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DOE/JPL/956061-6
(DE83007036)

INVESTIGATION OF THE HYDROCHLORINATION OF SiCl_4

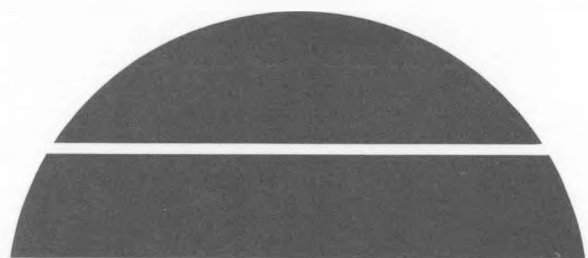
Quarterly Report for the Period October 9, 1982—January 8, 1983

By
Jeffrey Y. P. Mui

January 18, 1983

Work Performed Under Contract No. NAS-7-100-956061

Solarelectronics, Inc.
Bellingham, Massachusetts



U.S. Department of Energy



Solar Energy

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INVESTIGATION OF THE HYDROCHLORINATION OF SiCl_4
FLAT-PLATE SOLAR ARRAY PROJECT
ADVANCED MATERIALS RESEARCH TASK

Quarterly Report Covering the Period October 9, 1982-January 8, 1983

By
Jeffrey Y. P. Mui

January 18, 1983

JPL Contract No. 956061

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FLAT-PLATE SOLAR ARRAY PROJECT

ADVANCED MATERIALS RESEARCH TASK

"Investigation of the Hydrochlorination of SiCl_4 "

SIXTH QUARTERLY REPORT

January 18, 1983.

by

Jeffrey Y. P. Mui

SOLARELECTRONICS, INC.

Bellingham, Mass.

ABSTRACT

A basic, experimental study on the hydrochlorination of silicon tetrachloride and metallurgical grade silicon with hydrogen gas to form trichlorosilane has been carried out to greatly expand the range of reaction conditions. These reaction kinetic measurements were reported in previous Quarterly Reports. During this quarter, the equilibrium constant, K_p , for the hydrochlorination reaction was measured as a function of temperature, pressure and concentration. The variation of the equilibrium constant as a function of temperature provided the measurement on the heat of reaction, ΔH , by the Second Law Method. The value of ΔH was measured to give 10.6 Kcal/mole. The equilibrium constant was also studied as a function of concentration. In agreement with the theory, the equilibrium constant remained constant with respect to the varying H_2/SiCl_4 feed ratios. On the other hand, the effect of pressure on the equilibrium constant was found to be more complex. At the lower pressure range of 25 psig to 100 psig, the equilibrium constant remained constant within experimental error. However, at the higher pressure range of 150 psig to 500 psig, the equilibrium constant showed a much higher value. This phenomenon is not

fully understood at the present time.

Previous kinetic modeling of the hydrochlorination reaction has shown that the experimental rate data obeyed a pseudo-first order kinetics. The rate constant, k_1 , for the pseudo-first order rate equation was then measured as a function of temperature, pressure and concentration. The variation of the rate constants as a function of temperature provided the measurement on the activation energy, ΔE , which was reported in the last Quarterly Report to give a value of 13.2 Kcal/mole. The effect of pressure on the rate constant was studied this quarter. The rate constant, k_1 , decreases as a function of increasing pressure. On the other hand, the concentration ($H_2/SiCl_4$ feed ratio) shows a small effect on the reaction rate. The rate constant slightly increases at a higher $H_2/SiCl_4$ feed ratio. An attempt to develop a generalized rate equation applicable to the entire range of reaction conditions is in progress.

Construction of the quartz hydrochlorination reactor system has been completed. This quartz reactor is designed for the deuterium kinetic isotope effect study. The reactor system has been successfully started up. Some preliminary experiments on the deuterium kinetic isotope effects were carried out. More experimental work is in progress.

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I. INTRODUCTION

A basic research and development program has been carried out to study the hydrochlorination of SiCl_4 and metallurgical grade (m.g.) silicon to form SiHCl_3 . The hydrochlorination reaction was shown to be an efficient process for the production of trichlorosilane which is an important starting material for the manufacturing of high purity, electronic grade silicon metal. Experimental work was carried out in accordance with the SC-1 Program Plan in the Appendix. The laboratory study was expanded to include a wide range of reaction conditions. These additional reaction kinetic measurements provided the needed experimental data for the subsequent theoretical studies to develop a rate equation for the hydrochlorination reaction and to provide a basic understanding on the reaction mechanism. This Quarterly Report is the sixth in the series. Activities in this quarter includes the equilibrium constant and the rate constant measurements as a function of temperature, pressure and concentration. Thermodynamic functions, such as ΔH , are also determined from these experimental data. Results are summarized in the following discussion.

II. DISCUSSION

A. Equilibrium Constant Measurements

The hydrochlorination of SiCl_4 and m.g. silicon to form SiHCl_3 is an equilibrium reaction. The overall reaction may be written as,



The equilibrium constant, K , based on mole fraction of reactants and products, is defined in accordance with the stoichiometry of the hydrochlorination reaction (1).

$$K = \frac{(\text{SiHCl}_3)^4}{(\text{SiCl}_4)^3 (\text{H}_2)^2}$$

The activity (concentration) of elemental silicon is taken as unity. The equilibrium constant, K_p , expressed in terms of partial pressure of reactants and products, is given by,

$$K_p = \frac{(p_{\text{SiHCl}_3})^4}{(p_{\text{SiCl}_4})^3 (p_{\text{H}_2})^2}$$

The partial pressure is obtained by multiplying the mole fraction with the total pressure, P. Thus,

$$K_p = \frac{K}{P}$$

The equilibrium constants were measured as a function of temperature, concentration and pressure.

(1) Equilibrium Constant as a Function of Temperature

A series of experiments on the hydrochlorination of SiCl_4 and m.g. silicon was carried out at 100 psig, H_2/SiCl_4 feed ratio of 2.0 and at various reaction temperatures. Sufficiently long residence times were allowed for the experiment so that the hydrochlorination reaction was well within equilibrium. The reaction product composition was then measured by the in-line gas chromatograph (G.C.) at the reaction temperature of 500°C , 525°C , 550°C and 575°C , respectively. Results of the G.C. measurements are summarized in Table I. The mole % of SiHCl_3 and of SiCl_4 in Table I was converted to mole fractions. The concentration of hydrogen in the reaction product mixture was not experimentally determined. However, it can be readily calculated. Since one mole of hydrogen is consumed for every two moles of SiHCl_3 produced and since one mole of hydrogen is consumed for every mole of SiH_2Cl_2 produced, the concentration of hydrogen at equilibrium is given by,

$$C_{\text{H}_2} = a_{\text{H}_2} - \frac{1}{2} C_{\text{SiHCl}_3} - C_{\text{SiH}_2\text{Cl}_2}$$

where a_{H_2} is the initial hydrogen concentration in the feed. The values of K and K_p were calculated from the mole fraction data and from the partial pressure data obtained at equilibrium. Results are summarized in Table II. As the results in Table II show, the equilibrium constants for the hydrochlorination reaction increase as a function of increasing reaction temperature.

(2) Heat of Reaction, ΔH

The heat of reaction, ΔH , is calculated by the Second Law Method. Starting from the equation,

$$\Delta F = -RT \ln K$$

by differentiation with respect to T ,

$$\frac{d \Delta F}{dT} = -S$$

one obtains the well-known Van't Hoff equation,

$$\Delta H = RT^2 \frac{d \ln K}{dT}$$

where, ΔF is the Free Energy, R is the ideal gas constant, T is the temperature and S is the Entropy. By substituting $dT = -T^2 d(1/T)$, one obtains,

$$\Delta H = -R \frac{d(\ln K)}{d\left(\frac{1}{T}\right)}$$

Thus, the slope of a $\ln K$ versus $(1/T)$ plot is $-\Delta H/R$. The logarithm of the equilibrium constant K in Table II is then plotted against the inversed temperature, $1/T$. Results are given in Figure I. The plot in figure I gives a straight line. The heat of reaction, ΔH , is then determined from the slope

of the straight line to give a value of 10.6 Kcal/mole for the hydrochlorination reaction. Thus, the hydrochlorination of SiCl_4 and m.g. silicon to SiHCl_3 is a slightly endothermic reaction.

(3) Equilibrium Constant as a Function of Concentration

A set of experimental data previously obtained from the hydrochlorination of SiCl_4 experiments at 100 psig, 500°C and at various H_2/SiCl_4 feed ratios (see Figure V, fourth Quarterly Report, April 9 to July 8, 1982) was analyzed. These experimental data are reproduced in Figure II. The equilibrium SiHCl_3 conversions at various H_2/SiCl_4 feed ratios were directly measured from the plots at the point where the kinetic curves level off. The mole % data were converted to mole fractions as shown in Table III. The equilibrium constants, K and K_p , were calculated in the same manner as described in Section A (1). Results are summarized in the last two columns in Table III. The equilibrium constants in Table III remain essentially constant within experimental error at the various H_2/SiCl_4 feed ratios ranging from 1.0 to 4.7. The standard deviations from this set of equilibrium constant values are well within $\pm 10\%$. Thus, the equilibrium constant for the hydrochlorination reaction is constant with respect to concentration. This observation is in agreement with the theoretical consideration.

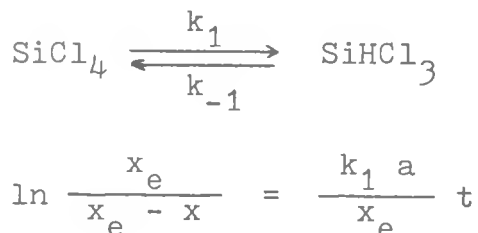
(4) Equilibrium Constant as a Function of Pressure

The equilibrium constant, K_p , expressed in terms of partial pressures should also be a constant value with respect to pressure. A collection of equilibrium data previously obtained from the hydrochlorination of SiCl_4 and m.g. silicon at 500°C and at various pressures (from 25 psig to 500 psig) and H_2/SiCl_4 feed ratios (from 1.0 to 4.7) is summarized in Table IV. The equilibrium mole% of SiHCl_3 was obtained directly from the various kinetic curves at the point where the % SiHCl_3 conversion leveled off at long residence times. These kinetic curves have been published in

previous Quarterly Reports and in the work carried out at the Massachusetts Institute of Technology⁽¹⁾. The mole % data were converted to mole fractions and partial pressures. The values of K and K_p were then calculated and listed in the last two columns in Table IV. Results in Table IV show that the effect of pressure on the equilibrium constant K_p is rather complex. At the lower pressure range of 25 psig to 100 psig, the value of K_p remains constant at about $0.65 \times 10^{-3} \text{ atm.}^{-1}$. However, at the higher pressure range of 150 psig to 500 psig, the value of K_p increases by a factor of two or more, e.g., $1.3 \times 10^{-3} \text{ atm.}^{-1}$ at 500 psig. The reason for the increase of the value of K_p at the higher pressure range is not fully understood at the present time. Nevertheless, the variation of K_p with respect to pressure is reproducible by similar experiments on the hydrochlorination reaction at a lower temperature. Table V summarizes the results of the equilibrium constant measurements at 450°C and at the similar ranges of pressures and H_2/SiCl_4 feed ratio. At the lower pressure range of 25 psig to 100 psig, the value of K_p remains constant within experimental error at about $0.35 \times 10^{-3} \text{ atm.}^{-1}$. Again, at the higher pressure range of 150 psig to 500 psig, the values of K_p increase to a much higher number, e.g., $0.66 \times 10^{-3} \text{ atm.}^{-1}$ at 500 psig.

B. Rate Constant Measurements

The experimental rate data obtained from the hydrochlorination of SiCl_4 and m.g. silicon was found to obey the psuedo-first order kinetics. The psuedo-first order rate equation for the hydrochlorination reaction was described in the last Quarterly Report.



where x is the concentration (or partial pressure) of SiHCl_3 at time t , x_e is the concentration of SiHCl_3 at equilibrium and a is the initial concentration of SiCl_4 in the feed. A plot of the logarithm of $x_e/x_e - x$ versus time t gives a straight line if the experimental rate data obey the pseudo-first order kinetics. The rate constant, k_1 , is then determined from the slope of the straight line, which equals to $k_1 a/x_e$.

