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**FLAT-PLATE SOLAR ARRAY PROJECT**

**TASK I SILICON MATERIAL**

**QUARTERLY REPORT**

**INVESTIGATION OF THE HYDROCHLORINATION OF  $SiCl_4$**

(Covering the Period July 9, 1982 to October 8, 1982.)

JPL CONTRACT NO. 956061

TO

JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY

BY

JEFFREY Y. P. MUI

October 15, 1982.



The JPL Flat-Plate Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

**SOLARELECTRONICS, INC.**

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FLAT-PLATE SOLAR ARRAY PROJECT

SILICON MATERIAL TASK

"Investigation of the Hydrochlorination of  $\text{SiCl}_4$ "

FIFTH QUARTERLY REPORT

October 15, 1982.

by

Jeffrey Y. P. Mui

SOLARELECTRONICS, INC.

Bellingham, Mass.

ABSTRACT

The JPL Contract No. 956061 to Solarelectronics, Inc. has been extended to April of 1983 to further the basic experimental study on the hydrochlorination of  $\text{SiCl}_4$  and m.g. silicon metal to produce  $\text{SiHCl}_3$ . The extended research and development work includes reaction kinetic measurements at the higher temperature range (up to  $650^\circ\text{C}$ ). These additional kinetic data are needed for the theoretical study to develop a rate equation and to determine important thermodynamic functions, such as,  $\Delta H$  and  $\Delta E$ . A reaction mechanism study includes experiments on the deuterium kinetic isotope effects. An experimental study on the effect of catalysts and impurities on the hydrochlorination reaction is also planned. The objective is to provide a basic understanding on the nature of the catalyst and to search for a still more effective catalyst for the hydrochlorination reaction.

Reaction kinetic measurements on the hydrochlorination of  $\text{SiCl}_4$  and m.g. silicon metal were carried out at two higher temperatures,  $550^\circ\text{C}$  and  $525^\circ\text{C}$ , and at two pressure ranges, 200

psig and 100 psig. These higher reaction temperature data are also used in the theoretical study for the development of a kinetic model and a rate equation for the hydrochlorination reaction. Preliminary results on the theoretical treatments of reaction rate data at 550°C, 500°C and 450°C show that the rate of formation of SiHCl<sub>3</sub> follows a pseudo-first order kinetics. The rate constants at these three temperatures and the activation energy, ΔE, are calculated and reported.

The design of a quartz hydrochlorination reactor for the planned experiments on deuterium kinetic isotope effects has been completed. This quartz reactor can also be used to measure reaction rate and the equilibrium conversion of SiHCl<sub>3</sub> at the higher temperature range where the present stainless steel reactor becomes unusable. More experimental work is in progress.

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## I. INTRODUCTION

A basic research and development program was initiated to study the hydrochlorination of  $\text{SiCl}_4$  and metallurgical grade (m.g.) silicon metal to produce  $\text{SiHCl}_3$ .



Experimental work was carried out in accordance with the revised Program Plan. The one-year JPL Contract No. 956061 to Solar-electronics, Inc. has been extended for nine months to April of 1983. The additional work plans are summarized in the revised Program Plan SC-1 in the Appendix. The objective of this research and development program is to carry out an experimental study to collect reaction kinetic data on the hydrochlorination reaction and to provide a basic understanding on the reaction mechanism. This Quarterly Report is the fifth in the series. Result of the experimental work performed during this quarter is summarized in the following discussion.

## II. DISCUSSION

### A. The Revised Program Plan

The Program Plan has been revised to include the additional nine months of contractual work. The extended work plans include basic research oriented experimental studies on the hydrochlorination of  $\text{SiCl}_4$  and m.g. silicon metal to produce  $\text{SiHCl}_3$ . The revised Program Plan SC-1 is shown in the Appendix. The objective is to provide a basic understanding on the reaction mechanism and to develop a rate equation for the hydrochlorination process. Additional experiments will be carried out to measure reaction rates and the equilibrium constant at the higher reaction temperature range of up to  $650^\circ\text{C}$ . These additional data are needed to determine important thermodynamic functions, such as, the activation energy,  $\Delta E$  and the heat of reaction,  $\Delta H$ . Previous studies <sup>1,2</sup> on the hydrochlorination reaction have shown that a

plausible reaction mechanism involves a slow, rate-determining step on the hydrogenation of the Si-Cl bond by hydrogen. Thus, hydrogen may be involved in the activation process. The planned reaction mechanism study on deuterium kinetic isotope effects provides a powerful tool to study the nature of the activated complex and on the mechanism of the activation process. The effect of the major impurities, iron and aluminum, in the m.g. silicon metal on the hydrochlorination reaction will be studied. A program to study the effect of catalyst on the reaction rate is also planned. The objective is to provide a basic understanding on the nature of the catalytic process and to search for a new, more effective catalyst for the hydrochlorination reaction.

#### B. Reaction Kinetic Measurements

Experiments were carried out at reaction temperature above 500°C to collect additional kinetic data on the hydrochlorination of SiCl<sub>4</sub> and m.g. silicon metal to SiHCl<sub>3</sub>. The reaction rate measurements were carried out in the two inch-diameter stainless steel reactor schematically shown in Figure I. The design and operation of the hydrochlorination apparatus were reported in detail in the first Quarterly Report (DOE/JPL 956061-1). The operating temperature of this stainless steel reactor is limited to about 550°C by the capacity of the electrical heaters. Also, the supporting structure for the reactor tube is made of aluminum (m.p. 660°C) and some stainless parts is silver-soldered (flow point 615°C) on the outside of the reactor wall. Thus, the stainless steel reactor is not usable for reaction temperature much above 550°C. A quartz hydrochlorination reactor has been designed for the planned experiments to study the deuterium kinetic isotope effect as described in Section C. This quartz reactor can also be used to collect reaction rate data and equilibrium conversion data at reaction temperature above 550°C. The reactions of chlorosilanes at low temperature (room temperature to 500°C) mostly involve a catalytic process<sup>3</sup>. On the other hand, at the much higher temperature range of 800°C to 1400°C, typically for the CVD and

