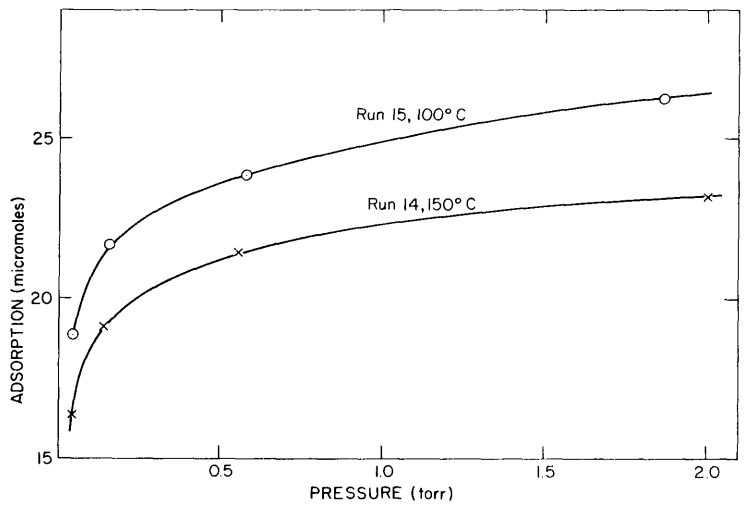


Fig. 9 - Adsorption isotherms of water vapor on pristine E-glass fiber

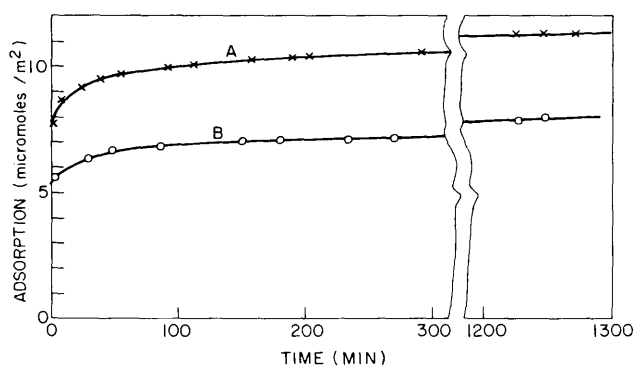


Fig. 10 - Water-vapor adsorption at 100°C before (B) and after (A) the treatment with liquid water

monolayer adsorption was 42 μmoles at 90°C and 41 μmoles at 120°C. The values are 1.7 greater than for the pristine fiber.

Examples of chemical attack on freshly fractured E glass in buffered aqueous media (pH 2-11) were reported by Levine and LaCourse (32) using electron microscopy. A uniform pitting of the glass surface occurred in the pH range 3 to 5, and at higher values the changes were accompanied by a phase separation of the glass attributed to random breaks in the networks in the boundary regions. However, the interaction of water vapor with a pristine E-glass fiber is considerably less destructive, and this is due to the lack of a means to remove nonvolatile reaction products from the reaction site. The present work demonstrates that a brief contact with liquid water alone provides such a means.