(1) Rate Constant as a Function of Temperature

The effect of temperature on the pseudo-first order rate constant, k_1 , was reported in the last Quarterly Report. The variation of k_1 with respect to reaction temperature provided a measurement on the activation energy, ΔE , for the hydrochlorination reaction by plotting the logarithm of k_1 versus the inverted temperature, $1/T$, in the Arrhenius equation. The value of ΔE was found to be 13.2 Kcal/mole. The effect of concentration (H_2/SiCl_4 feed ratio) and pressure on the reaction rate was studied this quarter.

(2) Rate Constant as a Function of Concentration

A set of rate data obtained from the hydrochlorination of SiCl_4 and m.g. silicon at 100 psig, 500°C and at various H_2/SiCl_4 feed ratios (1.0 to 4.7) was analyzed by the pseudo-first order kinetics. These experimental data are shown by the kinetic curves in Figure II. The % SiHCl_3 conversions at various residence times of 10, 20, 30, 40 and 60 seconds were directly measured from these kinetic curves. The mole % conversion data were converted to mole fractions and partial pressures as summarized in Table VI, Table VII, Table VIII and Table IX for the experiments with the H_2/SiCl_4 feed ratio of 4.7, 4.0, 2.8, 2.0 and 1.0, respectively. The equilibrium composition of SiHCl_3 , x_e , was taken at the point where the kinetic curves leveled off. The initial partial pressure of SiCl_4 , a , was calculated from the composition of the H_2/SiCl_4 feed. The logarithm of $x_e/x_e - x$ was calculated from the partial pressure data and plotted against the reaction time t as shown

in Figure III, Figure IV, Figure V, Figure VI and Figure VII for the experiments with the $H_2/SiCl_4$ feed ratio of 4.7, 4.0, 2.8, 2.0 and 1.0, respectively. Results in these Figures show that a straight line was obtained in each of the plot. The rate constant, k_1 , was calculated from the slope of the straight line, which equaled to $k_1 a/x_e$. Results are summarized in Table XI. Data in Table XI show that the rate constant slightly increases at a higher $H_2/SiCl_4$ feed ratio. These results suggest that the hydrochlorination of $SiCl_4$ and m.g. silicon to $SiHCl_3$ proceeds at a slightly faster rate at a higher concentration of hydrogen gas.

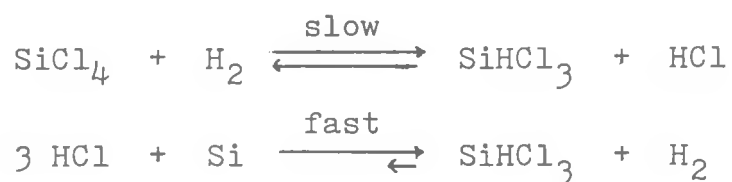
(3) Rate Constant as a Function of Pressure

A similar theoretical treatment of the reaction kinetic data obtained from the hydrochlorination of $SiCl_4$ and m.g. silicon at various pressures was performed. A set of kinetic curves obtained at $500^\circ C$ and with a $H_2/SiCl_4$ feed ratio of 2.0 at various pressures of 25 psig, 100 psig and 200 psig is reproduced in Figure VIII. The rate of $SiHCl_3$ formation (in mole% conversion) was directly read from these smooth kinetic curves at 10, 20, 30, 40 and 60 seconds residence time. The mole % data were converted to mole fractions and partial pressures for H_2 , $SiHCl_3$ and $SiCl_4$ and summarized in Table XII, Table XIII and Table XIV for the corresponding experiments at 25 psig, 100 psig and 200 psig, respectively. The equilibrium conversion of $SiHCl_3$, x_e , was measured at the point where the kinetic curves leveled off at long residence times. The initial $SiCl_4$ partial pressure, a , was calculated from the $H_2/SiCl_4$ feed ratio and the reactor pressure. The logarithm of $x_e/x_e - x$ was calculated and plotted against the reaction time t as shown in Figure IX, Figure X and Figure XI for the corresponding experiments at 25 psig, 100 psig and 200 psig respectively. A straight line was obtained from each of the plot in these Figures. The rate constant, k_1 , was calculated from the slope

of the straight line, which equaled to $k_1 a/x_e$. Results of the rate constant measurements are summarized in Table XV. Two more data points on the rate constant at 73 psig and at 500 psig were obtained by the same reaction kinetic treatment. These experimental rate data were obtained at a slightly higher $H_2/SiCl_4$ feed ratio (2.8 instead of 2.0). The rate constants measured at 73 psig and at 500 psig are also summarized in Table XV. Results in Table XV show that the pseudo-first order rate constant, k_1 , gradually decreases as a function of increasing pressure. The rate constants in Table XV were plotted against the pressure (in atmospheres) as shown in Figure XII. The graph in Figure XII shows that the effect of pressure on the hydrochlorination reaction rate (rate constant) is not linear. An attempt is in progress to incorporate the pressure effect into the rate equation. The ultimate goal is to develop a generalized rate equation applicable to the entire range of reaction conditions studied thus far.

C. Reaction Mechanism Study

Previous experimental studies⁽¹⁾ on the hydrochlorination of $SiCl_4$ and m.g. silicon showed that a plausible reaction mechanism may involve two stepwise reactions,



The hydrogenation of a Si-Cl bond by hydrogen to form $SiHCl_3$ and HCl was postulated as the slow, rate-determining step. By replacing hydrogen with deuterium in the hydrochlorination reaction, a positive kinetic isotope effect may provide useful information on the nature of the activated complex and on the mechanism of the reaction pathway.

(1) The Quartz Hydrochlorination Reactor

Construction of the quartz hydrochlorination reactor system was completed. This quartz reactor was designed for the deuterium kinetic isotope effects study. The apparatus is schematically shown in Figure XIII. The design and operation of this quartz reactor system were described in detail in the last Quarterly Report. Instruments and flowmeters were calibrated and standardized. The reactor system was successfully started up. Hydrogen was used in the initial runs to check out the system. These initial experiments also served to "clean" and to stabilize the fresh silicon metal mass bed by consuming some silicon in the process. A series of experiments on the hydrochlorination of SiCl_4 and m.g. silicon with hydrogen and deuterium is planned. The relative reaction rates between hydrogen and deuterium will be studied as a function of temperature and H_2/SiCl_4 or D_2/SiCl_4 feed ratios. More experimental work is in progress.

D. Summary of Progress

Experimental work on the JPL Contract No. 956061 has progressed in accordance with the Program Plan. Theoretical treatment of experimental rate data on the hydrochlorination reaction was carried out for the development of a rate equation and for the determination of thermodynamic functions. Equilibrium constants for the hydrochlorination of SiCl_4 and m.g. silicon to SiHCl_3 were measured as a function of reaction temperature, pressure and concentration. The heat of reaction, ΔH , was determined from the change of the equilibrium constant as a function of temperature. The rate data obtained from the hydrochlorination reaction was found to obey the pseudo-first order kinetics. The rate constants for the pseudo-first order rate equation were measured as a function of temperature, pressure and concentration. Variation of the rate constants as a function of temperature provided a measurement on the

activation energy, ΔE , for the hydrochlorination reaction. More work is in progress in an attempt to develop a generalized rate equation for the hydrochlorination of SiCl_4 and m.g. silicon to include the entire range of reaction conditions studied so far. Construction of the quartz hydrochlorination reactor system has been completed. This quartz reactor was successfully started up. Experiments on the deuterium kinetic isotope effects are in progress.

III. PROJECTED SEVENTH QUARTER ACTIVITIES

Planned activities for the seventh quarter (January - March) include,

- complete the experiments on the deuterium kinetic isotope effects study,
- complete the theoretical treatment of the reaction kinetic data obtained from the hydrochlorination reaction,
- complete the reaction mechanism study on the hydrochlorination of SiCl_4 and m.g. silicon,
- Final Report.

IV. REFERENCES

- (1) Final Report, JPL Contract No. 955382, "Investigation of the Hydrogenation of SiCl_4 " by Jeffrey Y. P. Mui and Dietmar Seyferth, Massachusetts Institute of Technology, April 15, 1981.

V. APPENDIX

Program Plan SC-1

Table I to XV

Figure I to XIII

TABLE I

EQUILIBRIUM COMPOSITIONS OF CHLOROSILANE PRODUCTS FOR
THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL
AT 100 PSIG, $\text{H}_2/\text{SiCl}_4 = 2.0$ AND AT VARIOUS TEMPERATURES

| Sample No. | Reaction Temperature °C | Residence Time Second | Product Composition, Mole % | | |
|------------|-------------------------|-----------------------|-----------------------------|------------------|-----------------|
| | | | SiH_2Cl_2 | SiHCl_3 | SiCl_4 |
| I | 500 | 148 | 0.3726 | 22.29 | 77.33 |
| I | 500 | 148 | 0.3596 | 21.98 | 77.66 |
| I | 500 | 148 | 0.3779 | 22.15 | 77.47 |
| I | 500 | 148 | 0.3600 | 22.11 | 77.53 |
| | | Average = | 0.3675 | 22.13 | 77.50 |
| II | 525 | 138 | 0.4781 | 23.25 | 76.27 |
| II | 525 | 138 | 0.3651 | 22.98 | 76.66 |
| II | 525 | 138 | 0.4141 | 22.92 | 76.66 |
| II | 525 | 138 | 0.4359 | 22.93 | 76.64 |
| | | Average = | 0.4233 | 23.02 | 76.56 |
| III | 550 | 101 | 0.5750 | 24.05 | 75.38 |
| III | 550 | 101 | 0.5125 | 23.98 | 75.51 |
| III | 550 | 101 | 0.5099 | 24.21 | 75.28 |
| III | 550 | 101 | 0.5650 | 23.98 | 75.45 |
| | | Average = | 0.5406 | 24.06 | 75.40 |
| IV | 575 | 98 | 0.5857 | 24.89 | 74.53 |
| IV | 575 | 98 | 0.5294 | 24.84 | 74.63 |
| IV | 575 | 98 | 0.5070 | 24.85 | 74.64 |
| IV | 575 | 98 | 0.4828 | 24.92 | 74.60 |
| | | Average = | 0.5262 | 24.88 | 74.60 |

TABLE II EQUILIBRIUM CONSTANTS FOR THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 100 PSIG, $\text{H}_2/\text{SiCl}_4 = 2.0$ AND AT VARIOUS TEMPERATURES

| Expt'l No. | Reaction Temp. °C | Mole Fractions at Equilibrium | | | | Equilibrium Constant | |
|---------------|-------------------------|-------------------------------|------------------|-----------------|--------------|-------------------------|---|
| | | SiH_2Cl_2 | SiHCl_3 | SiCl_4 | H_2 | K $\times 10^{-3}$ | K_p $\times 10^{-4} \text{ Atm.}^{-1}$ |
| I | 500 | 0.001326 | 0.079855 | 0.27965 | 0.63916 | 4.55 | 5.83 |
| II | 525 | 0.001533 | 0.083363 | 0.27725 | 0.63786 | 5.57 | 7.14 |
| III | 550 | 0.001967 | 0.087535 | 0.27432 | 0.63618 | 7.03 | 9.01 |
| IV | 575 | 0.001920 | 0.090774 | 0.27218 | 0.63513 | 8.35 | 10.7 |

TABLE III EQUILIBRIUM CONSTANTS FOR THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 500°C , 100 PSIG AND AT VARIOUS H_2/SiCl_4 FEED RATIOS

| $\frac{\text{H}_2}{\text{SiCl}_4}$ Ratio | Equilibrium (1) Composition | | Mole Fractions at Equilibrium | | | Equilibrium Constant | |
|---|--------------------------------|---------------------------|-------------------------------|-----------------|--------------|-------------------------|--|
| | Mole % SiHCl_3 | Mole % SiCl_4 | SiHCl_3 | SiCl_4 | H_2 | K $\times 10^{-3}$ | K_p $\times 10^{-3} \text{Atm.}^{-1}$ |
| 4.7 | 28.0 | 72.0 | 0.05353 | 0.1376 | 0.8088 | 4.81 | 0.617 |
| 4.0 | 26.7 | 73.3 | 0.05806 | 0.1594 | 0.7825 | 4.58 | 0.587 |
| 2.8 | 24.5 | 75.5 | 0.06988 | 0.2153 | 0.7148 | 4.67 | 0.599 |
| 2.0 | 22.8 | 77.2 | 0.08225 | 0.2785 | 0.6392 | 5.19 | 0.665 |
| 1.0 | 18.5 | 81.5 | 0.09939 | 0.4379 | 0.4627 | 5.43 | 0.696 |

(1) Data from Figure V, fourth Quarterly Report, April 9 to July 8, 1982.