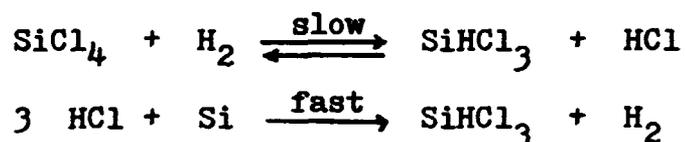
the Siemens process, homogeneous vapor phase reaction and/or non-catalyzed surface reaction are operative. Thus, by studying the hydrochlorination reaction over a wide temperature range of 350°C to 800°C, one may be able to observe a gradual change in the reaction pathway and shed some light on the very basic reaction kinetic process for the silicon-hydrogen-chlorosilane reaction system in general.

A series of experiments was carried out at 200 psig, H<sub>2</sub>/SiCl<sub>4</sub> feed ratio of 2.0 and at reaction temperature of 525°C and 550°C, respectively. Results are summarized in Table I (525°C) and Table II (550°C). The reaction rate data in these two tables are also presented in Figure II by plotting the % SiHCl<sub>3</sub> conversion versus residence time. As observed previously, a higher reaction temperature produces both a faster reaction rate and a higher equilibrium conversion of SiHCl<sub>3</sub>. Another series of experiments was carried out at the same reaction temperatures of 525°C and 550°C with a H<sub>2</sub>/SiCl<sub>4</sub> feed ratio of 2.0 but at a lower pressure of 100 psig. Results of these experiments are given in Table III (525°C) and Table IV (550°C). Data in Table III and Table IV are also plotted in the same graph in Figure II for the 200 psig experiments. The kinetic curves in Figure II show that, in addition to the large temperature effect, a significant pressure effect on the hydrochlorination reaction is also evident. The reaction rate, i.e., the rate at which the hydrochlorination reaction reaches its equilibrium conversion of SiHCl<sub>3</sub>, is considerably faster at lower pressures. For example, equilibrium is reached in about 60 seconds residence time at 100 psig, 550°C. On the other hand, about 150 seconds residence time is needed for the same reaction to reach its equilibrium conversion of SiHCl<sub>3</sub> at 200 psig (Figure II). As predicted by thermodynamics, a higher pressure produces a higher equilibrium conversion of SiHCl<sub>3</sub>. For example, the equilibrium conversion at 200 psig and at 550°C gives a 34% SiHCl<sub>3</sub> while 24.5% SiHCl<sub>3</sub> is observed at equilibrium at 100 psig. The reaction rate data obtained at the higher temperature of 550°C are also

used for the determination of the rate constants and the activation energy in Section D.

C. The Design of a Quartz Reactor for Studying the Deuterium Kinetic Isotope Effects

Previous experimental studies<sup>1,2</sup> on the hydrochlorination of  $\text{SiCl}_4$  and m.g. silicon metal showed that a plausible reaction mechanism may involve two stepwise reactions,



The hydrogenation of a Si-Cl bond by hydrogen to form  $\text{SiHCl}_3$  and HCl is postulated as the slow, rate-determining step. The reaction of HCl with silicon metal is a well-known reaction which occurs rapidly at about  $350^\circ\text{C}$ . At  $500^\circ\text{C}$ , the reaction of the HCl intermediate is expected to go very fast. Based on this postulated mechanism, one may propose an activation process involving hydrogen and  $\text{SiCl}_4$  to form an activated complex species which, through one or more reaction pathways, produces the product  $\text{SiHCl}_3$ . By replacing hydrogen with deuterium isotope in the hydrochlorination reaction, a positive kinetic isotope effect will not only produce the needed experimental evidence to prove the reaction mechanism, but also, it provides informations on the nature of the activated complex. Kinetic isotope effect is a powerful tool to study reaction mechanisms. It provides useful informations on the activation process and on the nature of the activated complex at the molecular level.

The two inch-diameter stainless steel reactor is primarily designed to study the hydrochlorination reaction under pressure. With a large internal volume and large size storage tanks, this apparatus is not suitable for the planned experiments to study the deuterium kinetic isotope effects. A small, 0.75 inch-diameter quartz reactor system has been designed with a minimum volume of dead space inside the apparatus in order to conserve the relatively

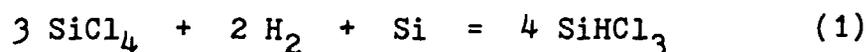
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expensive deuterium isotope (about \$2.00 per standard liter of gas). The apparatus is schematically shown in Figure III. The  $H_2/SiCl_4$  and the  $D_2/SiCl_4$  feed system is designed in such a way that either hydrogen gas or deuterium gas can be fed into the hydrochlorination reactor at any time during the experiment. This is accomplished by a 3-way ball valve as shown in Figure III. The cylinder pressure is reduced by a regulator to a few psig above atmospheric pressure. The flowrate of  $H_2$  or  $D_2$  is controlled by a fine metering needle valve and measured by a calibrated flowmeter. The gas is bubbled into a liquid column of  $SiCl_4$  maintained at a constant temperature. The  $H_2/SiCl_4$  or  $D_2/SiCl_4$  feed ratio can be readily adjusted by the  $SiCl_4$  liquid temperature. The gaseous mixture is fed into the quartz hydrochlorination reactor. The reaction product mixture coming out of the reactor is analyzed by the in-line gas chromatograph. The small amounts of chlorosilane and hydrogen gas are disposed of by venting into a scrubber. The reactor system at the right hand side of the flowmeter as shown in Figure III is made of Pyrex glass with the exception of the reactor tube and the heating jacket, which are made of quartz (Vycor). The  $H_2-D_2/SiCl_4$  feed system and the reactor assembly can be formed into a single piece of glassware by standard glass blowing technique. By using small diameter connecting tubing and by keeping the dead space inside the apparatus to a minimum, the residual gas inside the reactor can be readily flushed out with a small amount of deuterium. With this design feature, one can switch deuterium from hydrogen and vice versa for every data point in the reaction kinetic measurements. Past experience has shown that one can get a better reproducible data point measured within the span of a single experiment than that obtained in two separated experiments carried out under "identical" reaction conditions. In this way, one can accurately measure the relative reaction rate between hydrogen and deuterium.