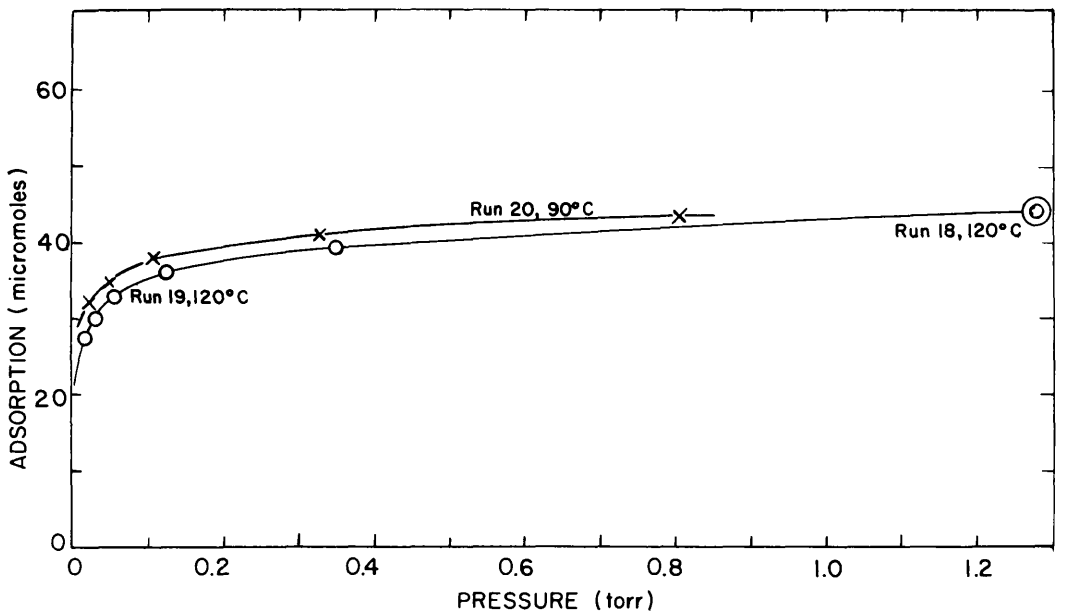


Fig. 11 - Adsorption isotherms of water vapor after treatment with liquid water

DISCUSSION

Reaction Mechanism

The linear Elovich plots over the range covered at first suggested that there might be a common kinetics for the water-vapor interaction with E glass. To calculate the corresponding energy factor for the reaction, the rates of adsorption at particular coverages were estimated at different temperatures and plots of log rate versus 1/T were made. The adsorption between n_a = 15 and n_a = 30 corresponds to an apparent surface coverage of 0.25 to 0.50. A typical plot for the E glass is shown in Fig. 12, and

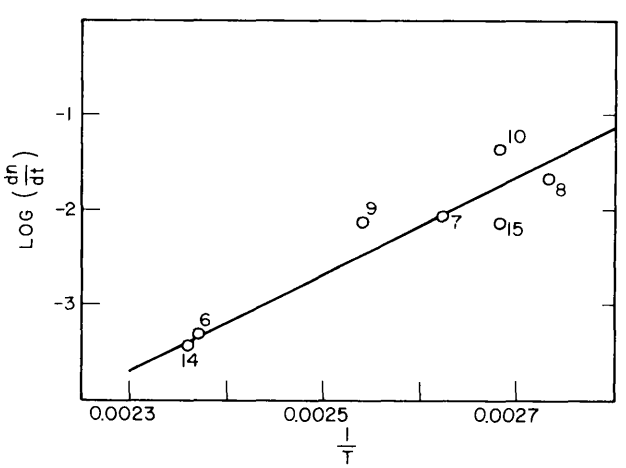


Fig. 12 - Log rates of adsorption versus 1/T(°K) for the adsorption of water vapor on E-glass fiber

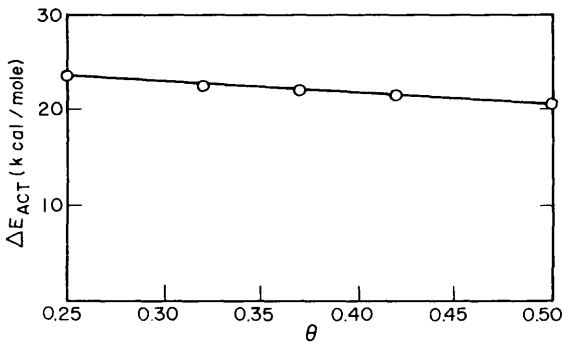


Fig. 13 - The apparent heat of activation as a function of surface coverage by water vapor

the dependence of E on coverage is given in Fig. 13. The apparent heat of activation of 20 to 24 kcal/mole is negative.

It is now possible to be highly critical of the above procedure. Taylor and Liang (33) pointed out 20 years ago that the significance of activation energy for adsorption on solids cannot be analogous to that for homogeneous reactions. When a surface is heterogeneous (all real solids appear to be on an atomic scale), there is no assurance that the two rates of adsorption observed at any two temperatures are concerned with the exactly same process. The activation energy has meaning only when the same number of gas molecules are adsorbed on equivalent surface sites at the two temperatures. A negative heat of activation, therefore, is without physical significance (34). When the above calculation was made for the E glass after contact with liquid water, a value of -75 kcal/mole was obtained at an apparent coverage of 0.3. This is a highly unlikely energy magnitude, and it is more reasonable to conclude that the process is not concerned with equivalent sites in the adsorption process at two temperatures and that the calculation, therefore, is not valid.