TABLE IV

EQUILIBRIUM CONSTANTS FOR THE HYDROCHLORINATION OF SiCl_4 AND M.G.
SILICON AT 500°C AND AT VARIOUS PRESSURES AND H_2/SiCl_4 FEED RATIOS

| Reactor Pressure | | $\frac{\text{H}_2}{\text{SiCl}_4}$ | Equilibrium Composition | | Mole Fraction at Equilibrium | | | Equilibrium Constant | |
|------------------|------|------------------------------------|----------------------------|---------------------------|------------------------------|-----------------|--------------|-----------------------|---|
| psig | Atm. | Ratio | Mole % SiHCl_3 | Mole % SiCl_4 | SiHCl_3 | SiCl_4 | H_2 | K $\times 10^{-3}$ | K_p $\times 10^{-3}\text{Atm.}^{-1}$ |
| 25 | 2.70 | 2.0 | 18.5 | 81.5 | 0.06572 | 0.2895 | 0.6448 | 1.85 | 0.685 |
| 73 | 5.97 | 2.8 | 23.7 | 76.3 | 0.06741 | 0.2170 | 0.7155 | 3.95 | 0.661 |
| 100 | 7.80 | 1.0 | 18.5 | 81.5 | 0.09939 | 0.4379 | 0.4627 | 5.43 | 0.696 |
| 100 | 7.80 | 2.0 | 22.8 | 77.2 | 0.08225 | 0.2785 | 0.6392 | 5.19 | 0.665 |
| 100 | 7.80 | 2.8 | 24.5 | 75.5 | 0.06988 | 0.2153 | 0.7148 | 4.67 | 0.599 |
| 100 | 7.80 | 4.0 | 26.7 | 73.3 | 0.05806 | 0.1594 | 0.7825 | 4.58 | 0.587 |
| 100 | 7.80 | 4.7 | 28.0 | 72.0 | 0.05353 | 0.1376 | 0.8088 | 4.81 | 0.617 |
| 150 | 11.2 | 2.0 | 27.9 | 72.1 | 0.1025 | 0.2650 | 0.6325 | 14.9 | 1.33 |
| 200 | 14.6 | 2.0 | 30.5 | 69.5 | 0.1132 | 0.2579 | 0.6289 | 24.2 | 1.65 |
| 300 | 21.4 | 2.8 | 35.0 | 65.0 | 0.1035 | 0.1923 | 0.7041 | 32.6 | 1.52 |
| 500 | 35.0 | 2.8 | 37.0 | 63.0 | 0.1102 | 0.1877 | 0.7020 | 45.3 | 1.29 |

TABLE V

EQUILIBRIUM CONSTANTS FOR THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 450°C AND AT VARIOUS PRESSURES AND H_2/SiCl_4 FEED RATIOS

| Reactor Pressure | | $\frac{\text{H}_2}{\text{SiCl}_4}$ Ratio | Equilibrium Composition Mole % | | Mole Fraction at Equilibrium | | | Equilibrium Constant | |
|------------------|------|---|-----------------------------------|-----------------|------------------------------|-----------------|--------------|-------------------------|--|
| psig | Atm. | | SiHCl_3 | SiCl_4 | SiHCl_3 | SiCl_4 | H_2 | K $\times 10^{-3}$ | K_p $\times 10^{-3} \text{Atm.}^{-1}$ |
| 25 | 2.70 | 2.0 | 16.2 | 83.8 | 0.05708 | 0.2953 | 0.6476 | 0.983 | 0.364 |
| 73 | 5.96 | 2.8 | 20.8 | 79.2 | 0.05858 | 0.2231 | 0.7183 | 2.06 | 0.345 |
| 100 | 7.80 | 2.0 | 20.4 | 79.6 | 0.07296 | 0.2847 | 0.6424 | 2.98 | 0.382 |
| 150 | 11.2 | 2.0 | 24.0 | 76.0 | 0.08696 | 0.2754 | 0.6377 | 6.73 | 0.601 |
| 150 | 11.2 | 2.8 | 26.5 | 73.5 | 0.07611 | 0.2111 | 0.7128 | 7.02 | 0.627 |
| 200 | 14.6 | 2.0 | 27.0 | 73.0 | 0.09890 | 0.2674 | 0.6337 | 12.5 | 0.854 |
| 300 | 21.4 | 2.8 | 31.0 | 69.0 | 0.09043 | 0.2013 | 0.7083 | 16.3 | 0.764 |
| 300 | 21.4 | 1.0 | 25.0 | 75.0 | 0.1379 | 0.4138 | 0.4483 | 25.4 | 1.19 |
| 500 | 35.0 | 2.8 | 33.0 | 67.0 | 0.09695 | 0.1968 | 0.7062 | 23.2 | 0.664 |

TABLE VI THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL TO SiHCl_3
 Pressure 114.7 psia, Temperature 500 °C, H_2/SiCl_4 Feed Ratio 4.7.

| Time t sec. | Composition Mole % | | Composition at Time t (psia)/Mole Fraction | | | Initial Partial Press. SiCl_4 a | Equil. Partial Press. SiHCl_3 x_e | $\ln \frac{x_e}{x_e - x}$ | Rate Constant k_1 $\times 10^{-3} \text{sec.}^{-1}$ |
|-------------------|-----------------------|-----------------|---|--------------------|-------------------|--|--|---------------------------|--|
| | SiHCl_3 | SiCl_4 | H_2 | SiHCl_3 | SiCl_4 | | | | |
| 10 | 19.9 | 80.1 | (93.30) 0.8137 | (4.250) 0.03708 | (17.12) 0.1493 | 20.12 | - | 1.180 | |
| 20 | 23.0 | 77.0 | (93.12) 0.8118 | (4.964) 0.04327 | (16.62) 0.1449 | 20.12 | - | 1.653 | |
| 30 | 24.7 | 75.3 | (93.00) 0.8108 | (5.359) 0.04673 | (16.34) 0.1424 | 20.12 | - | 2.063 | |
| 40 | 25.7 | 74.3 | (92.93) 0.8102 | (5.594) 0.04877 | (16.17) 0.1410 | 20.12 | - | 2.422 | |
| 60 | 26.9 | 73.1 | (92.85) 0.8095 | (5.878) 0.05124 | (15.97) 0.1393 | 20.12 | - | 3.158 | |
| Eq. | 28.0 | 72.0 | (92.77) 0.8088 | (6.139) 0.5353 | (15.79) 0.1376 | 20.12 | 6.139 | - | 12.7 |
| | | | | | | | | | |
| | | | | | | | | | |

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Reference To: Figure V, fourth Quarterly Report, April 9 - July 8, 1982.

TABLE VII THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL TO SiHCl_3
 Pressure 114.7 psia, Temperature 500 °C, H_2/SiCl_4 Feed Ratio 4.0.

| Time t sec. | Composition Mole % | | Composition at Time t (psia)/Mole Fraction | | | Initial Partial Press. SiCl_4 a | Equil. Partial Press. SiHCl_3 x_e | $\ln \frac{x_e}{x_e - x}$ | Rate Constant k_1 $\times 10^{-3} \text{sec.}^{-1}$ |
|-------------------|-----------------------|-----------------|---|--------------------|-------------------|--|--|---------------------------|--|
| | SiHCl_3 | SiCl_4 | H_2 | SiHCl_3 | SiCl_4 | | | | |
| 10 | 18.0 | 82.0 | (90.45) 0.7886 | (4.365) 0.03806 | (19.88) 0.1734 | 22.94 | - | 1.058 | |
| 20 | 21.3 | 78.7 | (90.19) 0.7864 | (5.220) 0.04551 | (19.29) 0.1681 | 22.94 | - | 1.518 | |
| 30 | 23.1 | 76.9 | (90.05) 0.7851 | (5.694) 0.04964 | (18.95) 0.1653 | 22.94 | - | 1.909 | |
| 40 | 24.4 | 75.6 | (89.95) 0.7842 | (6.039) 0.05265 | (18.71) 0.1631 | 22.94 | - | 2.337 | |
| 60 | 25.7 | 74.3 | (89.84) 0.7833 | (6.388) 0.05569 | (18.47) 0.1610 | 22.94 | - | 3.114 | |
| Eq. | 26.8 | 73.2 | (89.75) 0.7825 | (6.685) 0.05829 | (18.26) 0.1592 | 22.94 | 6.685 | - | 12.2 |
| | | | | | | | | | |
| | | | | | | | | | |

Reference To: Figure V, fourth Quarterly Report, April 9 - July 8, 1982.

TABLE VIII THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL TO SiHCl_3

Pressure 114.7 psia, Temperature 500 °C, H_2/SiCl_4 Feed Ratio 2.8 .

| Time t sec. | Composition Mole % | | Composition at Time t (psia)/Mole Fraction | | | Initial Partial Press. SiCl_4 a | Equil. Partial Press. SiHCl_3 x_e | $\ln \frac{x_e}{x_e - x}$ | Rate Constant k_1 $\times 10^{-3} \text{sec.}^{-1}$ |
|-------------------|-----------------------|-----------------|---|--------------------|-------------------|--|--|---------------------------|--|
| | SiHCl_3 | SiCl_4 | H_2 | SiHCl_3 | SiCl_4 | | | | |
| 10 | 17.0 | 83.0 | (82.80) 0.7219 | (5.422) 0.04728 | (26.47) 0.2308 | 30.18 | - | 1.128 | |
| 20 | 19.8 | 80.2 | (82.50) 0.7193 | (6.375) 0.05558 | (25.82) 0.2251 | 30.18 | - | 1.587 | |
| 30 | 21.5 | 78.5 | (82.32) 0.7177 | (6.962) 0.06070 | (25.42) 0.2216 | 30.18 | - | 2.030 | |
| 40 | 22.6 | 77.4 | (82.20) 0.7166 | (7.346) 0.06404 | (25.16) 0.2193 | 30.18 | - | 2.483 | |
| 60 | 23.7 | 76.3 | (82.08) 0.7156 | (7.697) 0.06711 | (24.92) 0.2172 | 30.18 | - | 3.227 | |
| Eq. | 24.5 | 75.5 | (81.98) 0.7148 | (8.015) 0.06988 | (24.70) 0.2153 | 30.18 | 8.015 | - | 11.4 |
| | | | | | | | | | |
| | | | | | | | | | |

Reference To: Figure V, fourth Quarterly Report, April 9 - July 8, 1982.