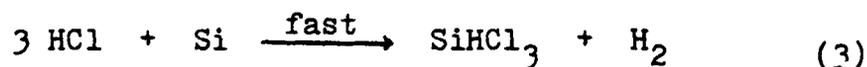
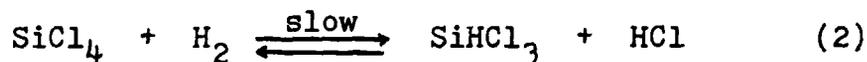
D. Development of a Rate Equation, the Rate Constants and the Activation Energy

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A theoretical treatment of experimental reaction kinetic data is to express the reaction rate in terms of an equation which relates the rate to the concentration of reactants, and sometimes of products or other substance present (e.g. of catalyst). If the reaction has a simple order, one must determine what the order is, and also the rate constant. The hydrochlorination of  $\text{SiCl}_4$  and m.g. silicon metal frequently expressed as equation (1),



is merely a balanced equation to show the stoichiometry of the overall equilibrium reaction. Previous experimental studies<sup>1,2</sup> showed that a plausible reaction mechanism involves the following stepwise reactions,

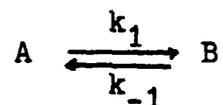


The hydrogenation of a Si-Cl bond with hydrogen in equation (2) is postulated as the slow, rate-determining step. The reaction of HCl and silicon metal is a known reaction which occurs rapidly to form  $\text{SiHCl}_3$  and  $\text{H}_2$ . The objective of the planned theoretical analysis is to determine whether equation (2) and (3) are the correct reaction mechanism and, if not, what other reaction mechanism is operative. A preliminary study to develop a kinetic model and a rate equation for the hydrochlorination of  $\text{SiCl}_4$  and m.g. silicon metal to  $\text{SiHCl}_3$  was carried out. A number of models for the treatment of experimental rate data was tested. Results are not conclusive at this point. However, preliminary results show that the reaction kinetics on the rate of formation of  $\text{SiHCl}_3$  fits reasonably well in the pseudo-first order rate equation. Results obtained from this theoretical treatment are presented in the following. As more theoretical calculations are made and as

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more experimental rate data are collected, a better rate equation may be developed to also include other reaction parameters, such as, pressure and catalyst.

To start with the simplest situation in which both the forward and reverse reactions are of first order,



If the reaction is started using pure A, of concentration a, and if after time t the concentration of B is x, that of A is a-x, the rate from left to right is then  $k_1(a-x)$ , and that from right to left is  $k_{-1}x$ ; the net rate of production of B is thus

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}x$$

At equilibrium, the net rate of production of B is zero, and if the concentration of x is then  $x_e$ ,

$$k_1(a - x_e) = k_{-1}x_e$$

Elimination of  $k_{-1}$  between these two equations give rise to

$$\frac{dx}{dt} = \frac{k_1 a}{x_e} (x_e - x)$$

The solution to this differential rate equation is

$$\ln \frac{x_e}{x_e - x} = \frac{k_1 a}{x_e} t$$

This simple rate equation can sometimes be applied to a more complex reaction involving more than one reactant and more than one product. It is then called pseudo-first order kinetics. For the rate of conversion of  $\text{SiCl}_4$  to  $\text{SiHCl}_3$ , x is the concentration of  $\text{SiHCl}_3$  at time t,  $x_e$  is the equilibrium concentration of

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of  $\text{SiHCl}_3$  and  $a$  is the initial concentration of  $\text{SiCl}_4$ .

One set of experimental data collected at 100 psig,  $\text{H}_2/\text{SiCl}_4$  feed ratio of 2.0 and at various reaction temperatures of  $550^\circ\text{C}$ ,  $500^\circ\text{C}$  and  $450^\circ\text{C}$  was applied to the pseudo-first order rate equation. This set of reaction rate data is summarized in Figure IV by plotting the %  $\text{SiHCl}_3$  conversion versus residence time,  $t$ . The  $550^\circ\text{C}$  experiment was obtained from Section B above. The  $500^\circ\text{C}$  and the  $450^\circ\text{C}$  experiments were obtained from a separated study (see Figure IV, fourth Quarterly Report, July 12, 1982). The %  $\text{SiHCl}_3$  conversion at 10, 20, 30, 40 and 60 seconds residence time were taken from the smooth kinetic curves at  $550^\circ\text{C}$ ,  $500^\circ\text{C}$  and  $450^\circ\text{C}$ , respectively in Figure IV. The equilibrium concentration of  $\text{SiHCl}_3$  was measured at the point where the kinetic curves leveled off at long residence times. The partial pressures of the reactant and the product were calculated from the experimentally determined mole% concentrations. These experimental rate data were then applied to the integrated rate equation on page 7. Results of this analysis are presented in Figure V by plotting the  $\ln x_e/x_e - x$  versus the reaction time  $t$ . A straight line is obtained from these plots. Thus, the results in Figure V show that the rate of formation of  $\text{SiHCl}_3$  fits reasonably well in the pseudo-first order rate equation. The rate constants,  $k_1$ , at  $550^\circ\text{C}$ ,  $500^\circ\text{C}$  and  $450^\circ\text{C}$  were then determined from the slope of the straight lines, which equal to  $k_1 a/x_e$ . Substitution of the known value of  $a$  and  $x_e$ , the rate constant  $k_1$  were calculated to give  $19.2 \times 10^{-3} \text{ sec}^{-1}$ ,  $12.7 \times 10^{-3} \text{ sec}^{-1}$  and  $6.50 \times 10^{-3} \text{ sec}^{-1}$  at the reaction temperatures of  $550^\circ\text{C}$ ,  $500^\circ\text{C}$  and  $450^\circ\text{C}$ , respectively. The activation energy,  $\Delta E$ , was determined by plotting the log of  $k_1$  versus the inverse temperature,  $1/T$ , in the Arrhenius equation,

