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Reaction of Fused Silica With Hydrogen Gas

by

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ABSTRACT

The reaction between fused silica and hydrogen gas in the experimental temperature range of 1200 to 1400°C forms SiO and H₂O vapors. At a sufficiently high constant flow rate of hydrogen gas the reaction rate is not transport controlled. The rate limiting step is deduced to be the desorption of the product from the glass surface.

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

INTRODUCTION

In the coal gasification process, silicate refractory linings are corroded in the reducing atmosphere. Hydrogen gas is an important constituent of the reducing gas atmosphere (CO , CH_4 , H_2 , etc.). In order to develop a fundamental understanding of the complex corrosion processes, it is desirable to first understand relatively simple systems in order to design a practical corrosion resistant material. Therefore, this study dealing with the mechanisms and kinetics of the reaction between fused silica and hydrogen gas was undertaken.

EXPERIMENTAL

The gravimetric method was used to measure the reaction rate. A hydrogen furnace was built for corrosion testing of samples. A schematic of the hydrogen furnace system is shown in Fig. 1. Hydrogen gas, provided by Lawrence Berkeley Laboratory, had a reported purity of 99.999%, oxygen -1.5 ppm, water vapor -0.25 ppm, and a dew point of -84.4°C . Helium as a carrier gas was available. An ice water cold trap was found necessary to condense the reaction product (mostly H_2O) in order to prevent clogging of the flow valve and check valve. An alumina furnace tube was used because of its corrosion resistance to hydrogen gas, but it is vulnerable to thermal shock. Design features and proper control of heating and cooling rates had to be introduced to minimize thermal shock problems.

Inside the alumina tube (Fig. 2) baffles were introduced as a heat exchanger to heat the incoming hydrogen gas. They also reduced the heat loss from the ends of the furnace tube. A sample holder was designed

to effectively reduce the total cross-section of the tube so as to get a high linear gas flow velocity past the specimens with a reasonably low total volume flow rate to reduce the gas consumption rate as well as the power consumption rate.

The silica glass* used was analyzed^Δ spectrographically for impurities which are reported as oxides: Al_2O_3 - 0.045, FeO - 0.015, MgO - 0.0007, CaO - 0.0005 and CuO - 0.0005 wt.%. The silica glass was received as a 9 mm rod. It was cut into 2 mm thick discs and then treated with hydrofluoric acid solution to remove microcracks caused by abrasion of the diamond saw. The surfaces of the reacted samples were examined by an optical microscope and a scanning electron microscope (SEM). The presence of crystalline phases was determined by X-ray diffraction (XRD).

RESULTS AND DISCUSSION

(A) Devitrification of Silica Glass

It was observed that silica glass devitrified in the hydrogen atmosphere in the temperature range 1200 to 1400°C. Heating in air to the same temperature did not result in devitrification of the glass. The product of the devitrification reaction was identified as cristobalite by XRD. The extent of devitrification was found to be a function of reaction temperature and time. The formation of the cristobalite started at the surface of the glass sample and propagated towards the center. Upon cooling, the glass cracked in the temperature range of 270 to 200°C as a

* Obtained from Amersil Co.

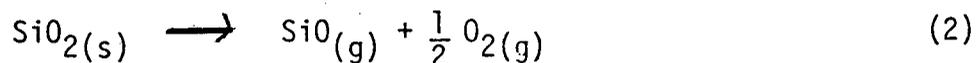
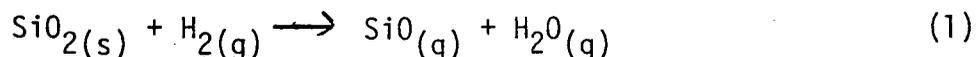
^ΔAmerican Spectrographic Laboratories

result of the $\beta \rightarrow \alpha$ cristobalite transformation.

It was found that the devitrification decreased in extent with continued use of the alumina furnace tube in hydrogen. The condensates in the cold trap of the hydrogen furnace (Fig. 1) contained sodium and a small amount of potassium as identified by Energy Dispersive X-ray Analysis. Their source was the sodium oxide and potassium oxide in the alumina tube which were reduced to sodium and potassium vapor and removed by the flowing hydrogen gas. Deposition of the vapors on the silica glass surface occurred as a result of the high concentration of water vapor near the glass sample in the furnace due to the reaction of silica and hydrogen. Formation of sodium silicate glass on the surface caused the formation of crystal nuclei which resulted in the propagation of devitrification. Therefore, removal of the sodium oxide from the tube should halt the devitrification of the silica glass. This hypothesis was verified by heating each new alumina tube in flowing hydrogen at 1500°C for 24 hours which resulted in complete elimination of the devitrification of the silica glass.

(B) Weight Loss Mechanism

In the presence of hydrogen gas, silica glass showed a weight loss at high temperatures. This loss may be due to a reaction with hydrogen gas according to reaction (1), or by decomposition in a low oxygen partial pressure according to reaction (2).



For reaction (1), using the thermodynamic data at 1600°K

$$\Delta G = -56.24 - 37.93 + 150.03 = 56.86 \text{ KCal}$$

$$\Delta G = -RT \ln K_{eq} = -RT \ln \frac{[SiO][H_2O]}{[H_2]}$$

$$[H_2] \cong 1$$

$$[H_2O][SiO] = 2.3 \times 10^{-8}$$

If $[H_2O] = [SiO]$ (i.e. $C_{H_2O} = C_{SiO} = 0$ in the incoming gas), then $[H_2O] = [SiO] = 1.5 \times 10^{-4}$ and relationship (3) holds which is the maximum equilibrium value.