TABLE IX THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL TO SiHCl_3

Pressure 114.7 psia, Temperature 500 °C, H_2/SiCl_4 Feed Ratio 2.0.

| Time t sec. | Composition Mole % | | Composition at Time t (psia)/Mole Fraction | | | Initial Partial Press. SiCl_4 a | Equil. Partial Press. SiHCl_3 x_e | $\ln \frac{x_e}{x_e - x}$ | Rate Constant k_1 $\times 10^{-3} \text{sec.}^{-1}$ |
|-------------------|-----------------------|-----------------|---|--------------------|-------------------|--|--|---------------------------|--|
| | SiHCl_3 | SiCl_4 | H_2 | SiHCl_3 | SiCl_4 | | | | |
| 10 | 15.1 | 84.9 | (74.44) 0.6490 | (6.079) 0.05300 | (34.18) 0.2980 | 38.23 | - | 1.034 | |
| 20 | 18.0 | 82.0 | (74.03) 0.6454 | (7.321) 0.06383 | (33.35) 0.2908 | 38.23 | - | 1.496 | |
| 30 | 19.6 | 80.4 | (73.79) 0.6433 | (8.018) 0.06990 | (32.89) 0.2867 | 38.23 | - | 1.896 | |
| 40 | 20.6 | 79.4 | (73.65) 0.6421 | (8.457) 0.07373 | (32.60) 0.2842 | 38.23 | - | 2.268 | |
| 60 | 21.9 | 78.1 | (73.46) 0.6404 | (9.032) 0.07875 | (32.21) 0.2808 | 38.23 | - | 3.156 | |
| Eq. | 22.8 | 77.2 | (73.32) 0.6393 | (9.434) 0.08225 | (31.94) 0.2785 | 38.23 | 9.434 | - | 10.9 |
| | | | | | | | | | |
| | | | | | | | | | |

Reference To: Figure V, fourth Quarterly Report, April 9 -July 8, 1982.

TABLE X THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL TO SiHCl_3
 Pressure 114.7 psia, Temperature 500 °C, H_2/SiCl_4 Feed Ratio 1.0.

| Time t sec. | Composition Mole % | | Composition at Time t (psia)/Mole Fraction | | | Initial Partial Press. SiCl_4 a | Equil. Partial Press. SiHCl_3 x_e | $\ln \frac{x_e}{x_e - x}$ | Rate Constant k_1 $\times 10^{-3} \text{sec.}^{-1}$ |
|-------------------|-----------------------|-----------------|---|--------------------|-------------------|--|--|---------------------------|--|
| | SiHCl_3 | SiCl_4 | H_2 | SiHCl_3 | SiCl_4 | | | | |
| 10 | 12.6 | 87.4 | (54.51) 0.4752 | (7.584) 0.06612 | (52.61) 0.4587 | 57.35 | - | 1.061 | |
| 20 | 15.0 | 85.0 | (53.93) 0.4702 | (9.115) 0.07947 | (51.65) 0.4503 | 57.35 | - | 1.541 | |
| 30 | 16.3 | 83.7 | (53.62) 0.4675 | (9.957) 0.08681 | (51.23) 0.4457 | 57.35 | - | 1.955 | |
| 40 | 17.1 | 82.9 | (53.42) 0.4657 | (10.48) 0.09136 | (50.80) 0.4429 | 57.35 | - | 2.338 | |
| 60 | 18.2 | 81.8 | (53.15) 0.4634 | (11.20) 0.09767 | (50.35) 0.4390 | 57.35 | - | 3.368 | |
| Eq. | 18.8 | 81.2 | (53.00) 0.4621 | (11.60) 0.1011 | (50.10) 0.4368 | 57.35 | 11.60 | - | 9.30 |
| | | | | | | | | | |
| | | | | | | | | | |

Reference To: Figure V, fourth Quarterly Report, April 9 - July 8, 1982.

TABLE X I RATE CONSTANTS FOR THE HYDROCHLORINATION OF SiCl_4 AT
 100 PSIG, 500°C AS A FUNCTION OF H_2/SiCl_4 FEED RATIO

| H_2/SiCl_4 Feed Ratio | Equilibrium Composition Mole % | | Rate Constant k_1 $\times 10^{-3} \text{ Sec.}^{-1}$ |
|---|-----------------------------------|-----------------|--|
| | SiHCl_3 | SiCl_4 | |
| 4.7 | 28.0 | 72.0 | 12.7 |
| 4.0 | 26.8 | 73.2 | 12.2 |
| 2.8 | 24.5 | 75.5 | 11.4 |
| 2.0 | 22.8 | 77.2 | 10.9 |
| 1.0 | 18.8 | 81.2 | 9.30 |

TABLE XII THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL TO SiHCl_3
 Pressure 39.7 psia, Temperature 500 °C, H_2/SiCl_4 Feed Ratio 2.0.

| Time t sec. | Composition Mole % | | Composition at Time t (psia)/Mole Fraction | | | Initial Partial Press. SiCl_4 a | Equil. Partial Press. SiHCl_3 x_e | $\ln \frac{x_e}{x_e - x}$ | Rate Constant k_1 $\times 10^{-3} \text{sec.}^{-1}$ |
|-------------------|-----------------------|-----------------|---|--------------------|-------------------|--|--|---------------------------|--|
| | SiHCl_3 | SiCl_4 | H_2 | SiHCl_3 | SiCl_4 | | | | |
| 10 | 15.0 | 85.0 | (25.77) 0.6491 | (2.089) 0.05263 | (11.84) 0.2983 | 13.23 | - | 1.636 | |
| 20 | 16.9 | 83.1 | (25.68) 0.6468 | (2.370) 0.05970 | (11.65) 0.2935 | 13.23 | - | 2.449 | |
| 30 | 17.6 | 82.4 | (25.64) 0.6459 | (2.474) 0.06232 | (11.58) 0.2918 | 13.23 | - | 3.073 | |
| 40 | 18.0 | 82.0 | (25.62) 0.6454 | (2.534) 0.06383 | (11.54) 0.2908 | 13.23 | - | 3.767 | |
| 60 | 18.3 | 81.7 | (25.61) 0.6450 | (2.580) 0.06496 | (11.51) 0.2900 | 13.23 | - | 5.222 | |
| Eq. | 18.4 | 81.6 | (25.60) 0.6449 | (2.594) 0.06534 | (11.50) 0.2898 | 13.23 | 2.594 | - | 14.5 |
| | | | | | | | | | |
| | | | | | | | | | |

Reference To: Figure III, fourth Quarterly Report, April 9 - July 8, 1982.

TABLE XIII THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL TO SiHCl_3

Pressure 114.7 psia, Temperature 500 °C, H_2/SiCl_4 Feed Ratio 2.0.

| Time t sec. | Composition Mole % | | Composition at Time t (psia)/Mole Fraction | | | Initial Partial Press. SiCl_4 a | Equil. Partial Press. SiHCl_3 x_e | $\ln \frac{x_e}{x_e - x}$ | Rate Constant k_1 $\times 10^{-3} \text{sec.}^{-1}$ |
|-------------------|-----------------------|-----------------|---|--------------------|-------------------|--|--|---------------------------|--|
| | SiHCl_3 | SiCl_4 | H_2 | SiHCl_3 | SiCl_4 | | | | |
| 10 | 12.2 | 87.8 | (74.85) 0.6525 | (4.862) 0.04239 | (34.99) 0.3051 | 38.23 | - | 0.7193 | |
| 20 | 18.1 | 81.9 | (74.01) 0.6453 | (7.365) 0.06421 | (33.32) 0.2905 | 38.23 | - | 1.500 | |
| 30 | 19.9 | 80.1 | (73.75) 0.6430 | (8.149) 0.07105 | (32.80) 0.2860 | 38.23 | - | 1.964 | |
| 40 | 20.9 | 79.1 | (73.60) 0.6417 | (8.589) 0.07488 | (32.51) 0.2834 | 38.23 | - | 2.366 | |
| 60 | 22.0 | 78.0 | (73.44) 0.6403 | (9.077) 0.07914 | (31.18) 0.2806 | 38.23 | - | 3.160 | |
| Eq. | 22.9 | 77.1 | (73.31) 0.6391 | (9.479) 0.08264 | (31.91) 0.2782 | 38.23 | 9.479 | - | 12.2 |
| | | | | | | | | | |
| | | | | | | | | | |

Reference To: Figure III, fourth Quarterly Report, April 9 - July 8, 1982.

TABLE XIV THE HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON METAL TO SiHCl_3

Pressure 214.7 psia, Temperature 500 °C, H_2/SiCl_4 Feed Ratio 2.0.

| Time t sec. | Composition Mole % | | Composition at Time t (psia)/Mole Fraction | | | Initial Partial Press. SiCl_4 a | Equil. Partial Press. SiHCl_3 x_e | $\ln \frac{x_e}{x_e - x}$ | Rate Constant k_1 $\times 10^{-3} \text{sec.}^{-1}$ |
|-------------------|-----------------------|-----------------|---|--------------------|-------------------|--|--|---------------------------|--|
| | SiHCl_3 | SiCl_4 | H_2 | SiHCl_3 | SiCl_4 | | | | |
| 20 | 14.7 | 85.3 | (139.4) 0.6495 | (11.06) 0.05152 | (64.19) 0.2990 | 71.57 | - | 0.5925 | |
| 40 | 21.0 | 79.0 | (137.7) 0.6416 | (16.16) 0.07527 | (60.79) 0.2832 | 71.57 | - | 1.059 | |
| 60 | 24.3 | 75.7 | (136.8) 0.6373 | (18.92) 0.08814 | (58.95) 0.2746 | 71.57 | - | 1.447 | |
| 80 | 26.7 | 73.3 | (136.1) 0.6341 | (20.98) 0.09769 | (57.58) 0.2682 | 71.57 | - | 1.884 | |
| 120 | 29.4 | 70.6 | (135.4) 0.6305 | (23.33) 0.1087 | (56.02) 0.2609 | 71.57 | - | 2.865 | |
| Eq. | 31.0 | 69.0 | (134.9) 0.6282 | (24.74) 0.1152 | (55.07) 0.2565 | 71.57 | 24.74 | - | 8.33 |
| | | | | | | | | | |
| | | | | | | | | | |

Reference To: Figure III, fourth Quarterly Report, April 9 - July 8, 1982.

TABLE XV

SUMMARY OF RATE CONSTANTS FOR THE HYDROCHLORINATION
OF SiCl_4 AT 500°C AS A FUNCTION OF REACTOR PRESSURE

| Reactor Pressure | | H_2/SiCl_4 Ratio | Equilibrium Mole % | | Rate Constant k_1 $\times 10^{-3}\text{sec.}^{-1}$ |
|------------------|------|-------------------------------------|--------------------|-----------------|--|
| psig. | Atm. | | SiHCl_3 | SiCl_4 | |
| 25 | 2.70 | 2.0 | 18.4 | 81.6 | 14.5 |
| 73 | 5.97 | 2.8 | 23.4 | 76.6 | 13.0 |
| 100 | 7.80 | 2.0 | 22.9 | 77.1 | 12.2 |
| 200 | 14.6 | 2.0 | 31.0 | 69.0 | 8.33 |
| 500 | 35.0 | 2.8 | 37.5 | 62.5 | 7.06 |

