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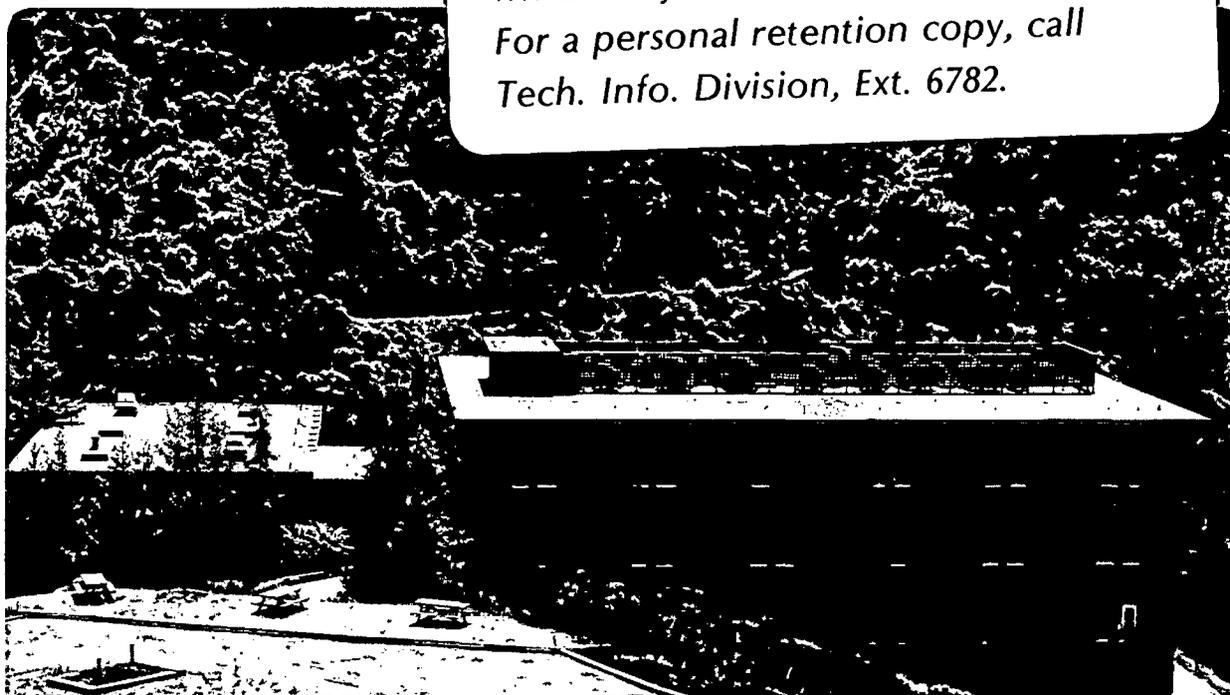
REACTION OF GLASSES WITH HYDROFLUORIC ACID SOLUTION

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REACTION OF GLASSES WITH HYDROFLUORIC ACID SOLUTION

by

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ABSTRACT

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. The corrosion resistance of the glass was found to decrease with addition of  $Al_2O_3$ , CaO or both.

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\*Now with Central Research Lab., Texas Instruments, Dallas, Texas

## INTRODUCTION

For the purpose of comparing the reactivity of fused silica<sup>†</sup> and silicate glasses with HF acid solution and with H<sub>2</sub> gas<sup>1,2</sup>, an investigation was carried out on the HF acid reaction. It was found that the reaction is transport controlled. This aspect was not discussed in previously published papers<sup>(3,4,5)</sup> on the mechanisms of this reaction, and some explanations were questionable. It is the purpose of this paper to present some reaction results and an interpretation of the reaction mechanism between silica glass and several silicate glasses with HF acid solution.

## EXPERIMENTAL PROCEDURE

Six silicate glasses\* were used in this study whose compositions are listed in Table 1. The silicate glasses were core drilled into 9 mm cylinders and cut into 2 mm-thick discs. The silica glass, received as a 9 mm diameter rod, was cut into 2 mm-thick discs. All of the discs were pre-etched with HF acid solution to remove surface irregularities and microcracks introduced in the cutting process. They were then stored in a desiccator.