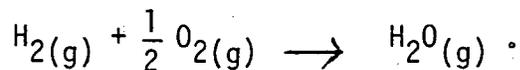
$$P_{H_2O} = P_{SiO} = 1.5 \times 10^{-4} \text{ atm} \quad (3)$$

For reaction (2) at 1600°K

$$\Delta G = 93.8 \text{ KCal} = -RT \ln [SiO][O_2]^{1/2}, \text{ and}$$

$$[SiO][O_2]^{1/2} = 1.54 \times 10^{-13} \quad (4)$$

in order to estimate the partial pressure of oxygen, the following reaction has to be considered:



At 1600°K

$$\Delta G = -37.9 \text{ KCal} = -RT \ln \frac{[H_2O]}{[H_2][O_2]^{1/2}}$$

Since the $P_{H_2} \cong 1 \text{ atm}$,

$$[O_2]^{1/2} = [H_2O] \times 6.58 \times 10^{-6}, \text{ and}$$

$$[O_2] = [H_2O]^2 \times 4.33 \times 10^{-11} \quad (5)$$

At equilibrium for reaction (1), the partial pressure of hydrogen is 1.5×10^{-4} atm (Eq. 3). Therefore the oxygen partial pressure will be $\sim 10^{-18}$ atm according to Eq. 5. In turn, the equilibrium partial pressure of SiO calculated from Eq. 4 is $[\text{SiO}] \sim 10^{-4}$. Without reaction (1), the water vapor partial pressure is reported to be less than 10^{-6} atm in the hydrogen gas. A higher SiO partial pressure is a possibility.

The above calculations give the maximum rate of reaction according to thermodynamic considerations. The experimental weight loss rate of SiO_2 at 1600°K is $\sim 2.5 \times 10^{-3}$ g/hr.cm² ($\sim 4.2 \times 10^{-5}$ mole/hr.cm²). Using Eq. (6), $P_{\text{SiO}} = 10^{-7}$ atm.

$$J = 44.33 \frac{P_{\text{SiO}}}{\sqrt{MT}} \quad (6)$$

From the calculated values for $P_{\text{SiO}} = [\text{SiO}]$, it can be seen that both reactions (1) and (2) are thermodynamically favorable. The weight loss is determined by the kinetics of these reactions.

The following experiment was conducted to determine whether reaction (1) or (2) was responsible for the experimental weight loss. A piece of silica glass was heated in a tantalum furnace in the presence of titanium wool at 1300°C ($P_{\text{total}} < 10^{-6}$ torr) for 24 hours. No weight loss was observed. As both tantalum and titanium are oxygen getters, a very low partial pressure of oxygen was probably achieved. The lack of weight loss indicates that reaction with hydrogen (Eq. 1) is the mechanism of weight loss at 1300°C . At higher temperatures ($>1600^\circ\text{C}$), the decomposition and volatilization of silica in vacuum is significant¹.

(C) Total Reaction Rate

With 100% hydrogen gas flow, the total reaction rate was found to be dependent on the gas flow rate as shown in Fig. 3. At a very low flow rate, the total reaction rate was negligible. As the flow rate increased, the total reaction rate also increased. In this transport influenced range, the higher flow rates decrease the thickness of the surface boundary layer. Beyond a certain flow rate, the total reaction rate became fairly constant and was independent of the flow rate. This behavior is explained as the transition of the slowest step of the reaction from transport controlled to kinetics controlled. At much larger flow rates large fluctuations were observed and experimental results became less reproducible. This phenomenon was probably due to the non-uniform cooling effect of hydrogen gas at very high flow rates.

The dependence of the reaction rate on the partial pressure of hydrogen gas was also studied by dilution with helium gas. The reaction rate vs. partial pressure of hydrogen is shown in Fig. 4.

(D) Surface Morphology

The reacted silica glass had an unusual surface morphology. The change in the surface morphology of a piece of as-sawed silica glass with increasing reaction time at 1300°C is shown in Fig. 5. The as-cut glass sample (Fig. 5A), which was not HF treated in this case, was not transparent because of surface roughness due to microcracks generated in the cutting process. As the reaction proceeded, this surface layer completely disappeared and the glass became transparent (Fig. 5B), then small holes started to form and developed into deep holes (Figs. 5C,D,E,F).

This kind of drilling effect was found to be unique to the transparent silica glass; it was not found on silicate glasses which were opaque. CaO-Al₂O₃-SiO₂ glasses became opaque² before the reaction due to phase separation at temperature while the Al₂O₃-SiO₂ glass became opaque after reaction due to Al₂O₃ residue left on the surface, higher than ~1000°C. Moreover, this drilling effect happened on both sides of the silica glass surface and developed perpendicular to the surface.

This morphology can be explained on the basis of the temperature gradient in the transparent glass sample. At high temperatures, silica glass has a low thermal conductivity coefficient, but radiation is the dominant heat transfer mechanism. With the combination of high radiative conductivity and low thermal conductivity, the bulk of the sample is at a higher temperature than the surface. The temperature gradient near the surface of the sample becomes even steeper due to cooling by the flowing hydrogen gas which is at a lower temperature. Accordingly, the reaction rate at the bottom of the hole is higher than at the surface. The difference in the reaction rate means that the hole develops into a deeper one and follows the steepest temperature gradient direction which is perpendicular to the surface. The product concentration at the tip of the hole is also higher than at the surface. This explanation is consistent with the observation that cristobalite was formed on the ridges as shown in Fig. 6. Apparently, silicon monoxide and water vapor on leaving the pits became oversaturated when they came into contact with the cooler hydrogen gas.