FIGURE I PLOT OF THE VAN'T HOFF EQUATION
LN K VERSUS INVERSED TEMPERATURE, 1/T

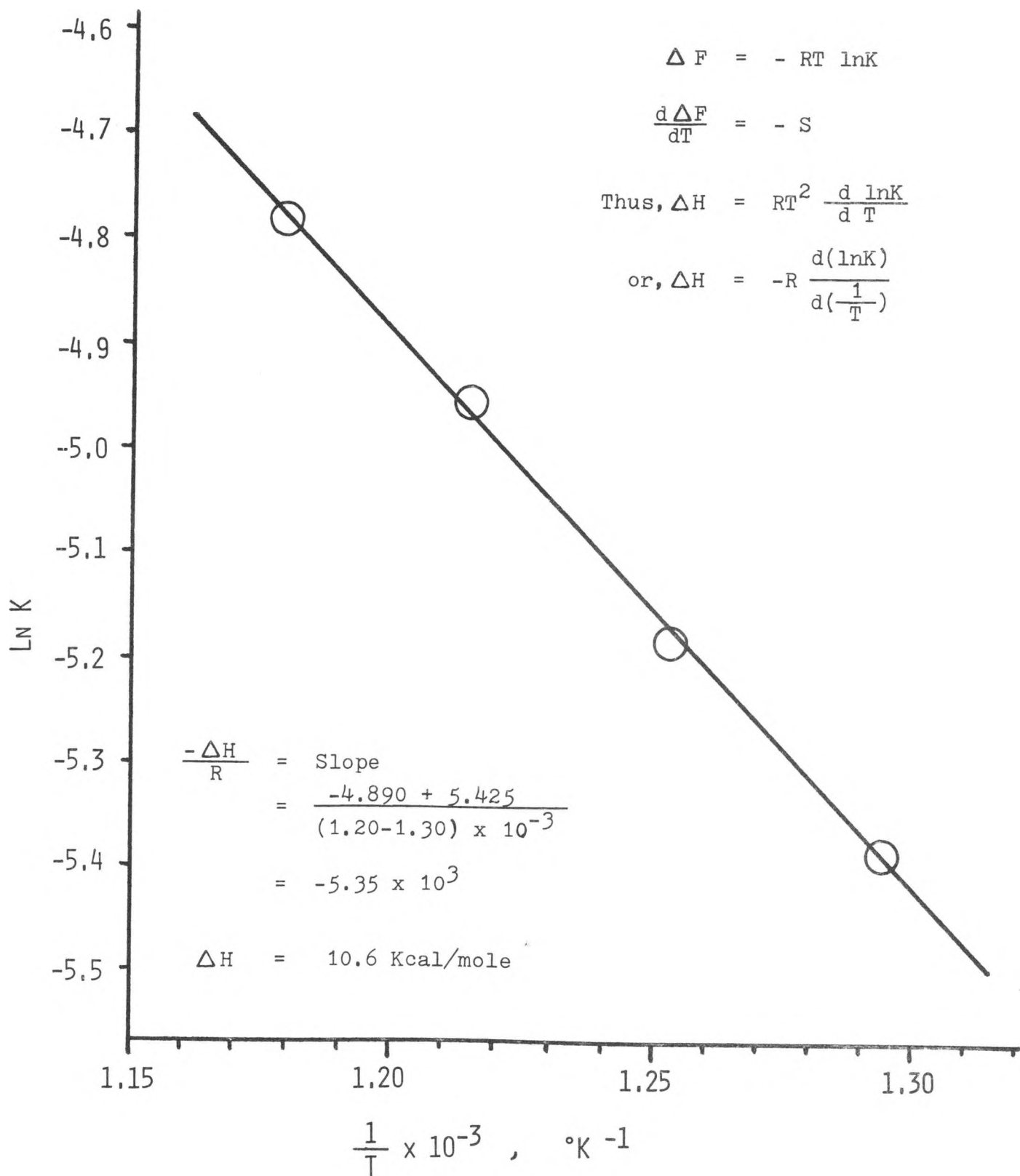


FIGURE II HYDROCHLORINATION OF SiCl_4 AT 100 PSIG, 500°C
AND AT VARIOUS MOLAR RATIOS OF $\text{H}_2 : \text{SiCl}_4$

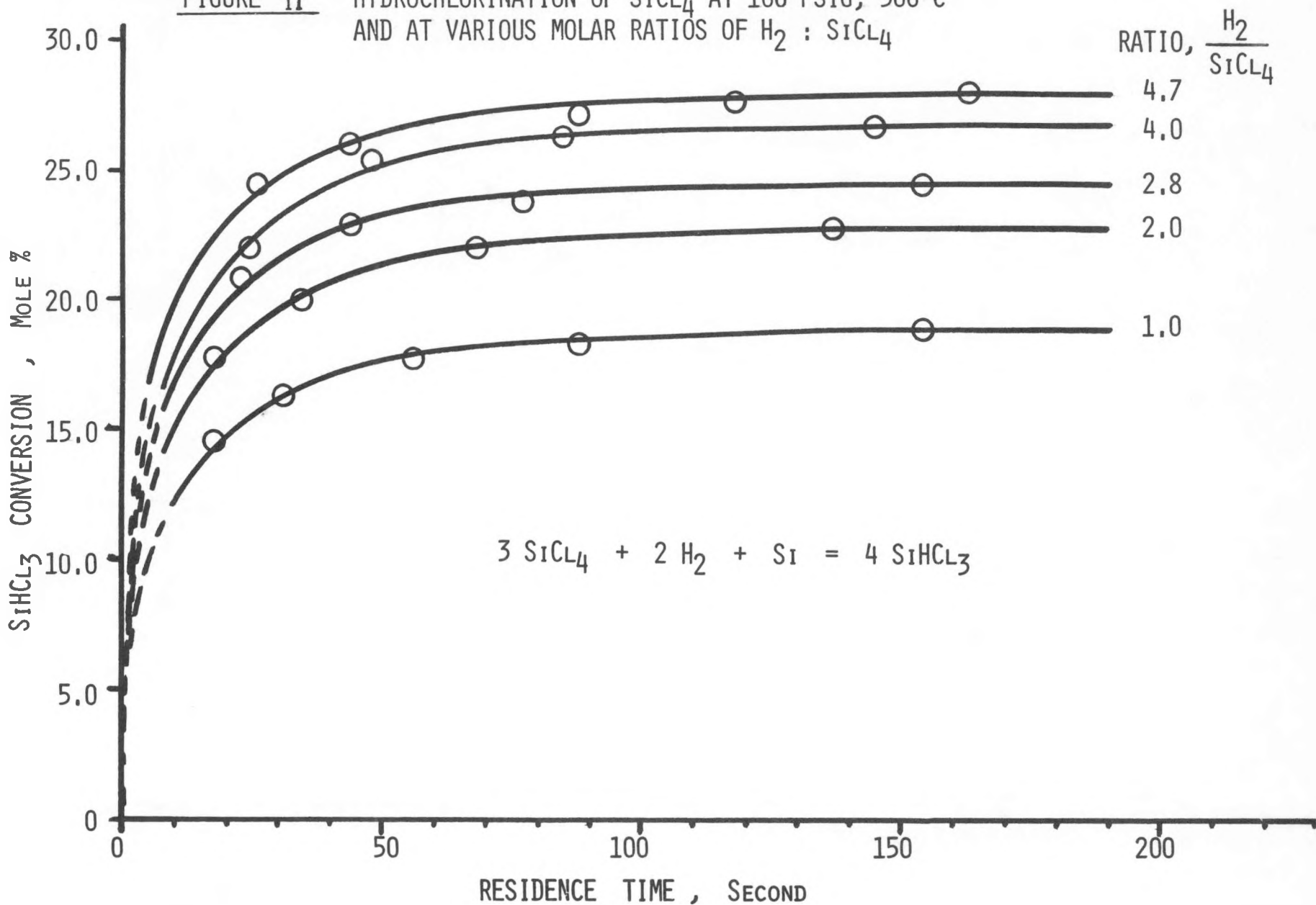


FIGURE III PLOT OF THE PSEUDO-FIRST ORDER RATE EQUATION
 FOR THE HYDROCHLORINATION OF SiCl_4 AT
100 PSIG, 500 °C AND H_2/SiCl_4 RATIO 4.7

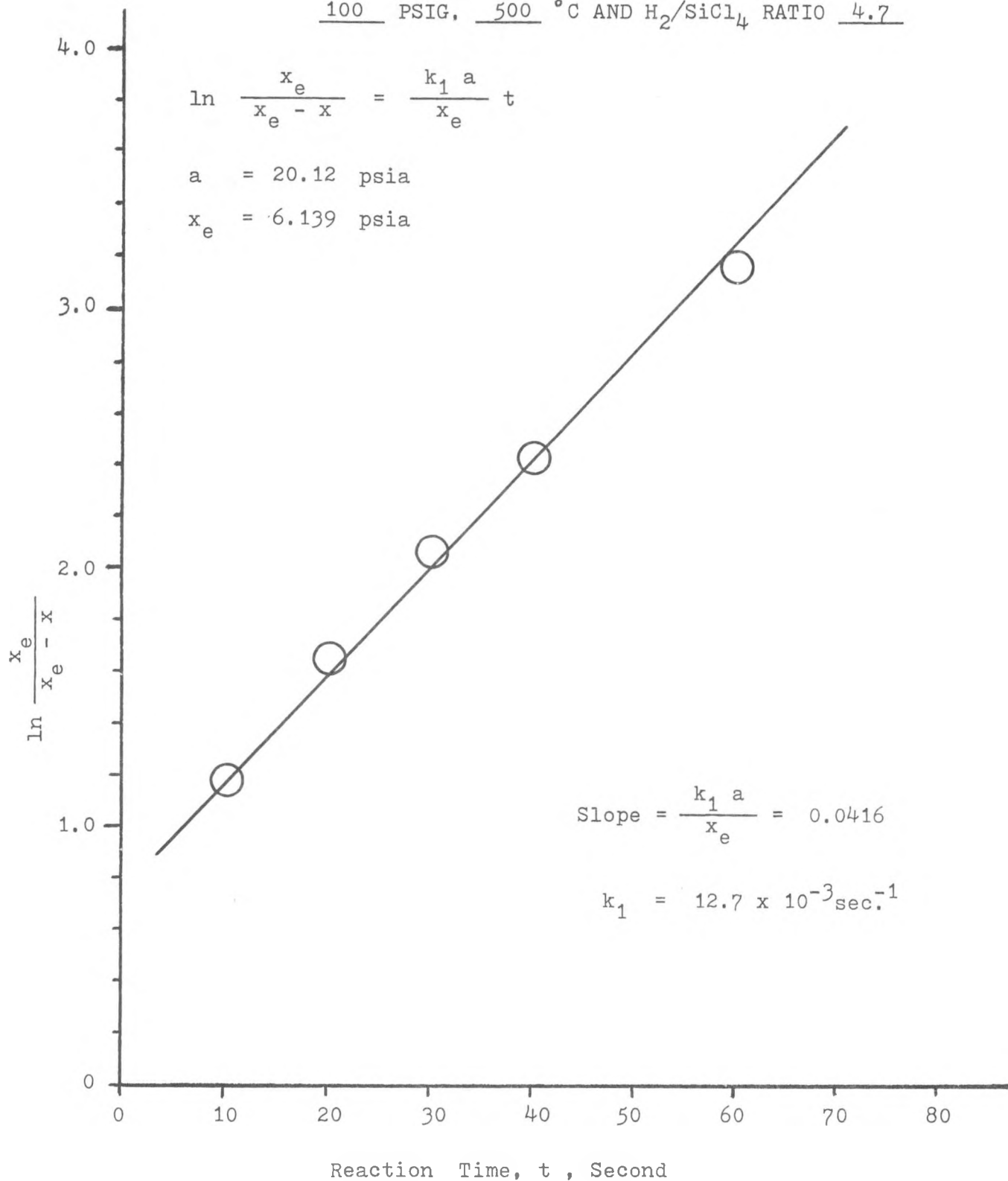


FIGURE IV PLOT OF THE PSEUDO-FIRST ORDER RATE EQUATION
 FOR THE HYDROCHLORINATION OF SiCl_4 AT
100 PSIG, 500 °C AND H_2/SiCl_4 RATIO 4.0