A realistic approach in developing a reaction mechanism for water-vapor adsorption on E glass is to recognize the existence and the variety of surface groups and their fractional surface coverage. Numerous infrared and structural studies of silica and porous glasses (35-38) combine to suggest the following molecular groups at the boundary surface:

Silanol terminal group	-SiOH
Aluminol terminal group	-AlOH
Borinol terminal group	-BOH
Silica network	-O-Si-O-Si-O-
Alumina network	-O-Al-O-Al-O-
Boria network	-O-B-O-B-O
Silicate ion	$-Si-O^-$
Aluminate ion	$-Al-O^-$
Borate ion	$-B-O^-$

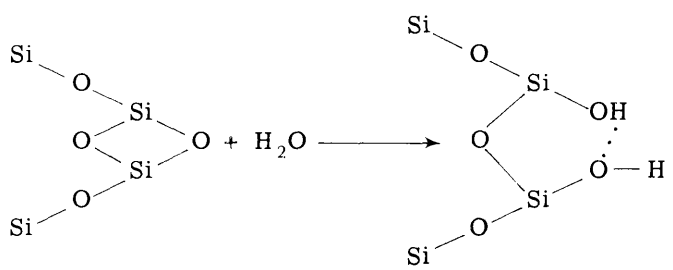
The cations Na^+, K^+, Ca^{++}, and Mg^{++} are also present in varying quantities, and these with the charged anions may be within and at the periphery of the network structure.

The water-vapor-glass interaction is viewed as many multiple-stage processes, which, in addition to a weaker van der Waal attraction, include the following groups of reactions:

I. Hydration of the surface cations
II. Hydrolyses of the surface anions

III. Hydrolyses of the surface networks
IV. Water-vapor adsorption by hydrogen bonding to the products of reactions I, II, and III

Accordingly, after the E-glass fiber has cooled from the outgassing temperature of 300°C to the experiment temperature, there is strong chemisorption according to reactions I, II, and III. This is followed by the reaction IV of water vapor interacting with the sites so formed. The hydrolysis of any one link in the silica network forms the adjacent silanol groups that have been shown to be required for water-vapor adsorption to silica. In the present work the coverage is always less than a monolayer, and there is no need to consider the formation of elaborate hydrogen bonding to form networks or cluster of water molecules. Similar considerations may be applied to the alumina and boria networks that may be part of the surface boundary:



The negative sign in the apparent heat of activation is readily explained by the negative temperature coefficients of the adsorption process (reaction IV). Reactions I, II, and III were too fast to follow in these studies. Similar situations with negative heats of activation have been reported for the reaction of ethylene and bromine catalysed by glass walls (39) and the reaction of nitric oxide and oxygen on glass (40).

An analogy may be drawn between reactions I, II, and III and known heats of reactions of water vapor with crystalline silicates, borates, and other inorganic solids. Table 5 contains the enthalpies of formation per mole of water of pertinent reactants and their well-defined products (41). The values are between -12 and -15 kcal for both the hydrolysis of the anions and for the hydration of the cations. It is, thus, reasonable to postulate that part of the initial fast water interaction with the heterogeneous E-glass surface containing many of these groups would involve bond energies of the same magnitude. It would be pertinent to determine the rates of water adsorption on some of the known crystalline species given in Table 5 to determine the activation energy of the water-vapor interaction with specific chemical groups.

The adsorption of water vapor to cations (e.g. Na^+) located in the boundary surface of a glass can be considerable. A qualitative estimate of the adsorption is possible from the hygroscopicity studies reported for a series of $Na_2O{\cdot}CaO{\cdot}SiO_2$ glasses (42). The amounts of water vapor adsorbed to powdered samples after periods of 1 and 2 hr were measured on exposure to 98% relative humidity (maintained by a saturated solution of $CaSO_4{\cdot}2H_2O$ at room temperature). These values are plotted in Fig. 14 as a function of the mole fraction of sodium in the glasses. It is reasonable that more sodium will be located at the surface with an increase of Na_2O in the glass. Of particular interest are the results at the lowest mole fraction of sodium which approach those reported by the same investigators for Pyrex and fused quartz, indicating that a negative adsorption of Na^+ at the glass boundary at low fractions. It may be noted that there is a considerable amount of water adsorbed on the $Na_2O{\cdot}CaO{\cdot}SiO_2$ glasses; monolayer coverage was estimated to be considerably less than 1 mg on the ordinate scale of Fig. 14. Any cleaning process that removes ionic constituents from the surface boundary can be

Table 5
Enthalpy Changes on Addition of Water Vapor to Various Inorganic Crystals (41)