(E) Apparent Activation Energy

The weight loss divided by the area of the sample calculated from its geometric shape (without considering the holes) is plotted against total reaction time (Fig. 7). By least squares fitting, the slopes of the curves represented reaction rates at the specified temperatures. The apparent activation energy was obtained by plotting the rate versus the reciprocal of temperature as shown in Fig. 8.

The reaction between silica and hydrogen gas in the temperature range studied is not mass transport controlled as evidenced by a lack of dependence of the reaction rate on the flow rate beyond a critical flow rate as well as the observed surface morphology. The total reaction rate varied as the square root of partial pressure of hydrogen gas when diluted by helium gas. Such a pressure dependence excludes adsorption as being the slowest step. Therefore, either surface reaction or desorption is the slowest step for this reaction. It is difficult to distinguish between them. Since water vapor is known to have a strong affinity for silica, the desorption process is more likely to be the slowest step.

However, the apparent activation energy can not be simply explained as the energy barrier for the slowest step. The complexity of the surface and the temperature gradient along the holes formed in the reaction offer no simple explanation of the apparent activation energy.

SUMMARY

Silica glass reacts with hydrogen gas at elevated temperatures. In the temperature range 1200°C-1400°C, the weight loss resulted from the formation and loss of SiO and H₂O vapors. Desorption was deduced

to be the rate limiting step. The apparent activation energy for the overall process was found to be 82 ± 8 kcal/mole. Devitrification of silica glass to cristobalite occurred well below the thermodynamic transformation temperature in the presence of sodium vapor. The surface morphology of reacted silica glass is unique as a result of the unusual heat transfer mechanism through the glass.

ACKNOWLEDGMENT

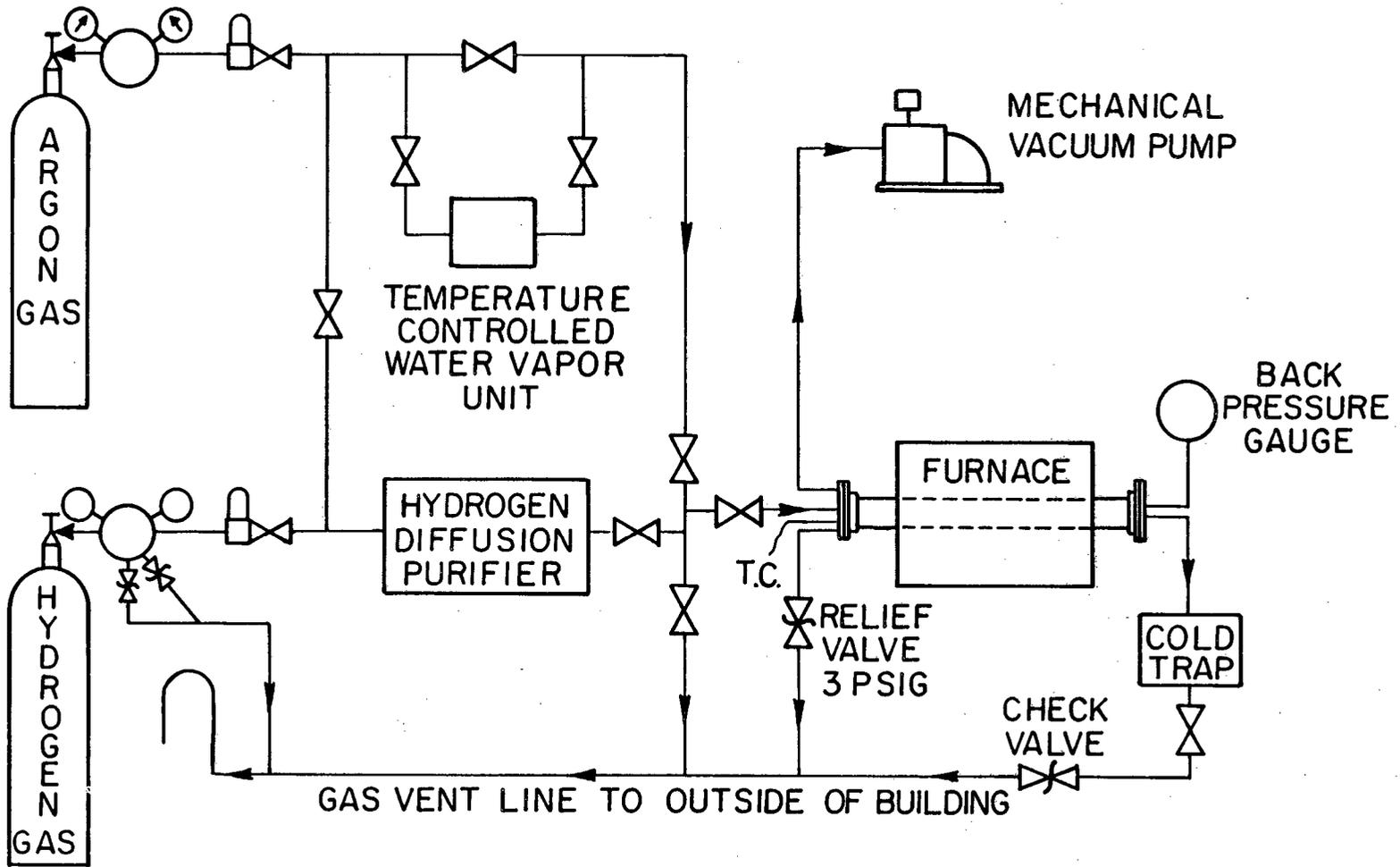
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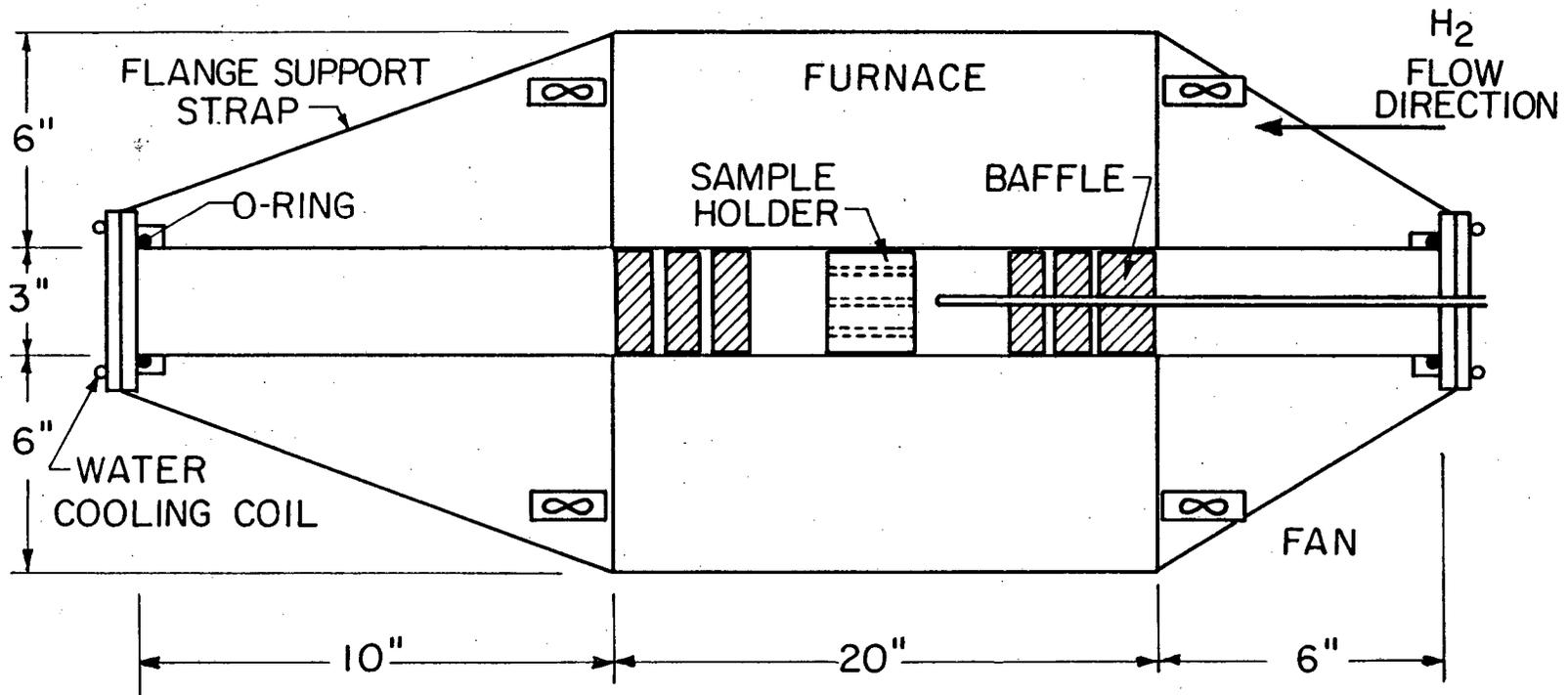
FIGURE CAPTIONS