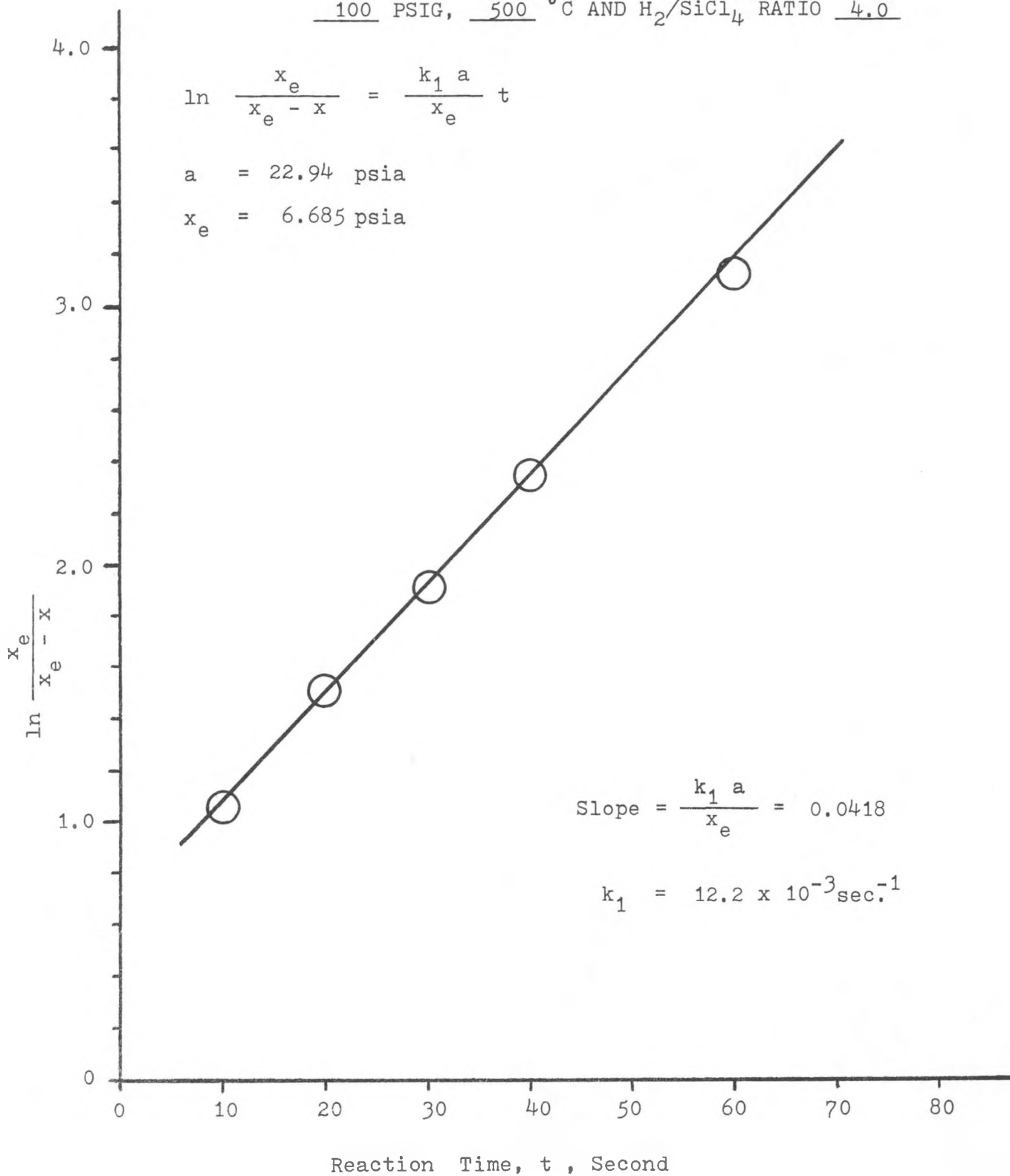


FIGURE V PLOT OF THE PSEUDO-FIRST ORDER RATE EQUATION
 FOR THE HYDROCHLORINATION OF SiCl_4 AT
100 PSIG, 500 °C AND H_2/SiCl_4 RATIO 2.8

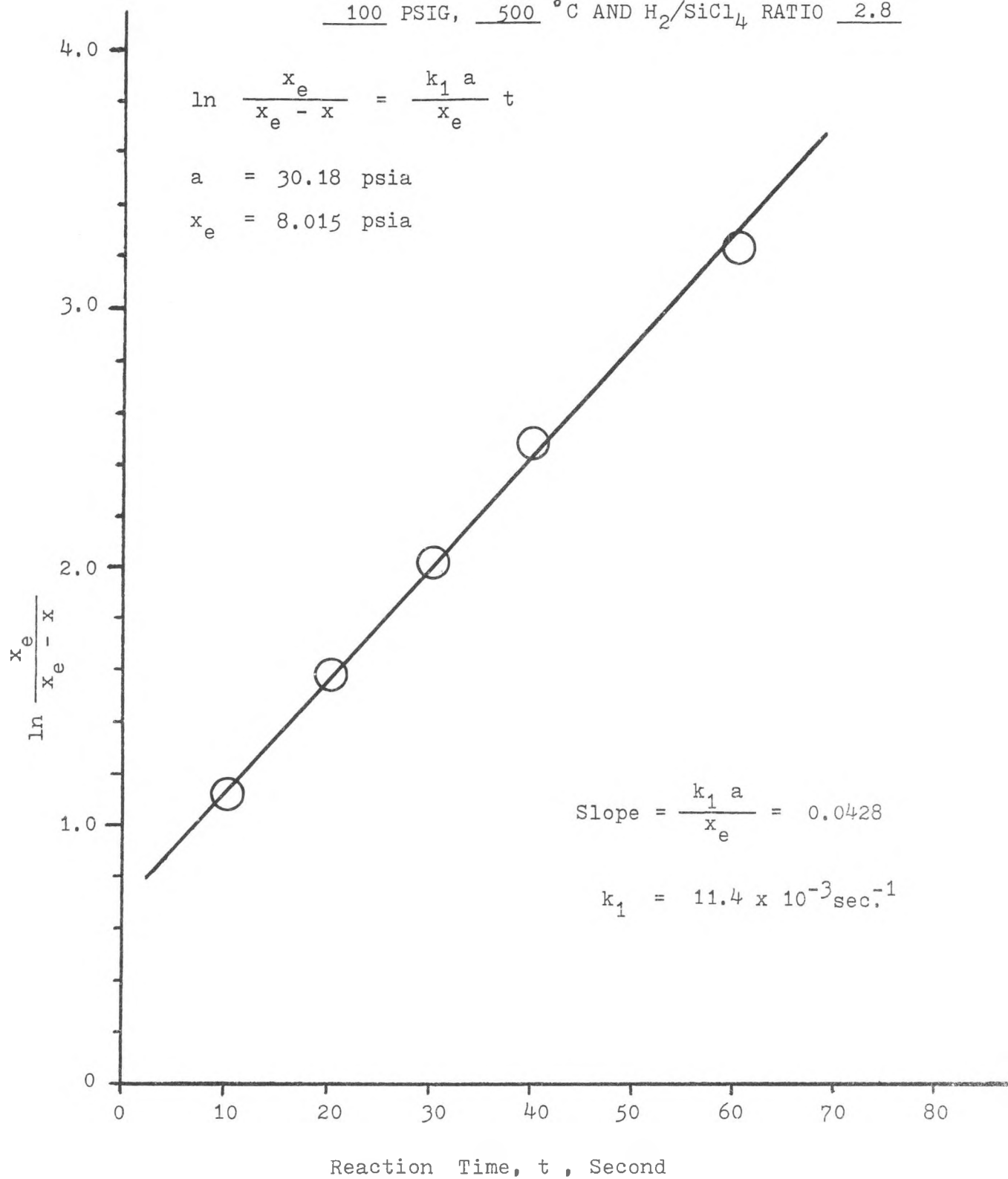


FIGURE V I PLOT OF THE PSUEDO-FIRST ORDER RATE EQUATION
 FOR THE HYDROCHLORINATION OF SiCl_4 AT
100 PSIG, 500 °C AND H_2/SiCl_4 RATIO 2.0

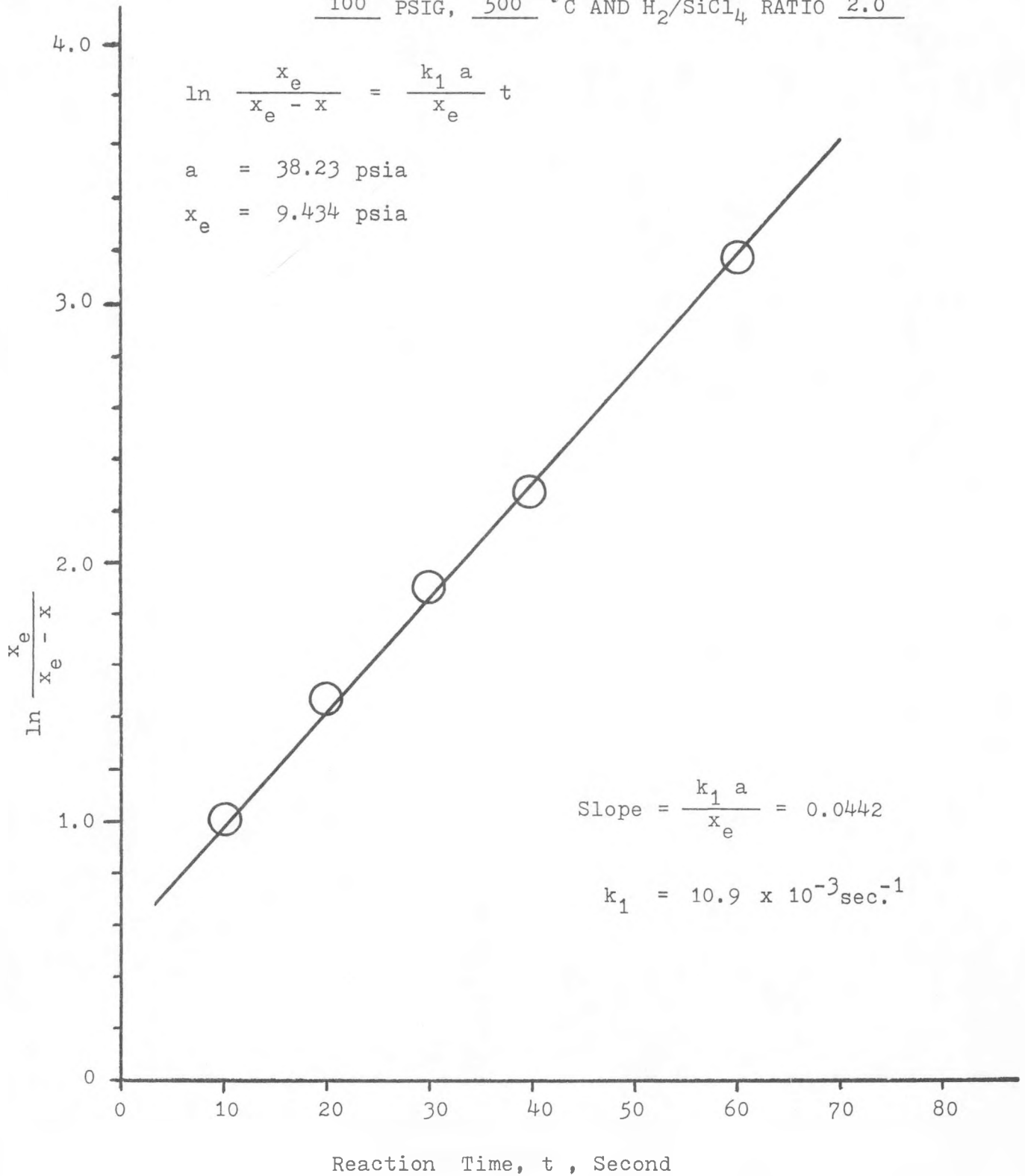


FIGURE VII PLOT OF THE PSEUDO-FIRST ORDER RATE EQUATION
 FOR THE HYDROCHLORINATION OF SiCl_4 AT
100 PSIG, 500 °C AND H_2/SiCl_4 RATIO 1.0

