The constants of combination are given by

$$c_{1k}=\frac{p_{1k}^2-a_1p_{1k}+a_0}{(p_{2k}-p_{1k})(p_{3k}-p_{1k})} \tag{D–11}$$

$$c_{2k}=\frac{p_{2k}^2-a_1p_{2k}+a_0}{(p_{1k}-p_{2k})(p_{3k}-p_{2k})} \tag{D–12}$$

$$c_{3k}=1-c_{1k}-c_{2k} \tag{D–13}$$

Finally,

$$c_z=\frac{(r_1-a_2)(1+r_2)}{(r_1-r_2)(1+a_2)} \tag{D–14}$$

$$c_0=\frac{(nr_1-1)(1+r_2)}{(r_1-r_2)(n+1)} \tag{D–15}$$

$$a_2=\frac{En+2}{n} \tag{D–16}$$

Effective relaxation times for the seal, τ_{kjr}, are defined by $\tau_{kjr}\equiv\tau_{\sigma r}/p_{kj}$.

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Reaction of Glasses with Hydrofluoric Acid Solution

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The gravimetric method was used to study the reaction between fused silica and silicate glasses with HF acid solution. The reaction was found to be transport-controlled. Additions of Al_2O_3, CaO, or both to fused silica caused a reduction in corrosion resistance of the resulting glasses.

I. Introduction

To COMPARE the reactivity of fused silica[†] and silicate glasses with HF acid solution and with H_2 gas,[1,2] the HF acid reaction was investigated. It was found that the rate-limiting step of the overall reaction is transport of product away from the glass into the liquid phase, i.e. transport- or diffusion-controlled. This aspect was not discussed in previously published papers[3–5] on the mechanisms of this reaction. It is the purpose of this paper to present these reaction results and to interpret the reaction mechanism between silica glass and several silicate glasses with HF acid solution.

II. Experimental Procedure

Six silicate glasses[‡] were used in this study (Table I). Slabs of glasses were core-drilled into 9-mm cylinders and cut into 2 mm-thick disks. The silica glass, received as a 9-mm-diameter rod, was cut into 2 mm-thick disks. All of the disks were pre-etched with HF acid solution, then stored in a desiccator. Commercial-grade HF acid solution was used and diluted with distilled water to the concentrations needed.

A constant-temperature water bath shaker was used. A solid state time-proportioning heat controller allowed precise temperature control from ambient temperature to 100°C. The oscillation speed varied between 20 and 200 cycles/min, which was the limit of the shaker. Polyethylene bottles were used as containers for the HF acid solution. In a reaction experiment glass samples were hung in a net of platinum wire from the top of the bottle. In each experiment a small piece of glass and a large amount of HF acid solution ($\approx$1.3 cm^2 per $\approx$40 cm^3 solution) were used. The reaction time was also limited (usually $<$1 h) so that the size reduction of the glass sample was insignificant and the HF acid concentration remained essentially unchanged.

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[†] Amersil Inc., Hillside, NJ (composition as oxides reported by American Spectrographic Laboratories, San Francisco, CA: SiO_2 major, Al_2O_3 0.045, FeO 0.015, MgO 0.0007, CaO 0.0005, and CuO 0.0005 wt%).

[‡] Prepared by George H. Beall, Corning Glass Works, Corning, NY, by a rapid quenching method.

Table I. Compositions of Glasses Studied

	Composition						
	Wt percent			Molar percent			
Glasses	SiO_2	Al_2O_3	CaO	SiO_2	Al_2O_3	CaO	Density
SiO_2	100	0	0	100	0	0	2.20
K	80	20	0	87.2	12.8	0	2.31
L	70	30	0	79.8	20.2	0	2.42
N	78.4	19.6	2	85.2	12.5	2.3	2.30
O	68.6	29.4	2	77.9	19.7	2.4	2.38
P	58.8	39.2	2	70.0	27.5	2.5	2.61
Q	76.2	19.1	4.8	82.4	12.1	5.5	2.32
S	57.1	38.1	4.8	67.5	26.5	6.0	2.52

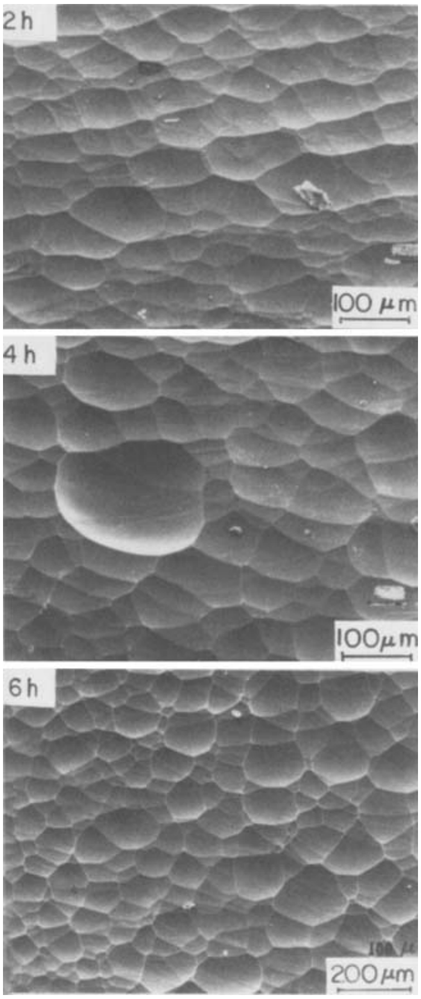

Fig. 1. Surface morphology of silica glass after reaction with HF solution for 2, 4, and 6 h.