- Fig. 1. Schematic of the hydrogen furnace set-up. (XBL 777-5872)
- Fig. 2. Cross-sectional schematic of the furnace tube. (XBL 777-5871)
- Fig. 3. Reaction rate between silica and hydrogen gas versus the flow rate of hydrogen gas. (XBL 789-5807)
- Fig. 4. Reaction rate between silica and hydrogen gas versus amount of hydrogen gas (diluted by helium gas). (XBL 797-6549, eliminate A)
- Fig. 5. Surface Morphology of silica glass after reaction with hydrogen gas at 1300°C. Photos A through F show how the surface morphology varies with increasing reaction time. (XBB 780-14504)
- Fig. 6. Deposition of cristobalite on the surface of silica glass during reaction with hydrogen gas. (XBB 780-14503)
- Fig. 7. Weight loss of silica glass per unit area versus reaction time for several temperatures. (XBL 789-5808)
- Fig. 8. Temperature dependence of the total reaction rate for silica glass with hydrogen gas. (XBL 789-5809)



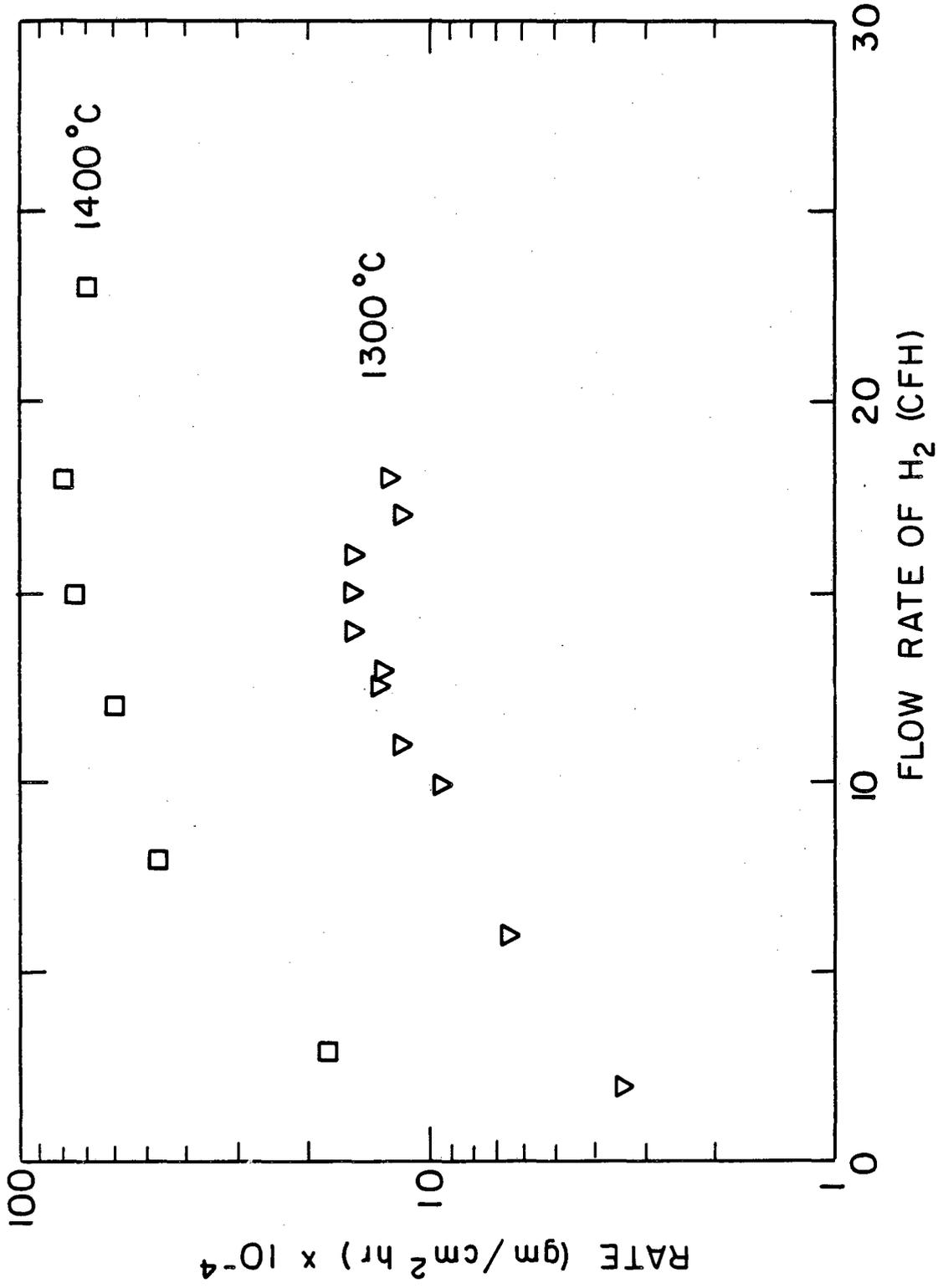
XBL 777-5872

Fig. 1