$$k_1 = C e^{-\Delta E/RT} \quad \text{or} \quad \ln k_1 = \ln C - \frac{\Delta E}{R} \left(-\frac{1}{T}\right)$$

where  $R$  is the gas constant (1.987 cal/mole/ $^\circ\text{K}$ ) and  $C$  is a constant. Results are presented in Figure VI. A straight line is drawn. The

activation energy is then calculated from the slope of the straight line, which equals to  $-\Delta E/R$ . Result of the calculation gives a value of 13.2 Kcal/mole for the activation energy.

#### E. Summary of Progress

Experimental work on the JPL Contract No. 956061 has progressed on schedule in accordance with the revised Program Plan. Reaction kinetic measurements were carried out to collect additional rate data at 525°C and 550°C. A theoretical study was carried out to provide a kinetic model and a rate equation for the hydrochlorination reaction. Results of this preliminary study show that the rate of formation of  $\text{SiHCl}_3$  follows a pseudo-first order kinetics. The rate constants were measured at three temperatures, 550°C, 500°C and 450°C, respectively. The activation energy was determined from the Arrhenius plot to give a value of 13.2 Kcal/mole. The design of a quartz reactor for the planned experiments to study the deuterium kinetic isotope effects has been completed. Equipment and material for this new reactor design have been ordered. This quartz reactor can also be used to measure reaction rates and equilibrium conversion of  $\text{SiHCl}_3$  at reaction temperature up to 650°C. More work is in progress.

### III. PROJECTED SIXTH QUARTER ACTIVITIES

Planned activities for the sixth quarter (October - December) include,

- Continue the theoretical study for the development of a rate equation for the hydrochlorination reaction,
- Construct and start-up the quartz hydrochlorination reactor,
- Carry out experiments to study the deuterium kinetic isotope effects,

- Carry out experiments on the reaction kinetic and equilibrium constant measurements at the higher reaction temperature range,
- Determine thermodynamic functions for the hydrochlorination reaction.

#### IV. REFERENCES

1. Final Report, JPL Contract No. 954334, "Feasibility of the Silane Process for Producing Semiconductor-Grade Silicon", Union Carbide Corporation, June, 1979.
2. Final Report, JPL Contract No. 955382, "Investigation of the Hydrogenation of  $\text{SiCl}_4$ " by Jeffrey Y. P. Mui and Dietmar Seyferth, Massachusetts Institute of Technology, April 15, 1981.
3. "Kinetics and Mechanisms of Chlorosilane Decomposition", presentation by Donald L. Bailey at the JPL "The Science of Silicon Material Preparation Workshop", August 23-25, Phoenix, Arizona.

#### V. APPENDIX

Program Plan

Table I to IV

Figure I to VI

SC-1 PROGRAM PLAN

(Revised August 9, 1982)

JPL Contract No. 956061

|   | Year |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
|---|------|---|---|----|------|----|---|---|------|----|----|----|----|----|----|----|----|----|----|----|----|----|
|   | 1981 |   |   |    | 1982 |    |   |   | 1983 |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Month of Year   | 7    | 8 | 9 | 10 | 11   | 12 | 1 | 2 | 3    | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 1  | 2  | 3  | 4  |
| Month of Contract   | 1    | 2 | 3 | 4  | 5    | 6  | 7 | 8 | 9    | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| I Program Plan, Baseline Cost Estimate, Transfer Apparatus from M.I.T., Design and Construct 2" Reactor, Safety Review                                    |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| II Reaction Kinetic Measurements as a Function of T, P, C. Mass Balance, HCl Analyses   |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| III Corrosion Study<br>(1) Copper, Nickel, Carbon Steel, Stainless Steel, Incoloy 800H, Alloy 400, Hastelloy B-2<br>(2) Corrosion Mechanism: SEM Analyses |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| IV Effect of Reactor Pressure: Reaction Kinetic Measurements, 25 to 500 psig, 350° to 500°C, H <sub>2</sub> /SiCl <sub>4</sub> Ratio 1.0 to 5.0           |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| V Reaction Kinetic Modeling of Previous Experimental Data   |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| VI Supplemental Reaction Kinetic Measurement with Reaction Temperature to 650°C   |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| VII Equilibrium Constant Measurements at Temperature Range 350°C to 650°C   |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| VIII Reaction Mechanism Study: Deuterium Kinetic Isotope Effects  |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| IX Develop Rate Equation, Thermodynamic Functions, ΔE, ΔH, ΔG, etc.   |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| X Catalyst Study: Electronic Grade Silicon v.s. the Presence of Ni and Co Catalyst  |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| XI Effect of Impurities: Electronic Silicon v.s. the Presence of Fe and Al  |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |
| XII Recommendations for Additional Development Work and Final Report  |      |   |   |    |      |    |   |   |      |    |    |    |    |    |    |    |    |    |    |    |    |    |