Commercial grade HF acid solution was used. It was diluted with distilled water to the concentration needed.

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\* Prepared by George H. Beall, Corning Glass Works by a rapid quenching method.

† Obtained from Amersil Co. (Composition as oxides reported by American Spectrographic Laboratories: SiO<sub>2</sub>-major, Al<sub>2</sub>O<sub>3</sub>-0.045, FeO-0.015, MgO-0.0007, CaO-0.0005, and CuO-0.0005 wt %).

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 to 200 cycles/min. 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 adequate amount of HF acid solution were used. The reaction time was also limited (usually <1 hr.) so that the size reduction of the glass sample could be neglected, and the HF acid concentration remained practically unchanged.

## RESULTS AND DISCUSSION

### (A) Reaction with Silica Glass

The as-cut glass specimens showed a higher initial reaction rate 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 similar surface morphologies which were invariant with reaction time, as shown in Fig. 1. The depth of the cusps was estimated by taking two photographs at different tilt angles and using a stereoscope. In Fig. 1, the depth of the cusps was 10 ~ 20  $\mu\text{m}$  and the diameter, 50 ~ 100  $\mu\text{m}$ . The true surface area of the etched glass samples calculated from these photos is only 4% higher than the projected flat surface area. Furthermore, because of the invariance of the surface morphology, the total surface area remains fairly constant. This feature makes the gravimetric study of the reaction rate attractive.

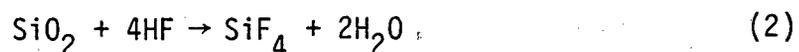
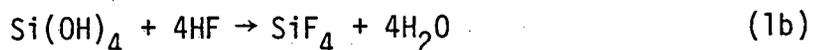
Experimental results revealed that the reaction rate varied with

agitation. Without agitation the reaction rate at the bottom of the container was lower due to precipitation of a silica gel formed during the reaction. A platinum wire hanger was used to raise the specimens above the bottom of the acid container. Also, a shaker was used to provide agitation to remove the reaction product from the surface of the sample. The reaction rate increased monotonically with the oscillation speed without leveling off at the maximum speed of the shaker (200 cycles/min.). This result and the surface morphology of the reacted silica glass specimens suggest that this reaction is transport controlled. In order to compare corrosion resistance among different glasses as well as 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.

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 was found to be proportional to concentration. In the more concentrated solutions, after a transition range, the reaction rate was greatly enhanced and also appeared to be linear. This increase in the reaction rate at higher concentrations is explained on the basis of the formation of considerably more active bifluoride ions ( $\text{HF}_2^-$ )<sup>(2,3,4)</sup>. 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 5.3 kcal/mole. This value of activation energy is low for a chemical reaction which therefore also suggests a transport controlled mechanism. The unique activation energy combined with the accelerated corrosion rate in the more concentrated solutions can be explained by the more active

bifluoride ion causing a higher equilibrium product concentration at the interface while diffusion remained the slowest step.

It was also found that although hydrogen ion ( $H^+$ ) was needed for the reaction to proceed, the reaction rate was not affected by the  $H^+$  concentration. On the other hand, the fluoride ion from other sources (such as  $CaF_2$ ) increased the reaction rate significantly. The silica glass had about twice the reaction rate in  $NH_4F \cdot HF$  than in HF acid solution of the same molarity. This observation can also be explained on the basis of 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, proposed as follows. The first step is the hydration of the silica surface which is enhanced by the presence of  $H^+$ . The second step is the reaction of the hydrated surface with HF acid to form  $SiF_4$ . This step involves a breaking of the electron bonds and removal of the fluorine product from the surface; it is therefore the slowest step. The step and total reactions can be written as



The fluoride and bifluoride concentrations play a dominating role in determining final product concentration at the interface.