III. Results and Discussion

(1) Reaction with Silica Glass

The as-cut glass specimens showed a higher initial reaction rate with HF solution as a result of a larger surface area due to the presence of microcracks generated during the cutting process; the pre-etching step removed the microcracks. The etched specimens had surface morphologies which were invariant with reaction time (Fig. 1). The cusps were estimated to have depths of 10 to 20 μm and diameters of 50 to 100 μm by taking two photographs at different tilt angles and using a stereoscope. The true surface area of the etched glass samples calculated from these photos is only ≈4% higher than the projected flat surface area and was assumed to remain constant.

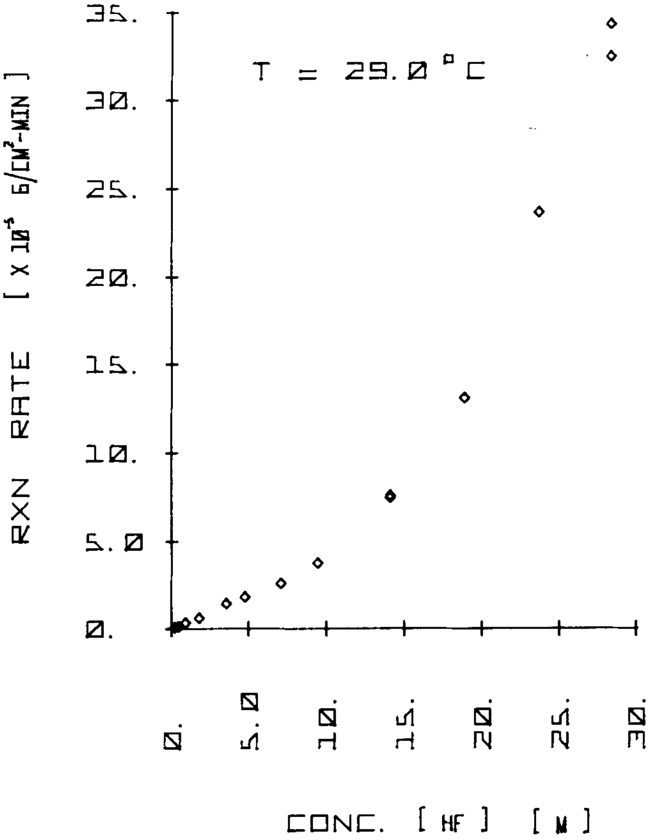

Fig. 2. Reaction rate of silica glass and HF solution vs molar HF concentration.

Experimental results revealed that the reaction rate varied with agitation and was slower at the bottom of the container due to precipitation of silica gel formed during the reaction. A platinum wire hanger was thus used to raise the specimens above the bottom of the acid container and a shaker provided agitation to remove the reaction product from the surface of the sample. Preliminary runs indicated that the reaction rate increased with oscillation speed without leveling off at the maximum speed of the shaker. To compare corrosion resistance of different glasses under different conditions (temperature, acid concentration), a fixed agitation rate of 120 cycles/min was arbitrarily chosen. All of the following data were recorded at this oscillation rate. This behavior and the invariant surface morphology of the reacted silica glass specimens (Fig. 2) suggest that this reaction is transport-controlled.

The effect of concentration of HF acid solution on the reaction rate of silica glass is shown in Fig. 2. At low HF acid concentrations the reaction rate appears to be proportional to concentration. With higher concentrations, after a transition range, the increase in reaction rate was greatly enhanced and also appears to be linear. This difference is assumed to be due to the dominance of fluoride ions at low concentrations followed by dominance of the more active bifluoride ions (HF_2^-), as reported in the literature.[3–5] However, the temperature dependence of the reaction rate (Fig. 3) remained the same at all concentration levels of 3 to 24*M* with an activation energy of 22.2 kJ/mol (5.3 kcal/mol). This value for activation energy, which is low for a chemical reaction, and its constancy also suggest a transport-controlled mechanism. The small activation energy combined with the accelerated corrosion rate in the more-concentrated solutions can be attributed to the more-active bifluoride ion causing a higher equilibrium-product concentration at the interface while diffusion through the surface product layer remained the slowest step.