Reaction	Enthalpy of Formation (kcal/mole H_2O)
$H_2Si_2O_5(c) + 2H_2O \longrightarrow H_6Si_2O_7(c)$	-11.6
$H_2SiO_3(c) + H_2O \longrightarrow H_4SiO_4(c)$	-12.1
HBO_2(rhombic) $+H_2O \longrightarrow H_3BO_3(c)$	-15.2
HBO_2(cubic) $+ H_2O \longrightarrow H_3BO_3$	-11.5
HBO_2(monoclinic) $+ H_2O \longrightarrow H_3BO_3$	-13.9
$CaHPO_4 + 2H_2O \longrightarrow CaHPO_4 \cdot 2H_2O$	12.6
$Ca(H_2PO_4)_2 + H_2O \longrightarrow Ca(H_2PO_4)_2 \cdot H_2O$	-15.8
$Al(NO_3)_3 \cdot 6H_2O + 3H_2O \longrightarrow Al(NO_3)_3 \cdot 9H_2O$	-14.4
$CaC_2O_4 \cdot H_2O + H_2O \longrightarrow CaC_2O_4 \cdot 2H_2O$	-12.2
$Ca(C_2H_3O_2)_2 + H_2O \longrightarrow Ca(C_2H_3O_2)_2 \cdot H_2O$	-12.3
$Sr(OH)_2 + H_2O \longrightarrow Sr(OH)_2 \cdot H_2O$	-15.2
$Sr(OH)_2 + 8H_2O \longrightarrow Sr(OH)_2 \cdot 8H_2O$	-13.7
$CaSO_4 + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O$	-12.5
$CaCl_2 + H_2O \longrightarrow CaCl_2 \cdot H_2O$	-17.3
$CaCl_2 + 2H_2O \longrightarrow CaCl_2 \cdot 2H_2O$	-15.0
$CaCl_2 + 4H_2O \longrightarrow CaCl_2 \cdot 4H_2O$	-14.7
$CaCl_2 + 6H_2O \longrightarrow CaCl_2 \cdot 6H_2O$	-14.4
$Al_2O_3 + H_2O \longrightarrow Al_2O_3 \cdot H_2O$	-21.1
$Al_2O_3 + 3H_2O \longrightarrow Al_2O_3 \cdot 3H_2O$	-13.9

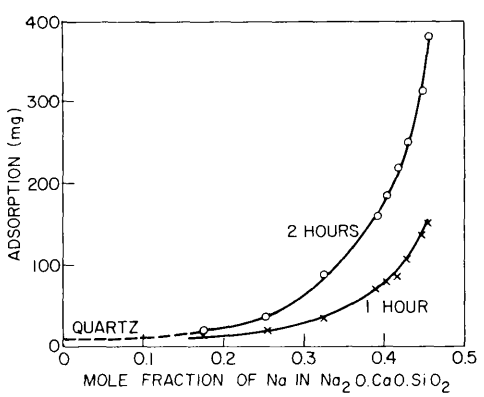


Fig. 14 - Water-vapor adsorption (Ref. 42) on a series of powdered glasses — $Na_2) \cdot CaO \cdot SiO_2$ — as a function of mold fraction of sodium

expected to reduce the water-vapor adsorption to this type of sample. The results of Rand (31) with leached porous glass is an example where the hygroscopic cations have been removed to decrease the water adsorption per unit area.

Concluding Remarks

Gas adsorption at fractional monolayer coverage is generally characterized by an extremely slow approach to a steady-state value. The interaction of water vapor with bare E-glass fiber in the range 90° to 150°C is no exception. There are strong rapid chemisorption processes accompanied or followed by physical adsorption.

Between the formation of the E-glass fiber used in the investigation and its evacuation, the sample had been briefly exposed to atmospheric moisture; it was then outgassed at 300°C. It is possible to draw the fiber in a water-free environment, but for the present there is considerably more to learn about the bare fiber using the current technique.

At 100°C the monolayer coverage of adsorbed water by the pristine E-glass fiber was reached at about 1.0 torr. This corresponds to a relative pressure range of 0.0013, and it is very unlikely under these conditions that capillary condensation plays any part in the adsorption process, as already suggested for even lower temperatures (43).

The comparison of the pristine E-glass fiber with that after exposure to liquid water shows pronounced differences in surface area and water-vapor adsorption. There is a small difference, only possibly significant, in the estimates of the heats of adsorption for the two cases. These were determined from the isotherms shown in Figs. 9 and 11. The heat of adsorption of water vapor on E-glass fiber and the pertinent results are summarized in Table 6. In the case of the pristine fiber there is good agreement between the heat of adsorption and the average heat of vaporization of liquid water. The water-washed fiber appears to have a lower value relative to the heat of vaporization.