#### (B) Reaction of Silicate Glasses

For comparison, all of the reaction rates for the silicate glasses (Table 1) were determined using a 6M HF acid solution at a fixed oscillation rate of 120 cycles/min. After etching, the same surface morphology as that of silica glass was observed for all these silicate glasses. The x-ray diffraction analysis showed no crystallinity and SEM did not show up any phase separation.

Experimental data indicated that the addition of either  $\text{Al}_2\text{O}_3$  or CaO to the silica glass increased the reaction rate. With the addition of  $\text{Al}_2\text{O}_3$  alone (K and L glasses) the glasses have only slightly higher reaction rates (Fig. 4). It has been reported<sup>(6)</sup> that aluminosilicate glasses show phase separation of mullite on heat treatment above 1000°C; but these crystals are so small that the specimens are still transparent or slightly translucent, being detected only by transmission electron microscopy. From a thermodynamic viewpoint this behavior means that the glasses are highly metastable and have a high internal energy. It would then be expected that they would have less resistance to corrosion. This situation is consistent with the reported corrosion resistance<sup>(7)</sup>: mullite >> silica glass > aluminosilicate glass.

The addition of only 2 wt% CaO increased the reaction rate considerably as seen by comparing glass K with N, and L with O (Fig. 4). The reaction rate also increased by increasing the  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio with CaO constant at 2 wt% (glasses N, O and P). Another relationship in

Fig. 4 showed an increase in reaction rate with an increase of CaO from 0 to 5 wt% in glasses with a constant  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio of 20/80 (glasses K, N and Q). These relationships are associated with the fact that CaO enhances the previously mentioned phase separation since the glasses become opaque upon heating below  $1000^\circ\text{C}$ ; glasses behave similarly with additions of  $\text{Al}_2\text{O}_3$ . The associated high internal energy in the presence of CaO and  $\text{Al}_2\text{O}_3$ , and the network modifying character of CaO, enhances reactivity which contributes to the reduction of corrosion resistance to HF acid solution.

#### SUMMARY

The reaction between silica and silicate glasses with HF acid solution is found to be transport controlled. Different reaction rates are considered to be due to a different equilibrium product concentration at the interface. Variation in the reactivity of the acid solution, e.g., polymerization of HF, or formation of bifluoride ions, and variation in the reactivity of the glass can result in a different equilibrium concentration and, in turn, a different reaction rate. In all cases no residue was found to remain on the specimen surfaces. Both  $\text{Al}_2\text{O}_3$  and CaO additions to the  $\text{SiO}_2$  glass increase the reactivity of the glass toward HF acid solutions.

#### ACKNOWLEDGMENT

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the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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FIGURE CAPTIONS

- Fig. 1. Surface morphologies of silica glass after reaction with HF acid solution for 2, 4 and 6 hours. (XBB 770-10487)
- Fig. 2. Reaction rate of silica glass and HF acid solution vs. the molar HF concentration. (XBL 7710-10329)
- Fig. 3. Temperature dependence of the reaction rate between silica glass and hydrofluoric acid solutions with increasing concentration. (XBL 7710-10331)
- Fig. 4. Reaction rates of  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  glasses with 6M HF acid solution at several temperatures. (XBL 7710-10330, XBL 7710-10332, and XBL 7710-10323---XBL 815-5817)

TABLE 1.

<u>GLASSES</u>	<u>[WT. PERCENT]</u>			<u>[MOLAR PERCENT]</u>			<u>DENSITY</u>
	<u>SiO<sub>2</sub></u>	<u>Al<sub>2</sub>O<sub>3</sub></u>	<u>CaO</u>	<u>SiO<sub>2</sub></u>	<u>Al<sub>2</sub>O<sub>3</sub></u>	<u>CaO</u>	
SILICA	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