Exploratory tests showed that although hydrogen ion (H^+) was needed for the reaction to proceed, the reaction rate did not change with H^+ if the F^- concentration remained constant. On the other

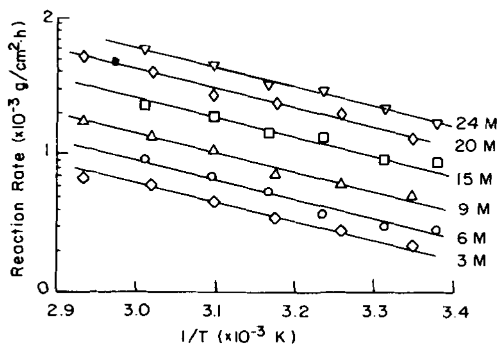

Fig. 3. Temperature dependence of rate of reaction between silica glass and HF solutions of concentrations indicated.

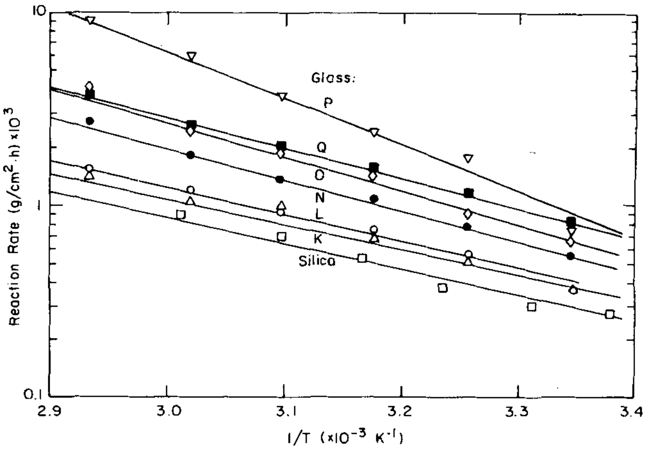

Fig. 4. Rates of reaction of CaO-Al_2O_3-SiO_2 glasses with 6*M* HF solution vs temperature.

hand, an increase of F^- from other sources (such as with addition of CaF_2) increased the reaction rate significantly, e.g. the reaction rate in $NH_4F{\cdot}HF$ was almost twice that in HF acid solution of the same molarity, which can be attributed to the bifluoride ion (HF_2^-) formation. The independence of the reaction rate relative to the H^+ concentration suggests at least a two-step reaction mechanism. The first step (Eq. (1*a*)) is the hydration of the silica surface which is enhanced by the presence of H^+. The second step (Eq. (1*b*)) is the reaction of the hydrated surface with HF acid to form SiF_4. The latter step involves a breaking of the electron bonds and removal of the fluorine product from the surface. The steps and total reaction (2) can be written as

$$SiO_2+2H_2O \rightarrow Si(OH)_4 \tag{1a}$$

$$Si(OH)_4+4HF \rightarrow SiF_4+4H_2O \tag{1b}$$

$$SiO_2+4HF \rightarrow SiF_4+2H_2O \tag{2}$$

(2) Reaction with Silicate Glasses

For comparison, all of the reaction rates for the silicate glasses (Table I) were determined using a 6*M* HF acid solution at a fixed oscillation rate of 120 cycles/min (Fig. 4). After reaction, the same surface morphology as that of silica glass was observed for all these glasses. No crystallinity or phase separation was observable by XRD or SEM.

Experimental data indicated that the addition of either Al_2O_3 or CaO to the silica glass increased the reaction rate. With the addition of Al_2O_3 alone (K and L in Fig. 4) the glasses had slightly higher reaction rates. It has been reported[6] that aluminosilicate glasses show phase separation of mullite when heat-treated above 1000°C, but these crystals are so small that the specimens are still transparent or slightly translucent, being detected only by TEM. Although the reported corrosion resistance[7] is mullite$\gg$silica glass$>$aluminosilicate glass, the presence of isolated small crystals of mullite causes a greater weight loss on reaction since they slough off with solution of the glass matrix.

The addition of only 2 wt% CaO increased the reaction rate considerably, as is seen by comparing glass K with N, and L with O (Fig. 4). The reaction rate also increased by increasing the Al_2O_3/SiO_2 ratio with CaO constant at 2 wt% (glasses N, O, and P). Another relation in Fig. 4 showed an increase in reaction rate with an increase of CaO from 0 to 5 wt% in glasses with a constant Al_2O_3/SiO_2 ratio of 20/80 (glasses K, N, and Q). These relations are associated with the fact that presence of CaO enhances phase separation since the glasses become opaque when heated at $T>1000$°C.

IV. Summary

The reaction between silica and silicate glasses with HF acid solution was considered to be transport- or diffusion-controlled from the glass into the liquid because of (1) an invariant surface morphology of the reacted glasses with time, (2) increase in reaction rates with agitation, and (3) the low activation energies for the overall reactions. Different reaction rates are considered to be due to a different equilibrium product concentration at the interface. Variations in the reactivity of the acid solution, e.g. polymerization of HF or formation of bifluoride ions, and variations in the reactivity of the glass can result in different equilibrium concentrations and, in turn, different reaction rates. In all cases no detectable residue remained on the specimen surfaces. Both Al_2O_3 and CaO additions to the SiO_2 glass increase the reactivity of the glass toward HF acid solutions. On the other hand, it is of interest to note that such additions to SiO_2 glass increase its resistance to hydrogen gas corrosion.[1,2]

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