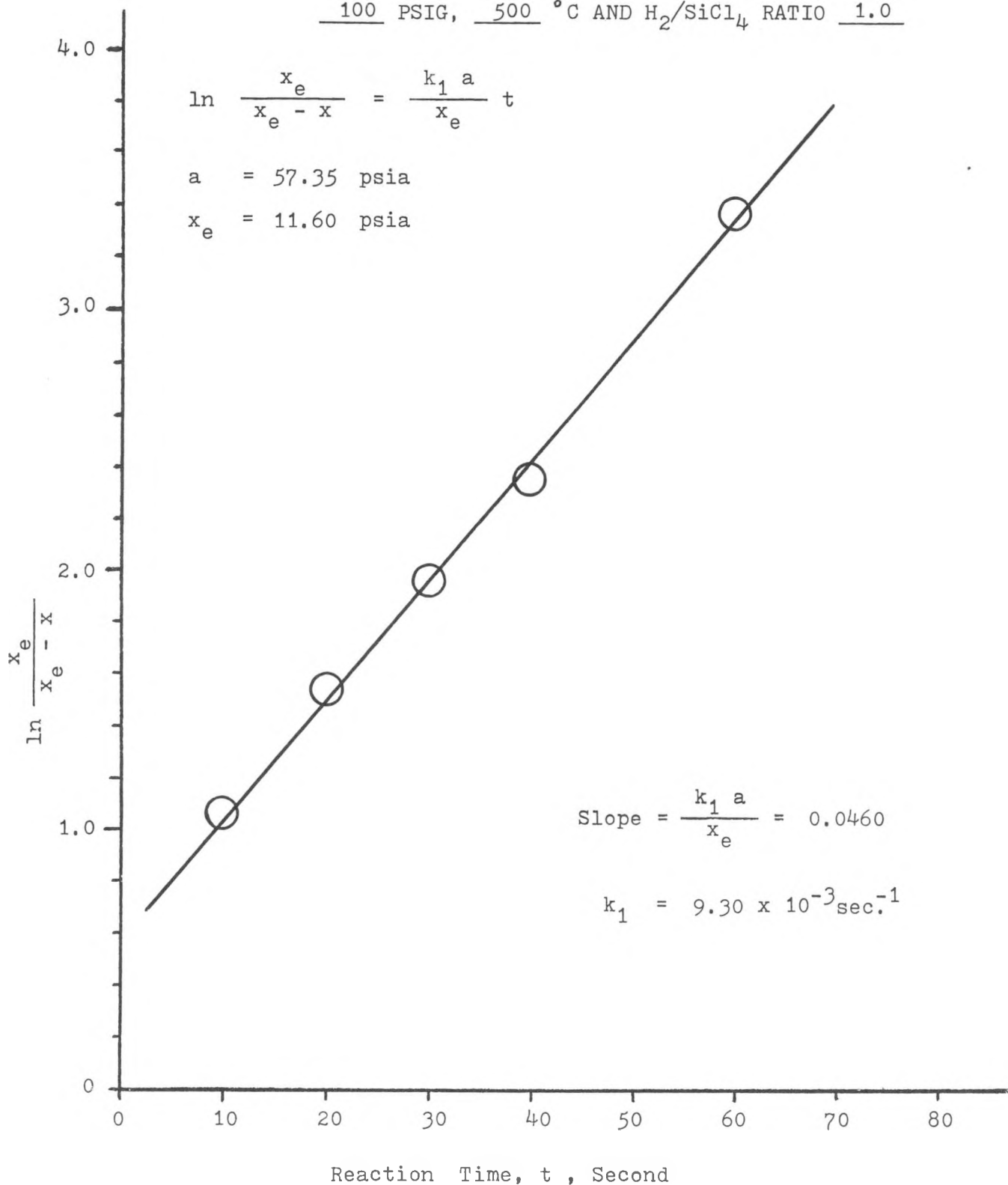


FIGURE VIII HYDROCHLORINATION OF SiCl_4 AND M.G. SILICON AT 500°C ,
 H_2/SiCl_4 RATIO OF 2.0 AND AT VARIOUS PRESSURES

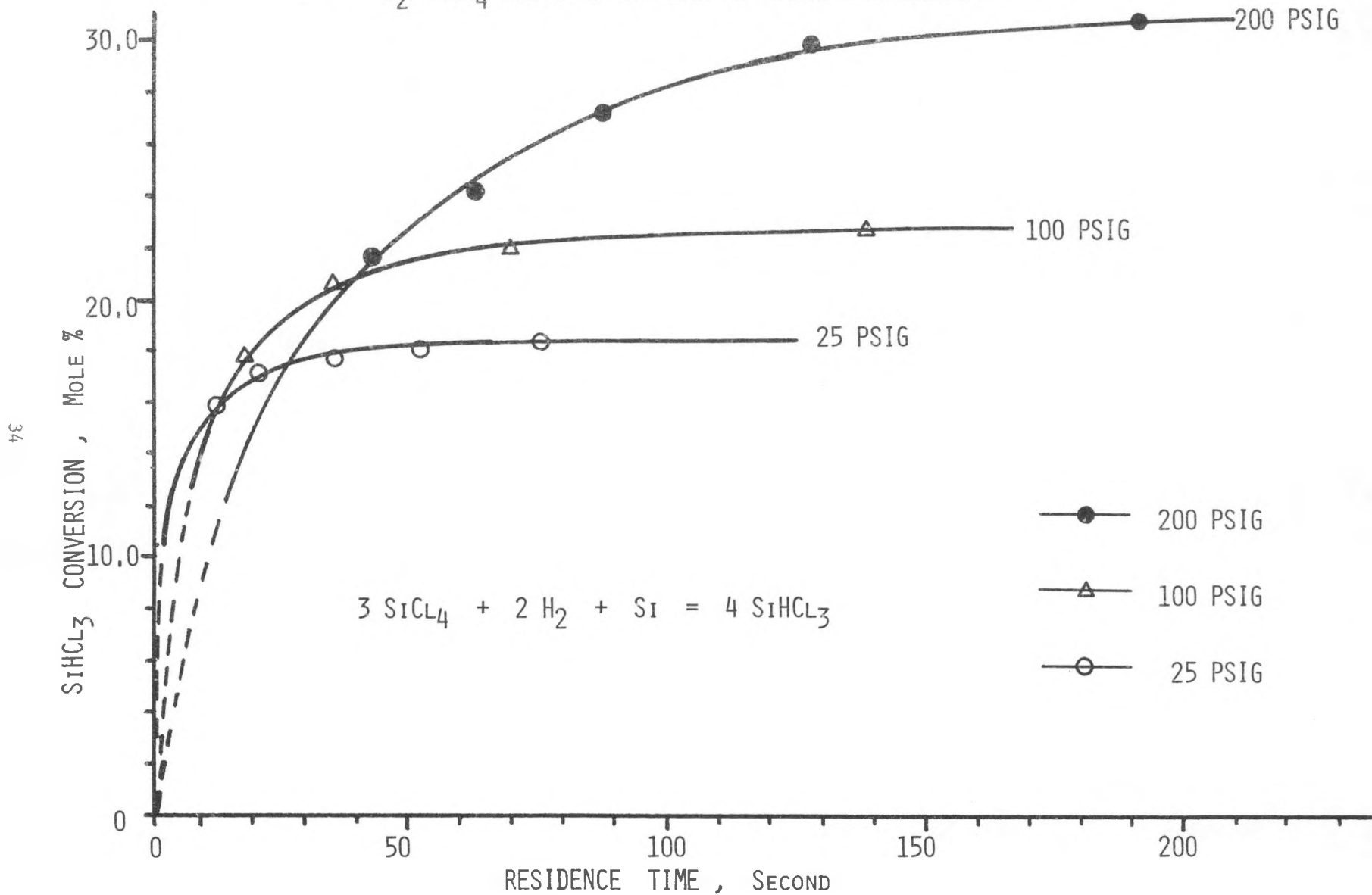


FIGURE IX

PLOT OF THE PSEUDO-FIRST ORDER RATE EQUATION
 FOR THE HYDROCHLORINATION OF SiCl_4 AT 25 PSIG
 500 °C AND H_2/SiCl_4 FEED RATIO OF 2.0

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

$$a = 13.23 \text{ psia}$$

$$x_e = 2.594 \text{ psia}$$

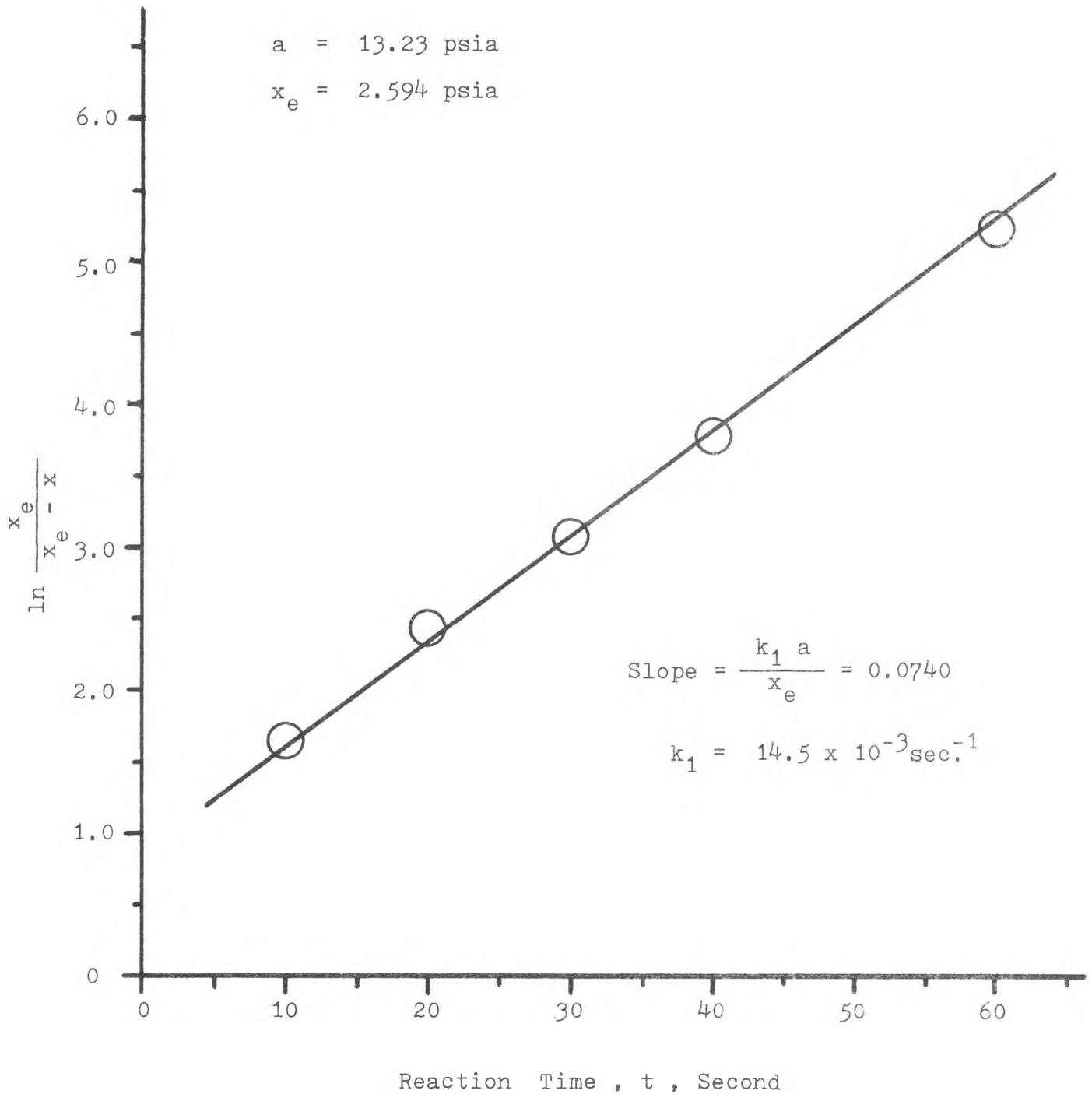


FIGURE X

PLOT OF THE PSEUDO-FIRST ORDER RATE EQUATION
 FOR THE HYDROCHLORINATION OF SiCl_4 AT
100 PSIG, 500 °C AND H_2/SiCl_4 RATIO 2.0