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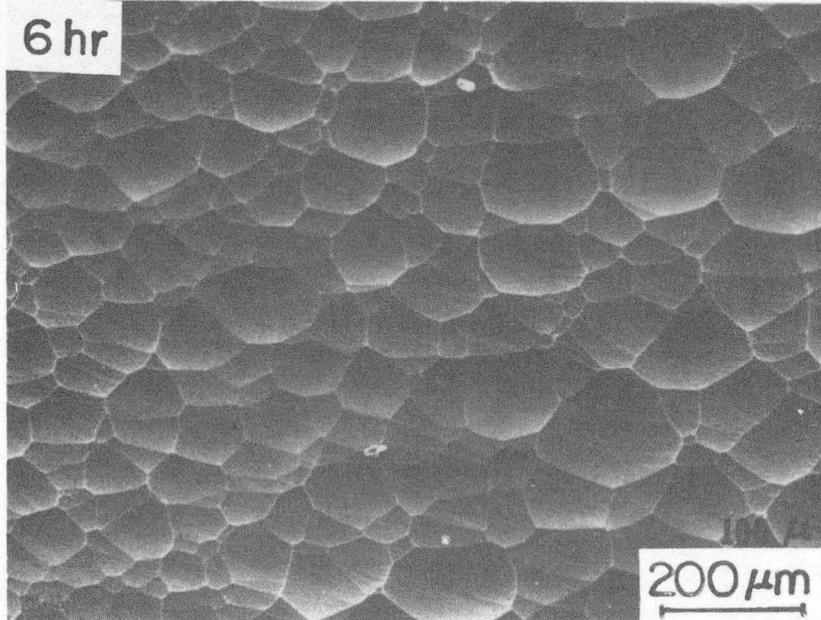