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TABLE I

THE HYDROCHLORINATION OF  $\text{SiCl}_4$  AND M.G. SILICON METAL  
AT  $525^\circ\text{C}$ , 200 PSIG AND  $\text{H}_2/\text{SiCl}_4$  FEED RATIO OF 2.0

| Sample<br>No. | Hydrogen<br>Feedrate<br>SLM (1) | Residence<br>Time<br>Second | Product Composition, Mole % |                  |                 |
|---------------|---------------------------------|-----------------------------|-----------------------------|------------------|-----------------|
|               |                                 |                             | $\text{SiH}_2\text{Cl}_2$   | $\text{SiHCl}_3$ | $\text{SiCl}_4$ |
| 1             | 0.80                            | 184                         | 0.9639                      | 33.09            | 65.95           |
| 2             | 0.80                            | 184                         | 0.7884                      | 32.86            | 66.35           |
| 3             | 0.80                            | 184                         | 1.098                       | 32.94            | 65.96           |
| 4             | 1.05                            | 140                         | 0.9986                      | 32.63            | 66.37           |
| 5             | 1.05                            | 140                         | 0.7667                      | 32.25            | 66.98           |
| 6             | 1.40                            | 105                         | 0.7814                      | 30.51            | 68.71           |
| 7             | 1.40                            | 105                         | 0.8403                      | 30.94            | 68.22           |
| 8             | 2.40                            | 61.3                        | 0.6544                      | 27.38            | 71.97           |
| 9             | 2.40                            | 61.3                        | 0.5852                      | 26.91            | 72.50           |
| 10            | 3.50                            | 42.1                        | 0.4765                      | 23.23            | 76.30           |
| 11            | 3.50                            | 42.1                        | 0.4557                      | 23.06            | 76.48           |

(1) SLM, Standard Liter per Minute

TABLE II

THE HYDROCHLORINATION OF  $\text{SiCl}_4$  AND M.G. SILICON METAL  
AT 550° C, 200 PSIG AND  $\text{H}_2/\text{SiCl}_4$  FEED RATIO OF 2.0

| Sample No. | Hydrogen Feedrate | Residence Time | Product Composition, Mole % |                  |                 |
|------------|-------------------|----------------|-----------------------------|------------------|-----------------|
|            | SLM               | Second         | $\text{SiH}_2\text{Cl}_2$   | $\text{SiHCl}_3$ | $\text{SiCl}_4$ |
| 1          | 0.80              | 172            | 0.8925                      | 34.02            | 65.09           |
| 2          | 0.80              | 172            | 1.125                       | 34.31            | 64.56           |
| 3          | 1.00              | 138            | 1.013                       | 33.83            | 65.15           |
| 4          | 1.00              | 138            | 1.007                       | 33.63            | 65.36           |
| 5          | 1.60              | 86.3           | 0.9775                      | 31.43            | 67.59           |
| 6          | 1.60              | 86.3           | 0.8721                      | 31.49            | 67.64           |
| 7          | 2.35              | 58.7           | 0.6559                      | 28.39            | 70.93           |
| 8          | 2.35              | 58.7           | 0.6463                      | 28.05            | 71.30           |
| 9          | 3.50              | 39.4           | 0.6110                      | 25.86            | 73.53           |
| 10         | 3.50              | 39.4           | 0.5613                      | 25.68            | 73.76           |

TABLE III

THE HYDROCHLORINATION OF  $\text{SiCl}_4$  AND M.G. SILICON METAL  
AT  $525^\circ\text{C}$ , 100 PSIG AND  $\text{H}_2/\text{SiCl}_4$  FEED RATIO OF 2.0

| Sample<br>No. | Hydrogen<br>Feedrate<br>SLM <sup>(1)</sup> | Residence<br>Time<br>Second | Product Composition, Mole % |                  |                 |
|---------------|--|-----------------------------|-----------------------------|------------------|-----------------|
|               |  |                             | $\text{SiH}_2\text{Cl}_2$   | $\text{SiHCl}_3$ | $\text{SiCl}_4$ |
| 1             | 0.65                                       | 111                         | 0.5872                      | 23.52            | 75.89           |
| 2             | 0.65                                       | 111                         | 0.5119                      | 23.18            | 76.31           |
| 3             | 1.00                                       | 72.2                        | 0.5519                      | 22.98            | 76.47           |
| 4             | 1.00                                       | 72.2                        | 0.5008                      | 23.25            | 76.25           |
| 5             | 1.60                                       | 45.1                        | 0.4871                      | 22.58            | 76.94           |
| 6             | 1.60                                       | 45.1                        | 0.5186                      | 22.17            | 77.31           |
| 7             | 2.40                                       | 30.1                        | 0.4864                      | 21.63            | 77.88           |
| 8             | 2.40                                       | 30.1                        | 0.4283                      | 21.45            | 78.12           |
| 9             | 3.40                                       | 21.2                        | 0.3766                      | 20.52            | 79.10           |
| 10            | 3.40                                       | 21.2                        | 0.4096                      | 20.84            | 78.75           |
| 11            | 5.10                                       | 14.1                        | 0.3733                      | 18.34            | 81.28           |
| 12            | 5.10                                       | 14.1                        | 0.3618                      | 18.09            | 81.55           |