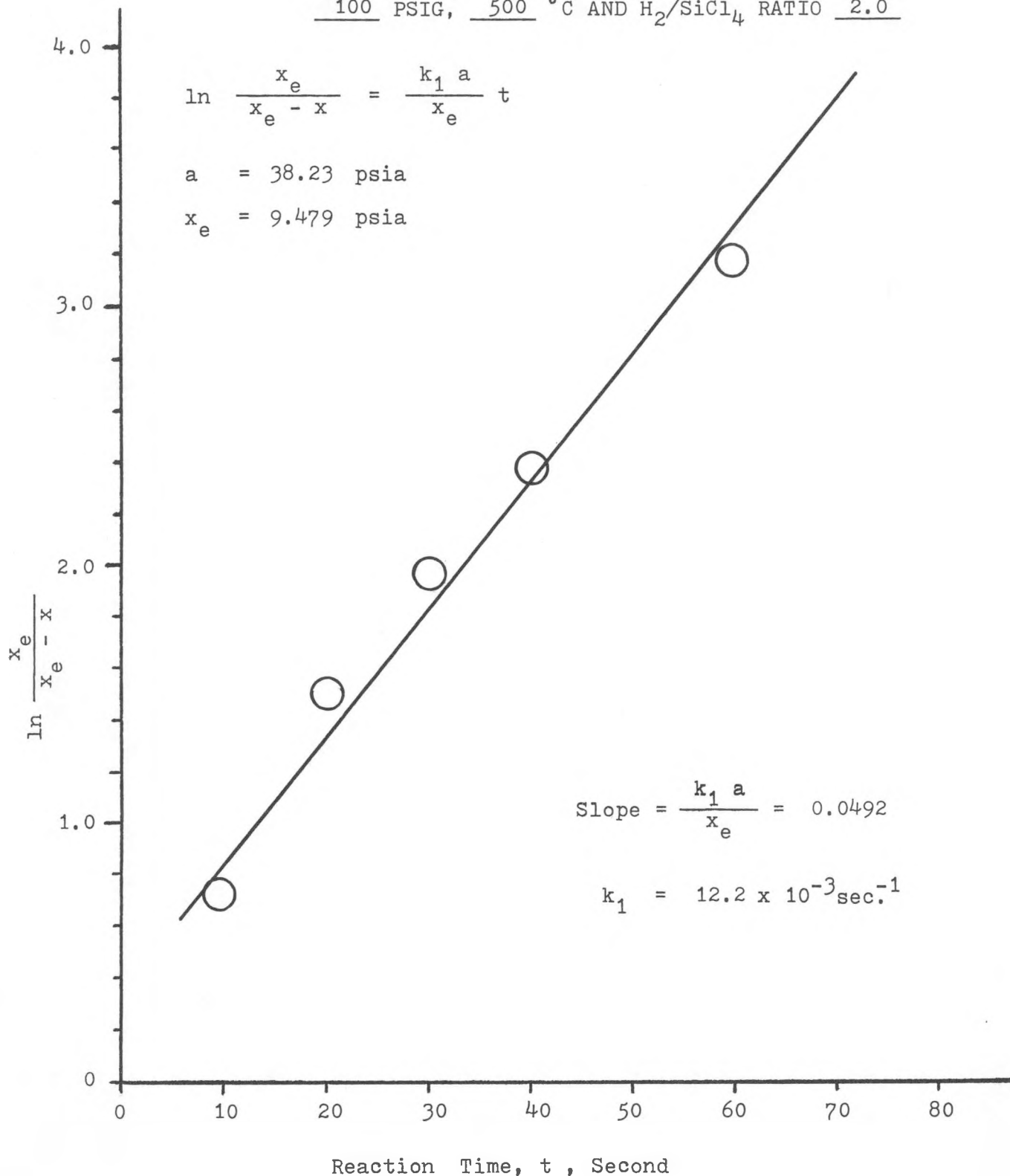


FIGURE XI PLOT OF THE PSEUDO-FIRST ORDER RATE EQUATION FOR THE HYDROCHLORINATION OF SiCl_4 AT 200 PSIG, 500 °C AND H_2/SiCl_4 RATIO 2.0

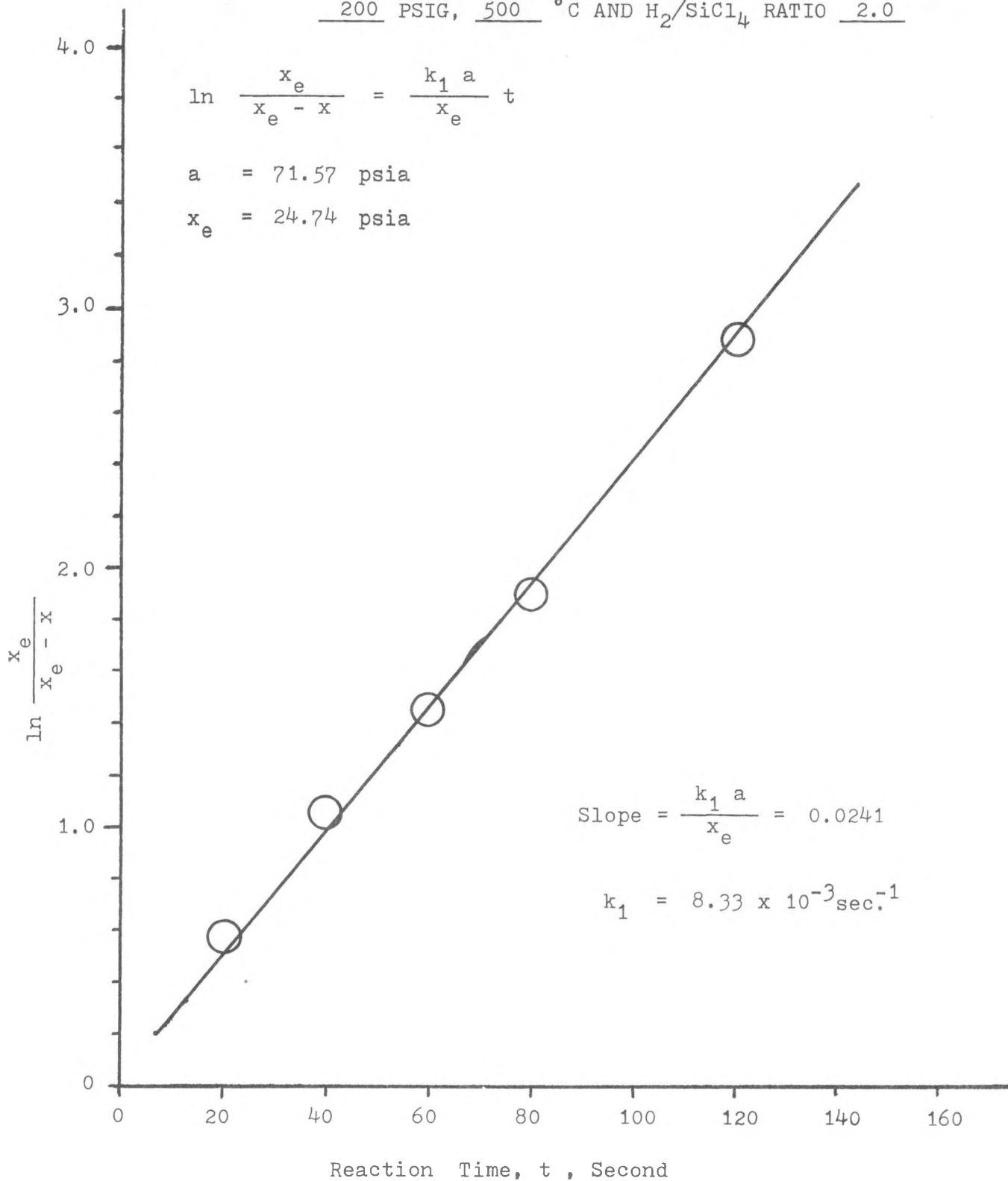


FIGURE XII PLOT OF THE PSEUDO-FIRST ORDER RATE CONSTANT k_1 VERSUS PRESSURE

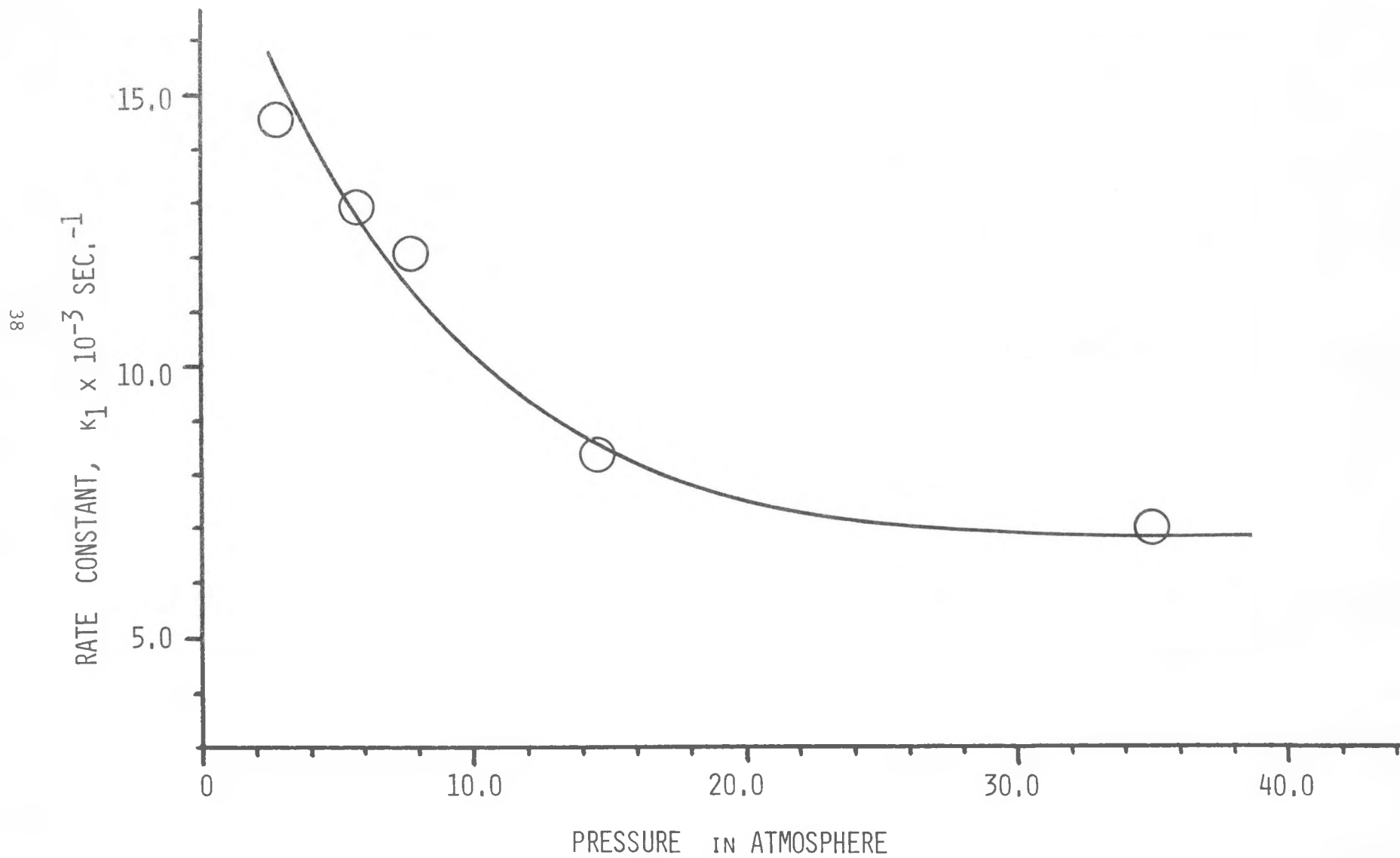


FIGURE XIII SCHEMATIC OF THE QUARTZ HYDROCHLORINATION REACTOR