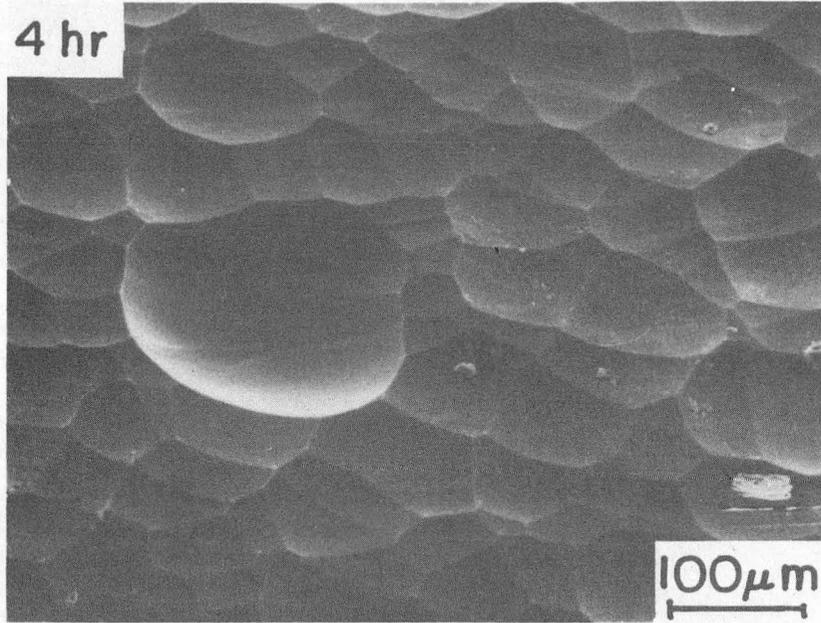
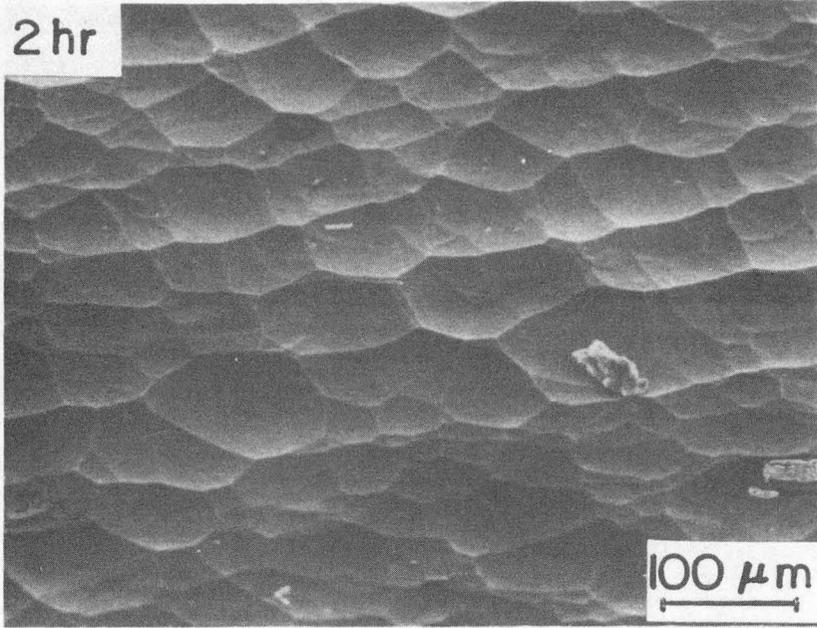
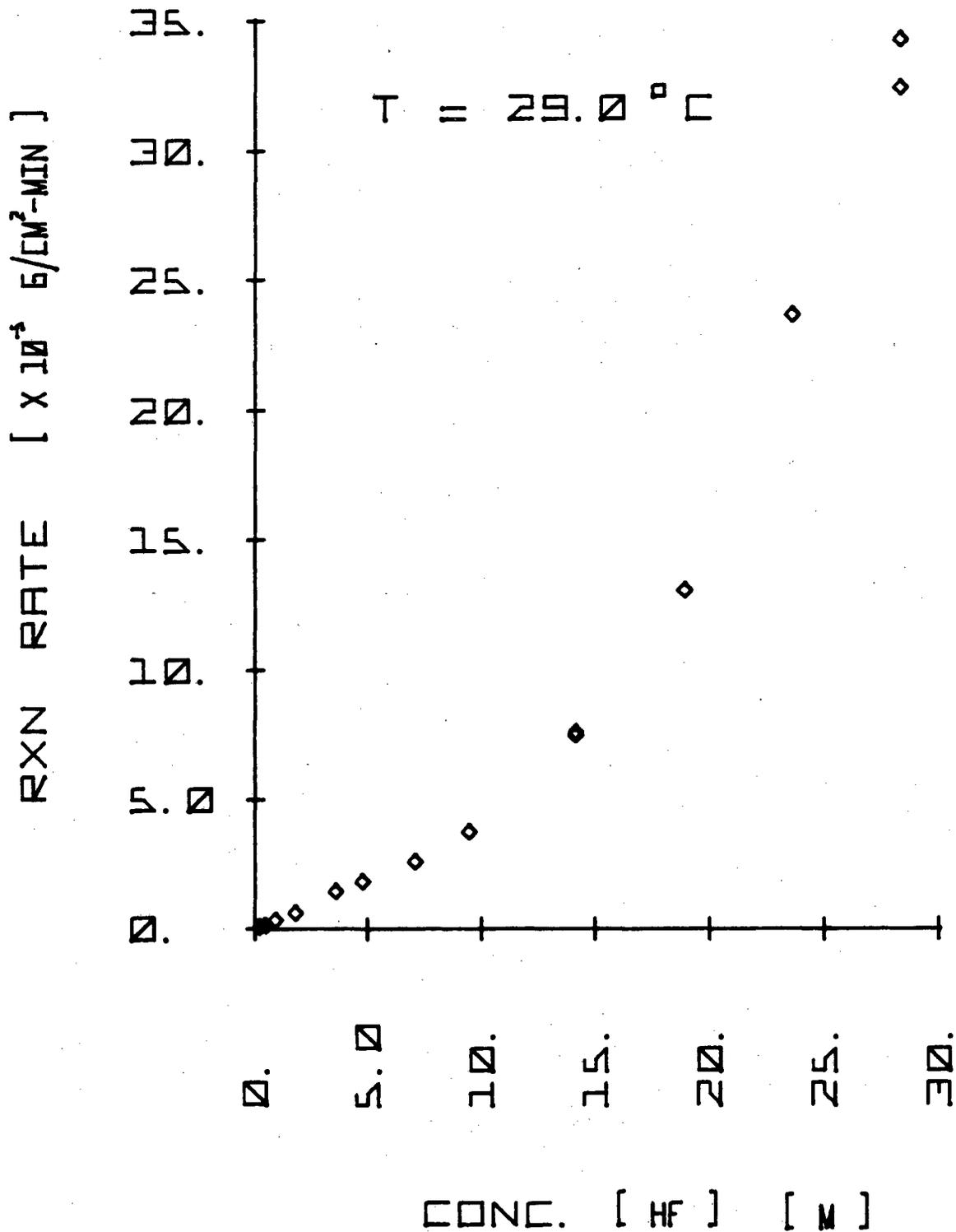