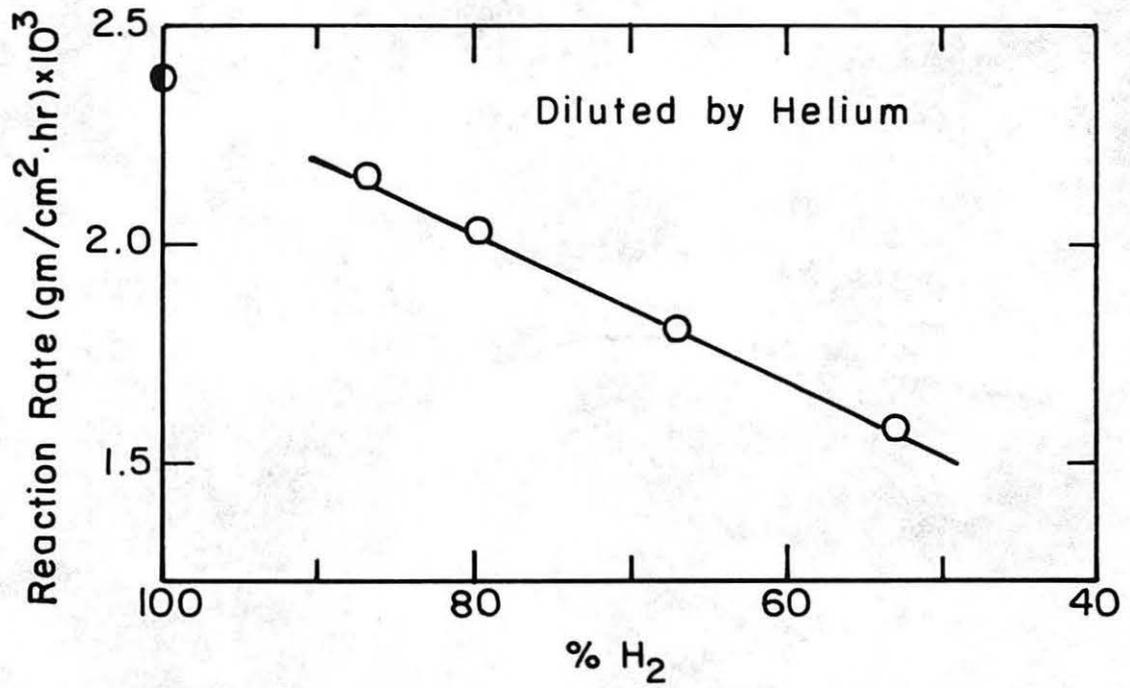
XBL 777-5871

Fig. 2



XBL 789-5807

Fig. 3



XBL 797-6549A

Fig. 4

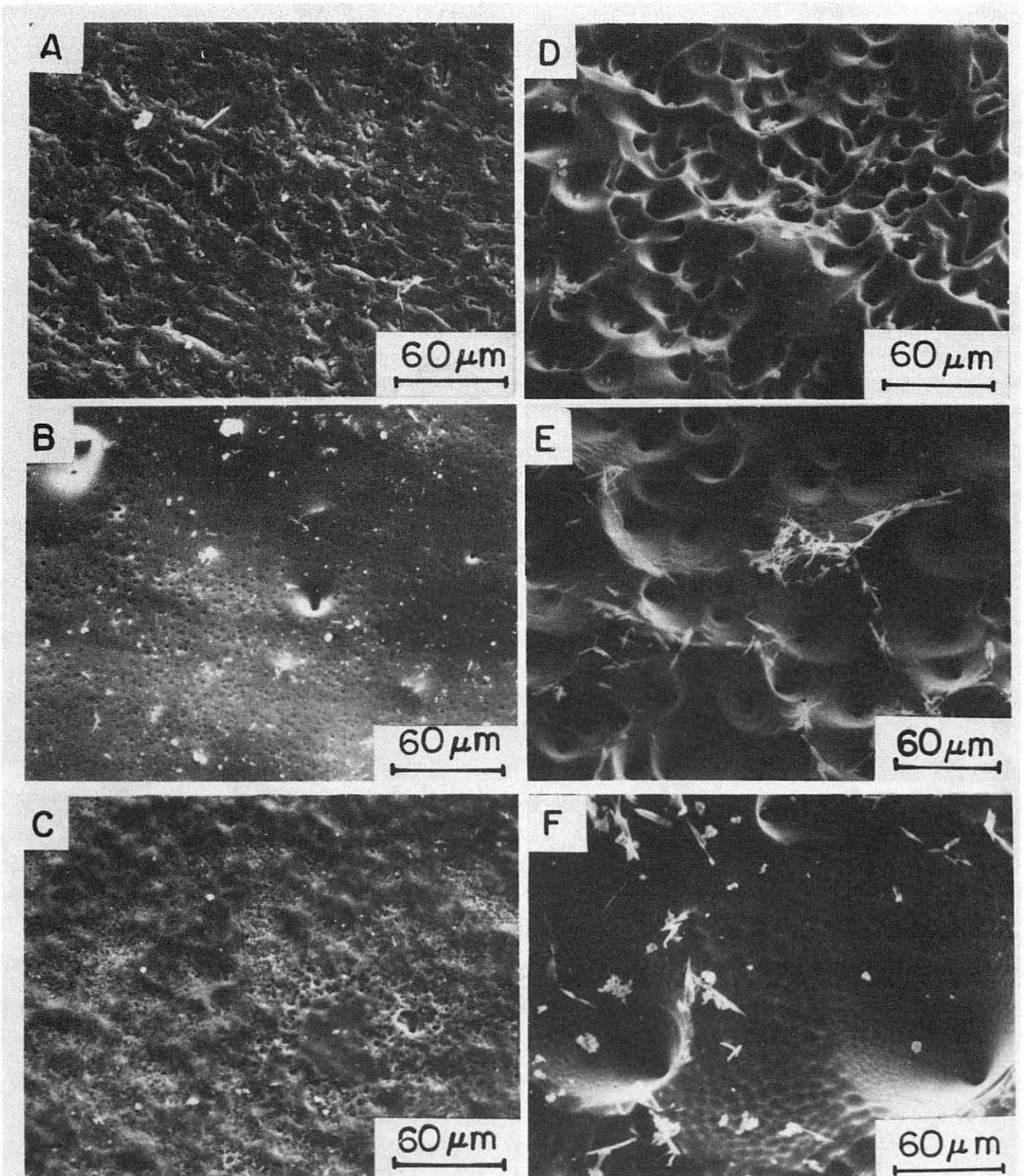


Fig. 5

XBB 780-14504

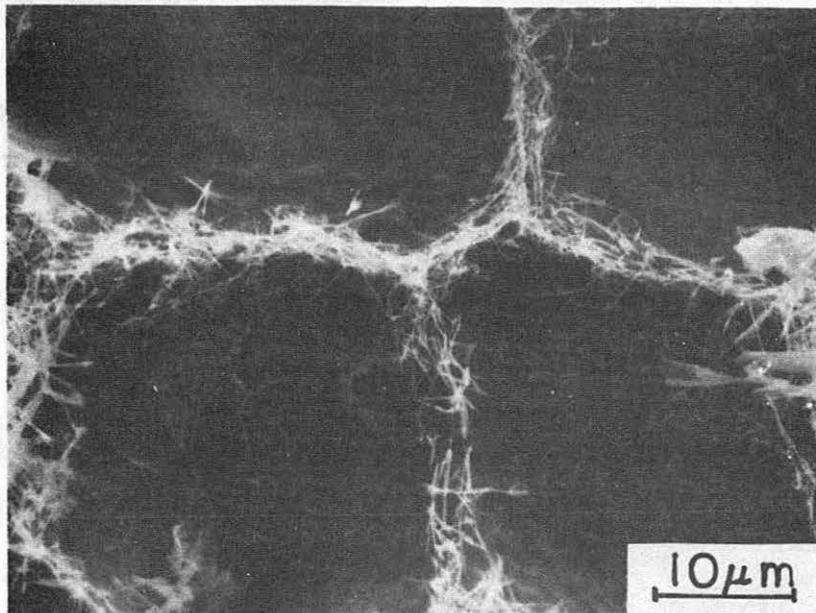
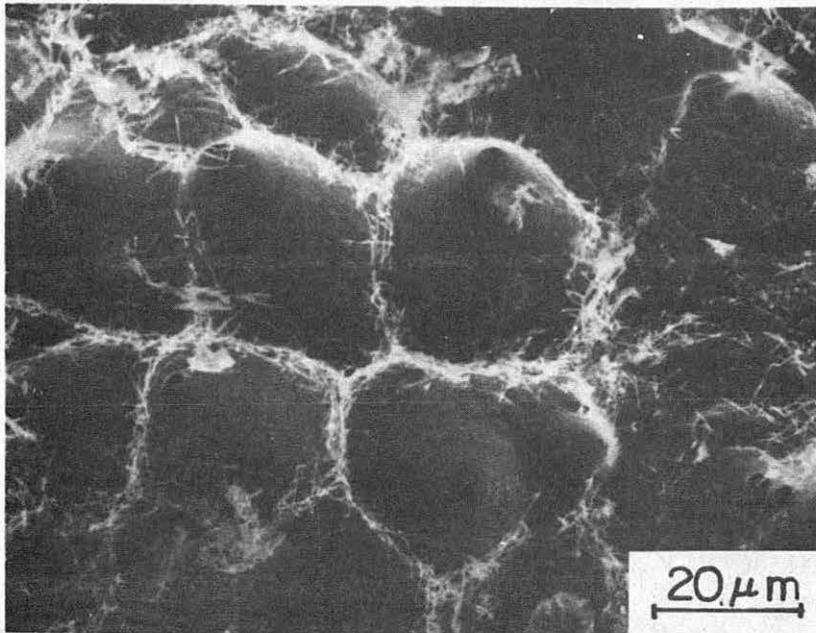
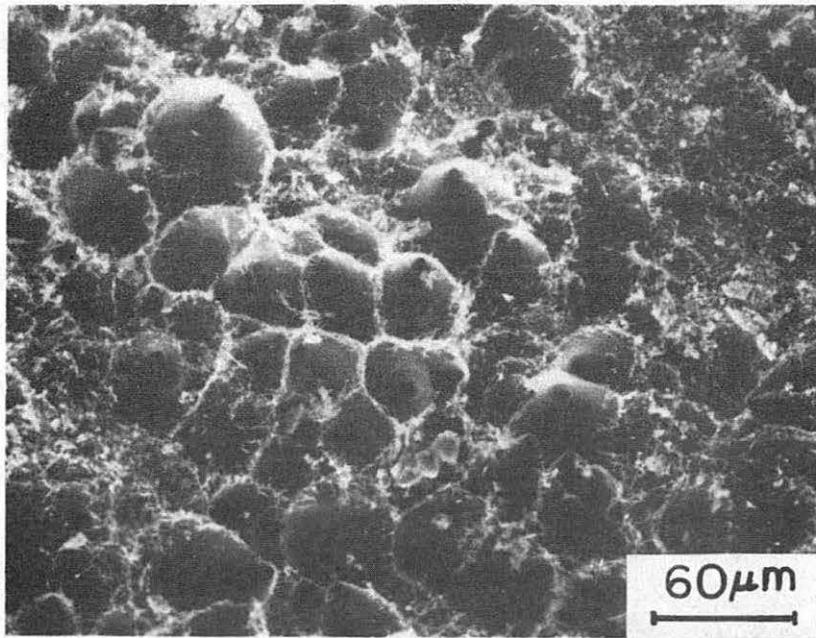
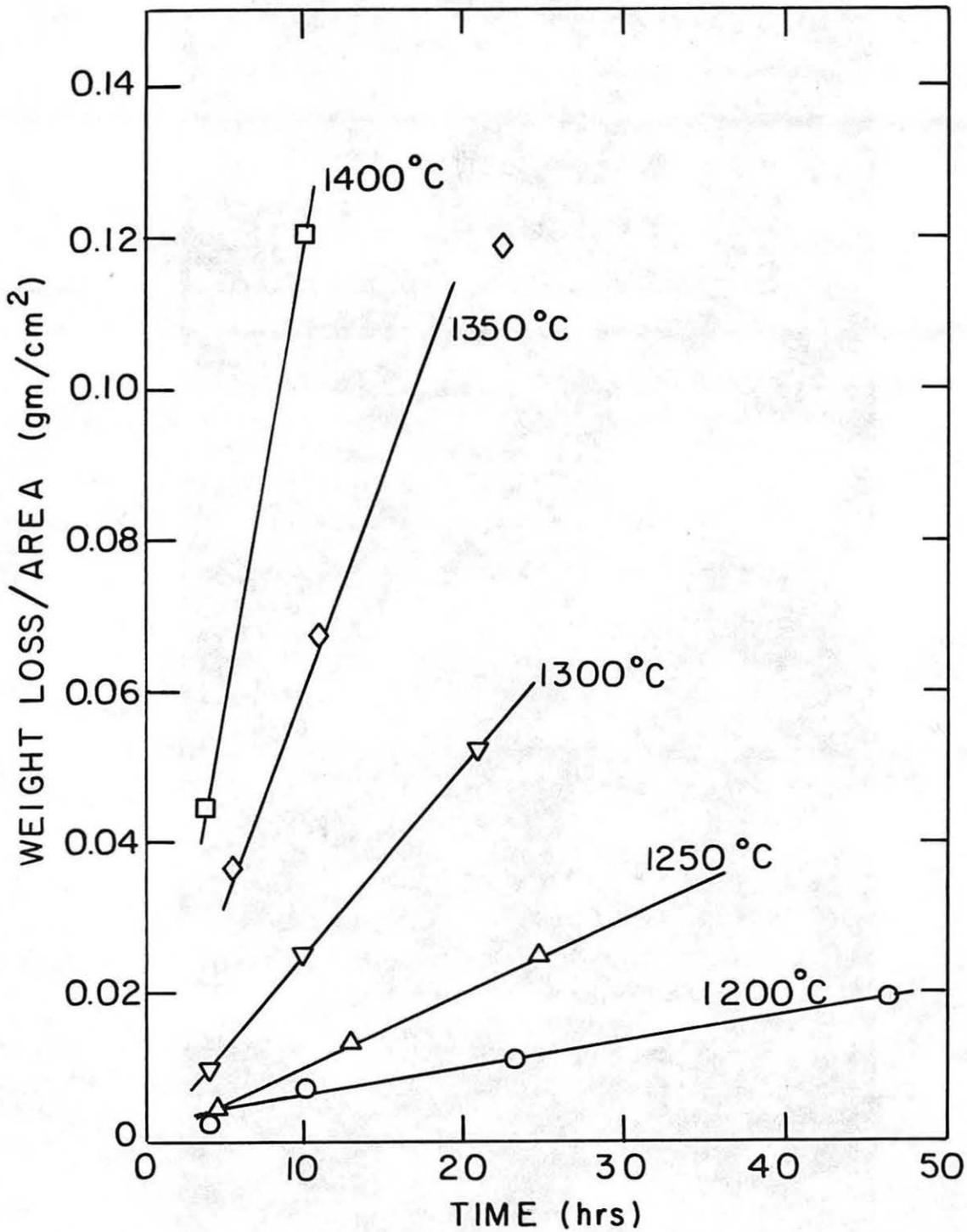