(1) SLM, Standard Liter per Minute

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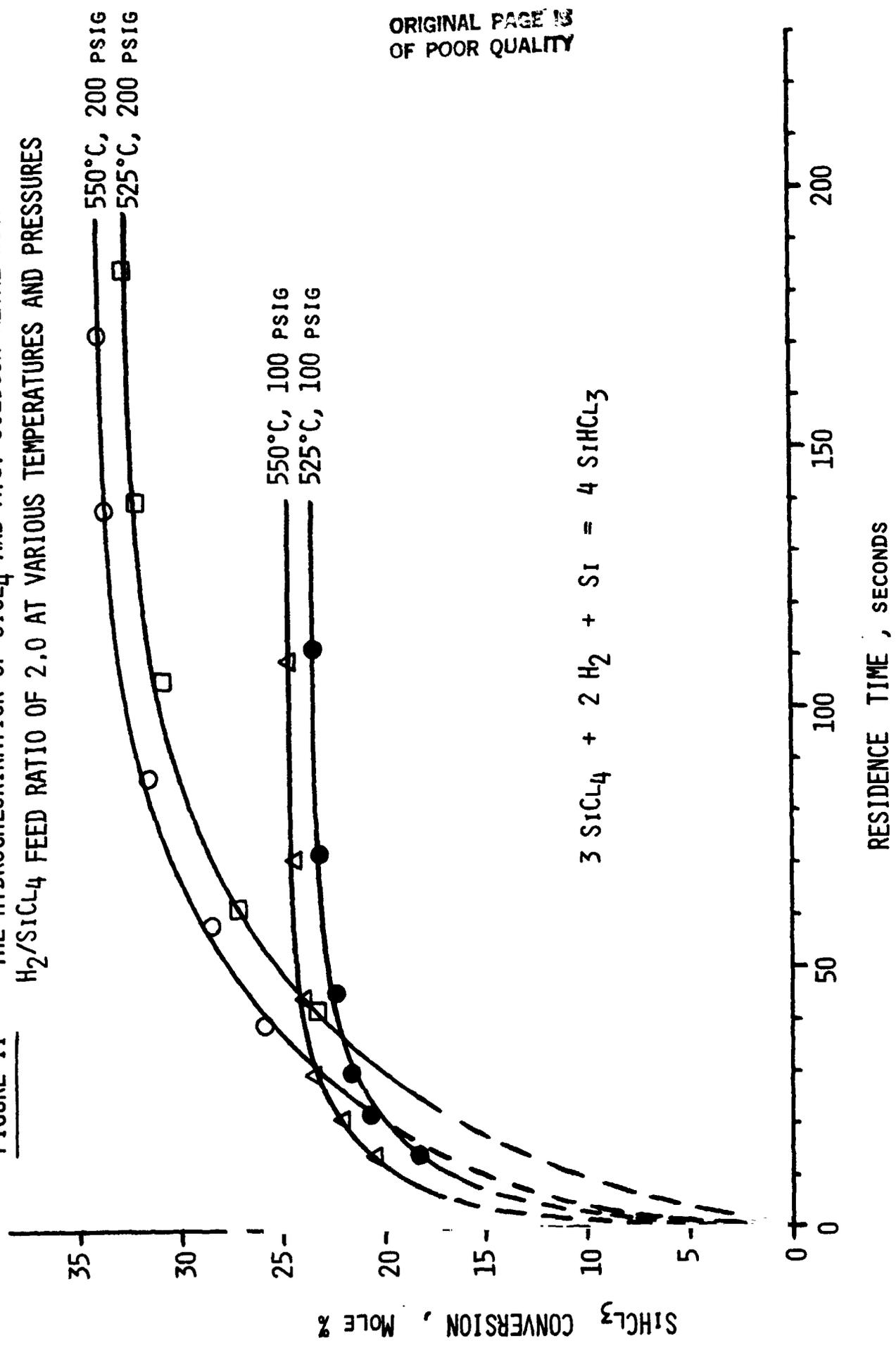
TABLE IV

THE HYDROCHLORINATION OF  $\text{SiCl}_4$  AND M.G. SILICON METAL  
AT 550 C, 100 PSIG AND  $\text{H}_2/\text{SiCl}_4$  FEED RATIO OF 2.0

| Sample<br>No. | Hydrogen<br>Feedrate | Residence<br>Time | Product Composition, Mole % |                  |                 |
|---------------|----------------------|-------------------|-----------------------------|------------------|-----------------|
|               | SLM                  | Second            | $\text{SiH}_2\text{Cl}_2$   | $\text{SiHCl}_3$ | $\text{SiCl}_4$ |
| 1             | 0.65                 | 109               | 0.6471                      | 24.72            | 74.64           |
| 2             | 0.65                 | 109               | 0.6821                      | 24.46            | 74.86           |
| 3             | 1.00                 | 70.9              | 0.6317                      | 24.36            | 75.00           |
| 4             | 1.00                 | 70.9              | 0.6733                      | 24.25            | 75.08           |
| 5             | 1.60                 | 44.3              | 0.6532                      | 23.61            | 75.74           |
| 6             | 1.60                 | 44.3              | 0.5337                      | 24.31            | 75.15           |
| 7             | 2.40                 | 29.5              | 0.5069                      | 23.29            | 76.21           |
| 8             | 2.40                 | 29.5              | 0.5456                      | 23.34            | 76.11           |
| 9             | 3.40                 | 20.8              | 0.4188                      | 22.08            | 77.50           |
| 10            | 3.40                 | 20.8              | 0.4848                      | 21.83            | 77.68           |
| 11            | 5.10                 | 13.9              | 0.3894                      | 20.16            | 79.45           |
| 12            | 5.10                 | 13.9              | 0.4431                      | 20.57            | 78.99           |