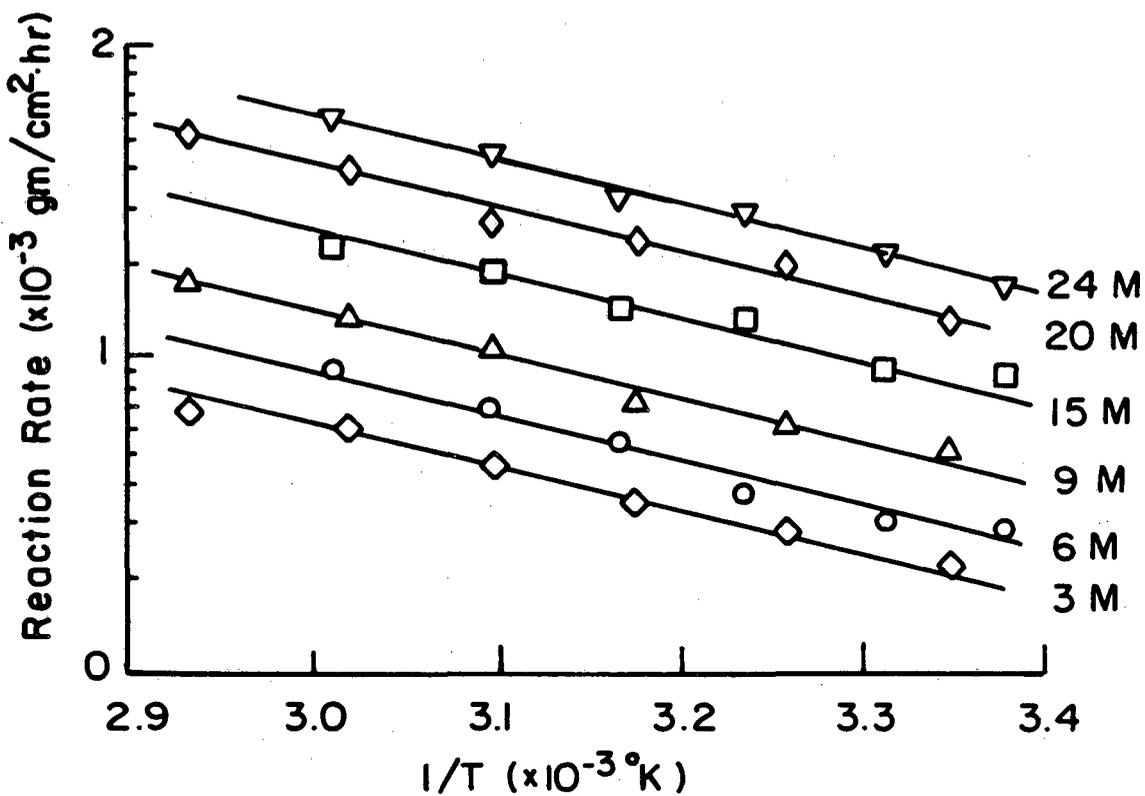
Fig. 1

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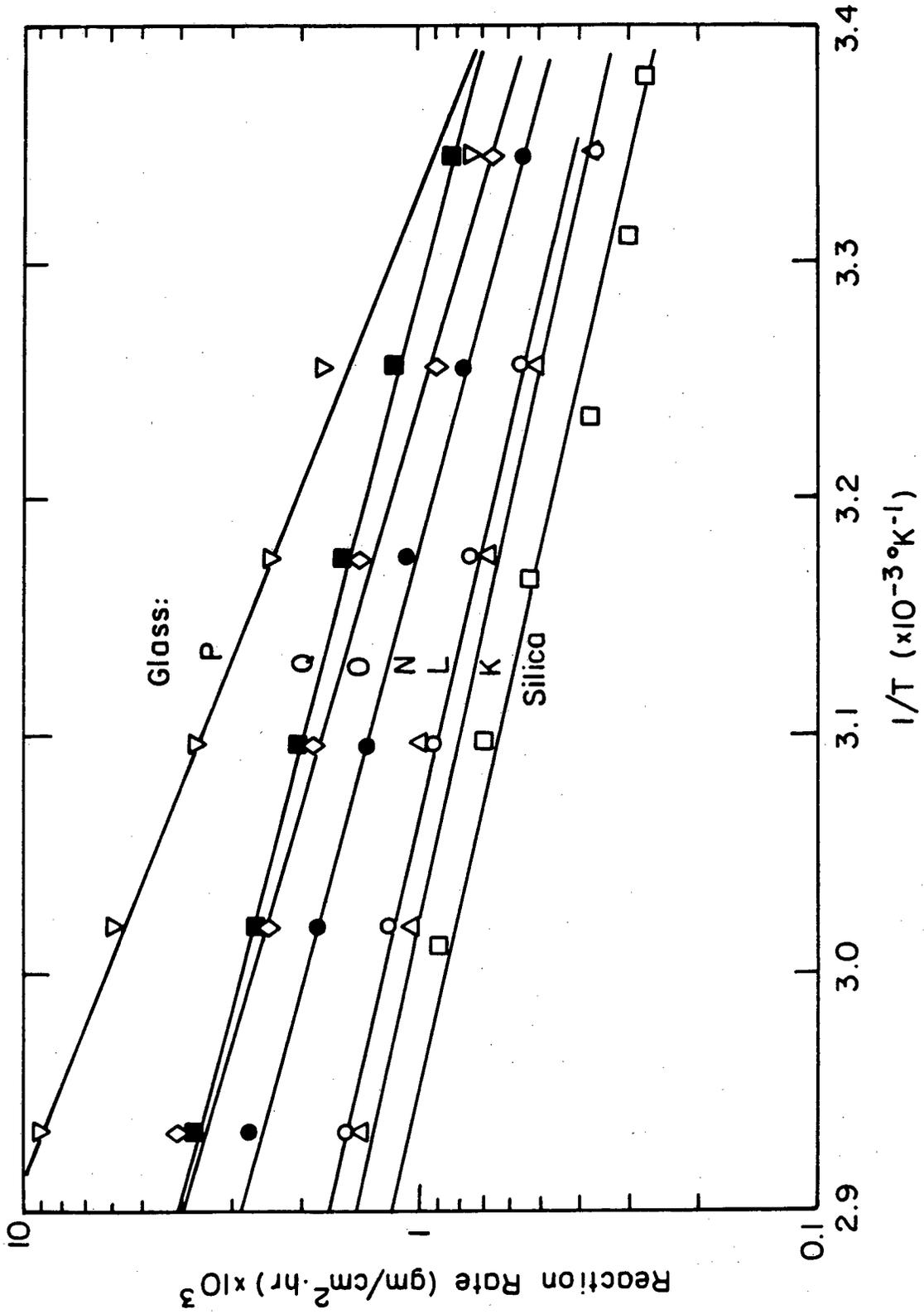
XBL 7710-10329

Fig. 2



XBL 7710-10331 A

Fig. 3



XBL 815-5817

Fig. 4

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