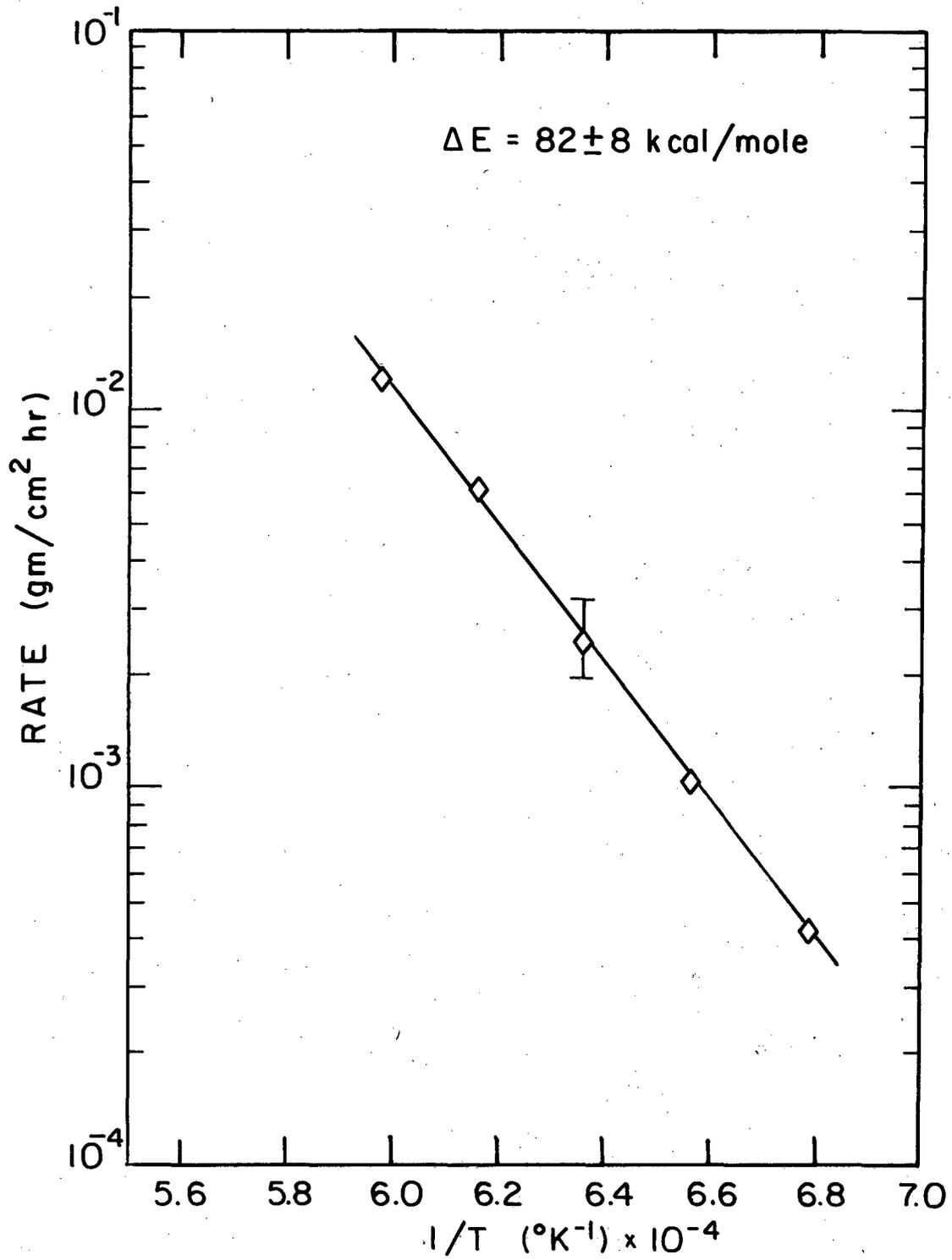
Fig. 6

XBB 780-14503



XBL 789-5808

Fig. 7



XBL 789-5809

Fig. 8

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