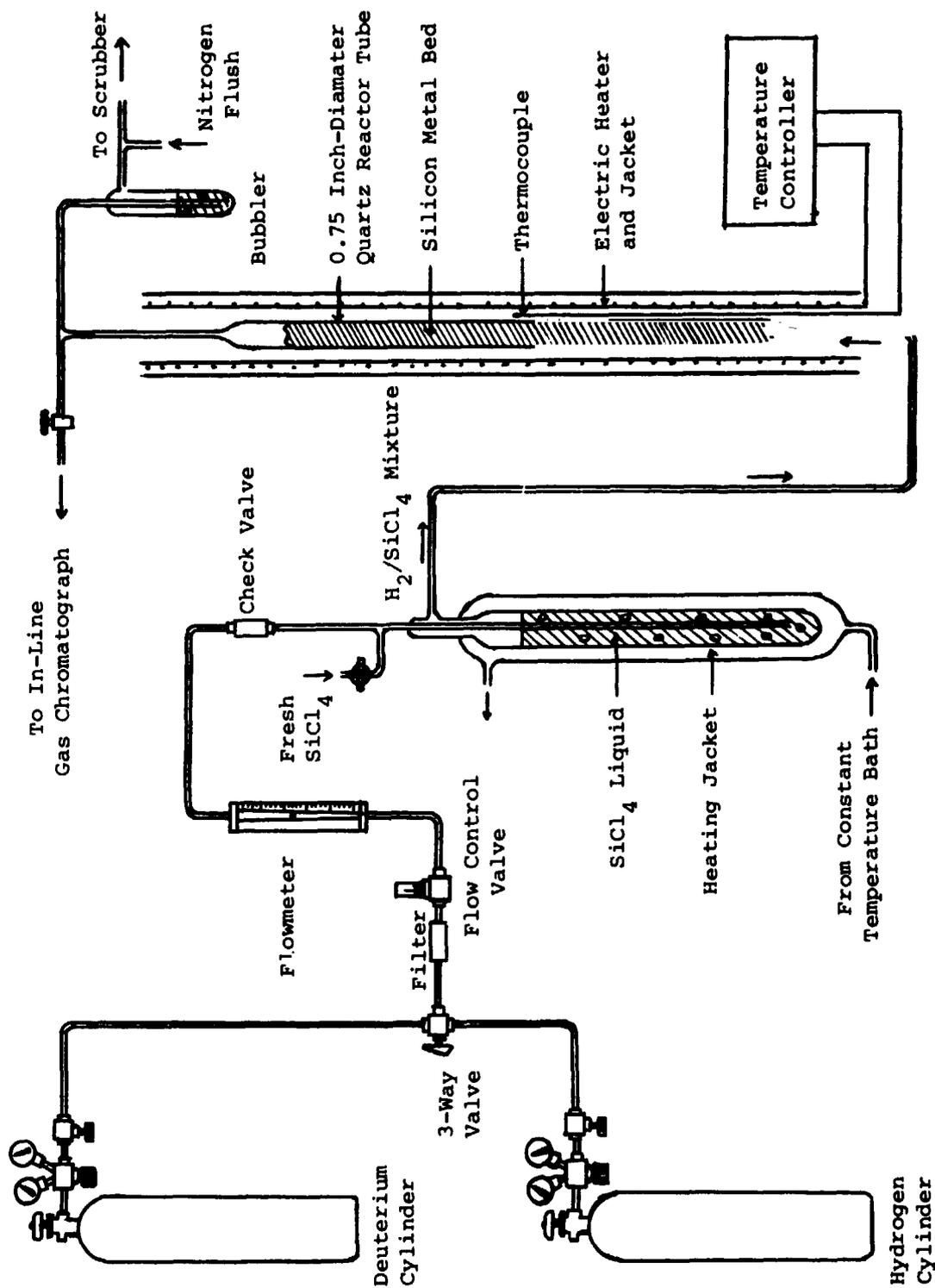


FIGURE II THE HYDROCHLORINATION OF  $\text{SiCl}_4$  AND M.G. SILICON METAL WITH A  $\text{H}_2/\text{SiCl}_4$  FEED RATIO OF 2.0 AT VARIOUS TEMPERATURES AND PRESSURES



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FIGURE III SCHEMATIC OF THE QUARTZ HYDROCHLORINATION REACTOR



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FIGURE IV HYDROCHLORINATION OF  $\text{SiCl}_4$  AT 100 PSIG AND  $\text{H}_2/\text{SiCl}_4$  RATIO OF 2.0