Table 6
The Heat of Adsorption of Water Vapor on E-Glass Fiber

Fiber	Monolayer Content (μ moles)	Temperature Range (°C)	Av $\Delta H_{vap.}$ (cal)	N_a (μ moles)	θ	ΔH_a (cal)	
Pristine	57.1	100-150	8000	20	0.35	7100	7900 av
			8000	21	0.37	8000	
			8000	22	0.38	8600	
Water-washed	91.3	90-120	8200	35	0.38	5600	5600 av
			8200	40	0.44	5600	

The explanation can take at least three forms. First, the primary data are not equilibrium values; therefore, the use of the Clausius-Clapeyron equation is not warranted. To go further into this aspect of the problem would require studies in nonequilibrium thermodynamics. Second, the lower value of ΔH_a for the water-washed (w-w) fiber might be explained in terms of an entropy change. The free energy of the reaction may be written as

$$\Delta F_{orig} = -7900 - T\Delta S_{orig.}$$

and

$$\Delta F_{w-w} = -5600 - T\Delta S_{w-w}.$$

Since the comparison is being made at a similar surface coverage and in the same pressure and temperature ranges, the free-energy changes may be considered to be about equal. If this is so, the difference can result only from a greater entropy change when water vapor is adsorbed to the water-washed fiber. This is not unreasonable since the water-washing process may yield a greater number of silanol groups positioned as close neighbors and thus result in a decreased random distribution of adsorbed water. An entropy change of 6 cal/degree is indicated for the above results.

A third explanation, however, also warrants consideration. The boundary surface of E glass has been shown to have great chemical complexity. Contact with liquid water definitely removes calcium and sodium ions, these having great affinity for water vapor. These changes are significant. As a result the above suggested explanations for the

difference between the two fibers may not be valid because a comparison of like with like is not being made. More data are needed using E-glass surfaces treated in a systematic manner to determine the nature of the adsorption sites that interact with water vapor.

If the bonding of a silane in a finishing agent to an E-glass fiber is via a chemical reaction with a silanol group (44,45), one may expect that the bonding would depend on the number of silanol groups in the surface. One result of this investigation suggests that a short exposure of the fiber to liquid water would do this. The exposure must be controlled so as to limit the reaction to a fraction of the surface and thus not jeopardize the integrity of the mechanical strength of the fiber. This is an intriguing possibility that merits further consideration. However, any silanol group that does not react with a component of the finishing agent remains as a water-adsorbing site and poses a threat to decreasing the wet strength of fiber composite.

The path followed by a crack traveling through bulk glass might well depend on the water-vapor-glass interaction. Wiederhorn (46) has shown the effect of water vapor on crack propagation in soda-lime glass. The hydration of the exposed cation at the crack tip may well be the primary reaction. The transport of the water molecules from the vapor to the crack tip would entail a chain-carrier mechanism, and the volume change that accompanies the hydration of a cation such as Na^+ would provide the strong gradient at atomic dimensions.

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13. ABSTRACT

The surface of the E-glass fiber is subject to subtle chemical changes, as are all glass surfaces. To start with an unmodified surface, pristine E-glass fiber was prepared directly from a melt of E-glass marbles. The experimental conditions were selected to measure adsorption on partially covered surfaces where the influence of surface groups can best be seen. The sample of E-glass fiber was selected so that the surface area was very much larger than the walls of the Pyrex container. The volumetric adsorption procedure employed for krypton was adapted for use with water vapor.

Knowing the length, weight, and density of the pristine E-glass fiber, an independent value was determined for the cross-sectional area of adsorbed krypton at -195°C. The adsorption and description of water vapor was followed between 90° and 150°C, and simple Elovich kinetics were observed for times up to 2000 min. Adsorption isotherms for water vapor were calculated after the fractional decrease in pressure ($\delta p/p$) became < 0.01. The heat of adsorption for an estimated surface coverage of 0.4 was 7900 cal/mole; the corresponding heat of vaporization of water was 8000 cal/mole. The behavior of pristine E-glass fiber was compared with the behavior after treatments with liquid water. The complexity of a glass surface is obviously compounded after aqueous treatments, and the influence of this on gas adsorption is pronounced.

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