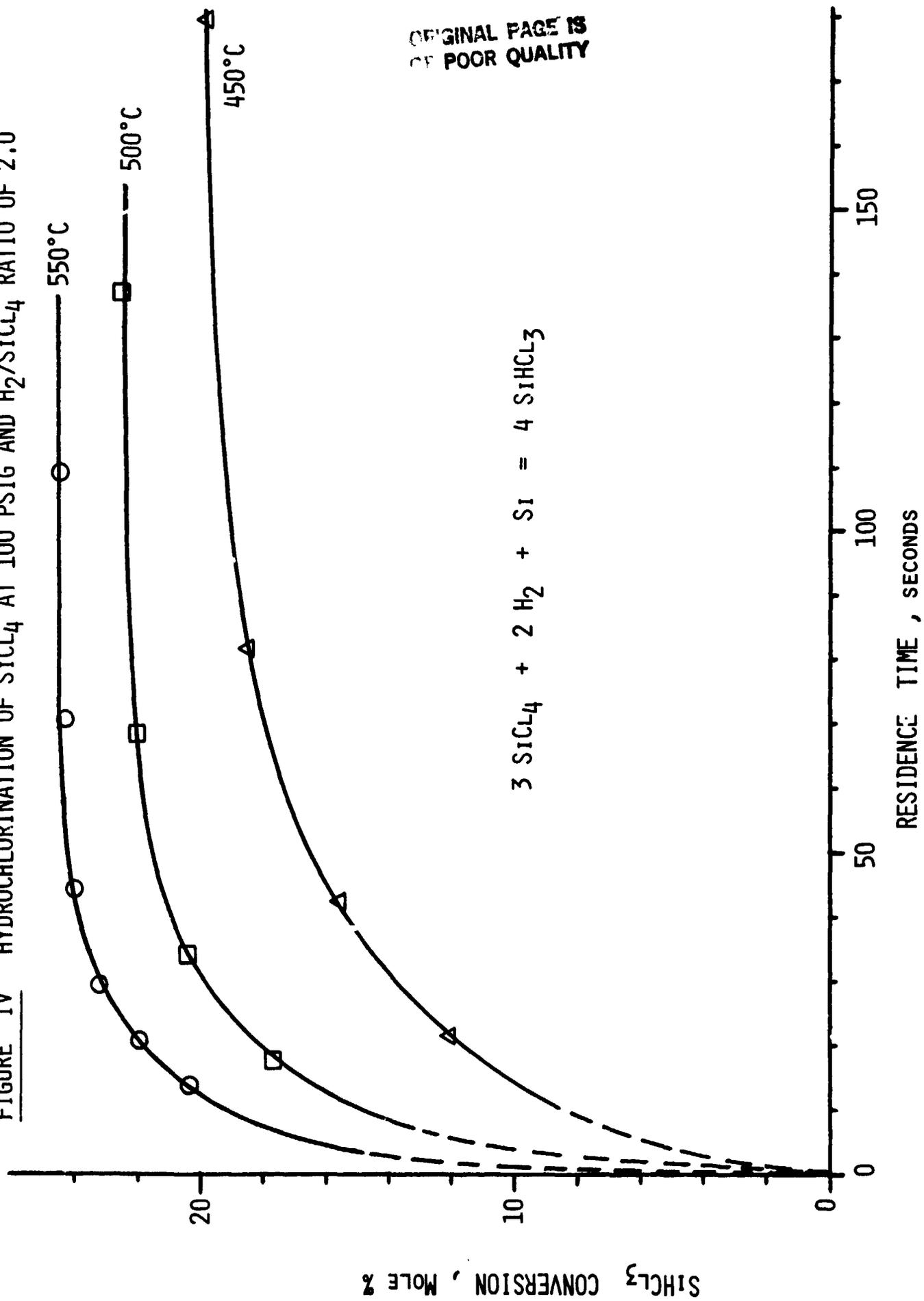


FIGURE V PLOT OF PSEUDO-FIRST ORDER RATE EQUATION

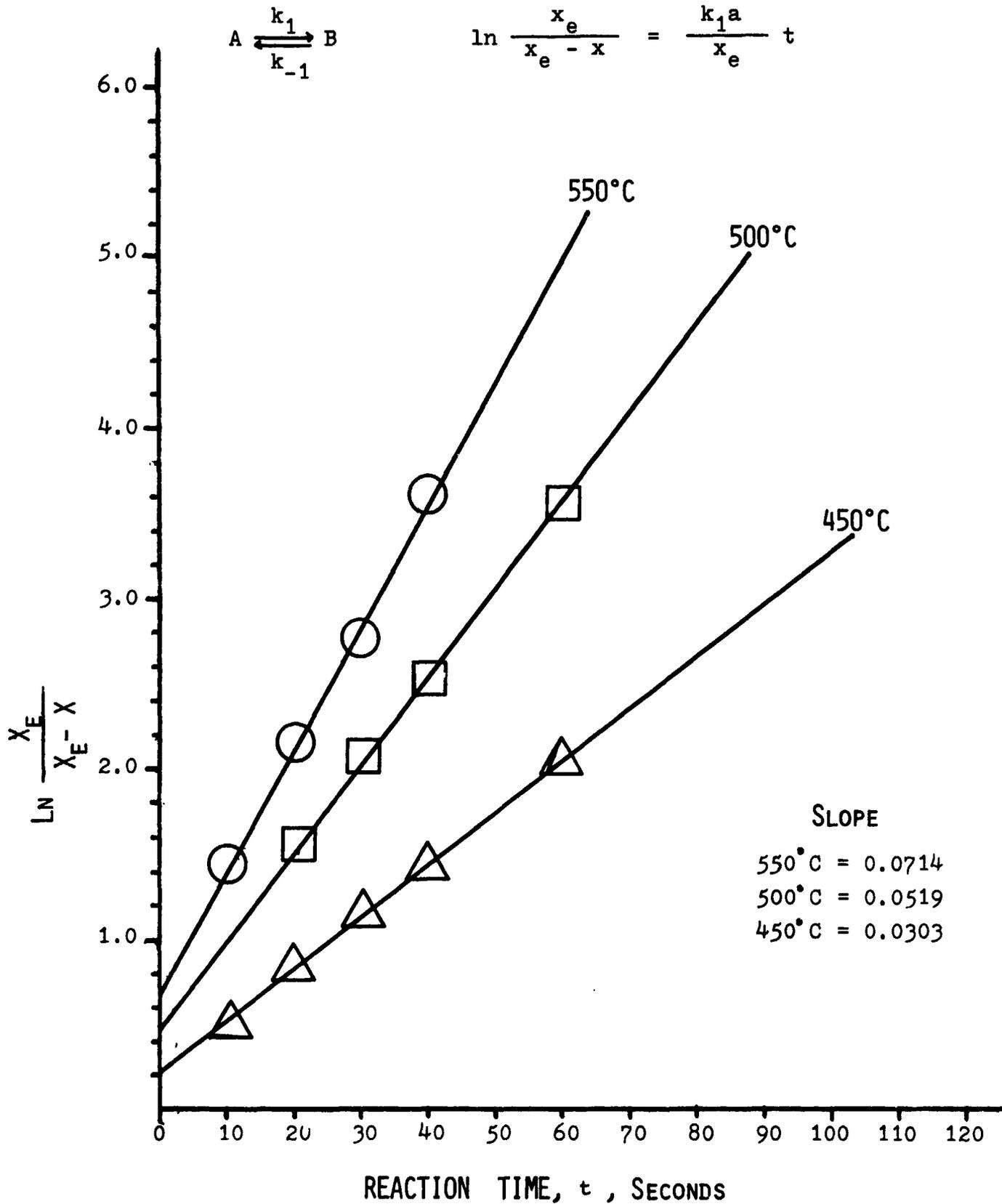


FIGURE VI PLOT OF THE ARRHENIUS EQUATION

