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FLAT-PLATE SOLAR ARRAY PROJECT

ADVANCED MATERIALS RESEARCH TASK

QUARTERLY REPORT

INVESTIGATION OF THE HYDROCHLORINATION OF $SiCl_4$

(Covering the Period October 9, 1982 to January 8, 1983.)

JPL CONTRACT NO. 956061

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JET PROPULSION LABORATORY
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BY

JEFFREY Y. P. MUI

January 18, 1983.

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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 studies 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 psuedo-first order kinetics. The rate constant, k_1, for the psuedo-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.

TABLE OF CONTENTS

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,

$$3\ SiCl_4 + 2\ H_2 + Si \rightleftharpoons 4\ SiHCl_3 \qquad (1)$$

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

$$K = \frac{(SiHCl_3)^4}{(SiCl_4)^3\ (H_2)^2}$$

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,

$$K_p = \frac{(p_{SiHCl_3})^4}{(p_{SiCl_4})^3 \, (p_{H_2})^2}$$

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,

$$C_{H_2} = a_{H_2} - \tfrac{1}{2} C_{SiHCl_3} - C_{SiH_2Cl_2}$$

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,

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

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,

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

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 ± 10%. Thus, the equilibrium constant for the hydrochlorination reaction is constant with respect to concentration. This observation is in agreement with the theoretcial 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 0.65×10^{-3} 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., 1.3×10^{-3} 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 0.35×10^{-3} 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., 0.66×10^{-3} 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.

$$SiCl_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SiHCl_3$$

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

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 psuedo-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 psuedo-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 inversed 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 psuedo-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 frations 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_1a/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°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 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_1a/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 psuedo-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,

$$SiCl_4 + H_2 \xrightleftharpoons{\text{slow}} SiHCl_3 + HCl$$

$$3\,HCl + Si \xrightleftharpoons{\text{fast}} SiHCl_3 + H_2$$

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 informations 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 psuedo-first order kinetics. The rate constants for the psuedo-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

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	7	8	9	10																		
II	Reaction Kinetic Measurements as a Function of T, P, C. Mass Balance, HCl Analyses				10	11	12	1	2														
III	Corrosion Study (1) Copper, Nickel, Carbon Steel, Stainless Steel, Incoloy 800H, Alloy 400, Hastelloy B-2						12	1	2	3													
	(2) Corrosion Mechanism: SEM Analyses								2	3	4												
IV	Effect of Reactor Pressure: Reaction Kinetic Measurements, 25 to 500 psig, 350° to 500°C, $H_2/SiCl_4$ Ratio 1.0 to 5.0										4	5	6	7									
V	Reaction Kinetic Modeling of Previous Experimental Data														8	9	10						
VI	Supplemental Reaction Kinetic Measurement with Reaction Temperature to 650°C															9	10	11	12	1			
VII	Equilibrium Constant Measurements at Temperature Range 350°C to 650°C																10	11	12	1			
VIII	Reaction Mechanism Study: Deuterium Kinetic Isotope Effects																	11	12	1			
IX	Develop Rate Equation, Thermodynamic Functions, $\Delta E, \Delta H, \Delta G$, etc.																		12	1	2	3	4
X	Catalyst Study: Electronic Grade Silicon v.s. the Presence of Ni and Co Catalyst																		12	1	2	3	
XI	Effect of Impurities: Electronic Silicon v.s. the Presence of Fe and Al																			1	2	3	4
XII	Recommendations for Additional Development Work and Final Report																						4

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TABLE I

EQUILIBRIUM COMPOSITIONS OF CHLOROSILANE PRODUCTS FOR THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL AT 100 PSIG, $H_2/SiCl_4$ = 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, $H_2/SiCl_4$ = 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 $\times 10^{-3}$	$K_p \times 10^{-4}$ 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

$\frac{H_2}{SiCl_4}$ Ratio	Equilibrium (1) Composition Mole %		Mole Fractions at Equilibrium			Equilibrium Constant	
	$SiHCl_3$	$SiCl_4$	$SiHCl_3$	$SiCl_4$	H_2	K x 10^{-3}	K_p x 10^{-3} 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		$\frac{H_2}{SiCl_4}$	Equilibrium Composition Mole %		Mole Fraction at Equilibrium			Equilibrium Constant	
								K	K_p
psig	Atm.	Ratio	$SiHCl_3$	$SiCl_4$	$SiHCl_3$	$SiCl_4$	H_2	x 10^{-3}	x 10^{-3} $Atm.^{-1}$
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		$H_2/SiCl_4$	Equilibrium Composition Mole %		Mole Fraction at Equilibrium			Equilibrium Constant	
psig	Atm.	Ratio	$SiHCl_3$	$SiCl_4$	$SiHCl_3$	$SiCl_4$	H_2	K x 10^{-3}	K_p x 10^{-3} 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 [illegible]90	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	Composition Mole %		Composition at Time t (psia)/Mole Fraction			Initial Partial Press. $SiCl_4$	Equil. Partial Press. $SiHCl_3$	$\ln \frac{x_e}{x_e - x}$	Rate Constant k_1
sec.	$SiHCl_3$	$SiCl_4$	H_2	$SiHCl_3$	$SiCl_4$	a	x_e		x 10^{-3} sec.$^{-1}$
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

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	Composition Mole %		Composition at Time t (psia)/Mole Fraction			Initial Partial Press. $SiCl_4$	Equil. Partial Press. $SiHCl_3$	$\ln \frac{x_e}{x_e - x}$	Rate Constant k_1
sec.	$SiHCl_3$	$SiCl_4$	H_2	$SiHCl_3$	$SiCl_4$	a	x_e		x 10^{-3}sec.$^{-1}$
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 x 10^{-3} 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	Composition Mole %		Composition at Time t (psia)/Mole Fraction			Initial Partial Press. $SiCl_4$	Equil. Partial Press. $SiHCl_3$	$\ln \frac{x_e}{x_e - x}$	Rate Constant k_1
sec.	$SiHCl_3$	$SiCl_4$	H_2	$SiHCl_3$	$SiCl_4$	a	x_e		x 10^{-3}sec.$^{-1}$
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	Composition Mole %		Composition at Time t (psia)/Mole Fraction			Initial Partial Press. $SiCl_4$	Equil. Partial Press. $SiHCl_3$	$\ln \frac{x_e}{x_e - x}$	Rate Constant k_1
sec.	$SiHCl_3$	$SiCl_4$	H_2	$SiHCl_3$	$SiCl_4$	a	x_e		$\times 10^{-3} sec.^{-1}$
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.	-	9.30

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

TABLE XI 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 x 10^{-3} 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 x 10^{-3} 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	[illegible].6	82.4	(25.64) 0.6459	(2.474) 0.06232	(11.58) 0.2918	13.23	-	3.073	
40	[illegible].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	Composition Mole %		Composition at Time t (psia)/Mole Fraction			Initial Partial Press. $SiCl_4$	Equil. Partial Press. $SiHCl_3$	$\ln \frac{x_e}{x_e - x}$	Rate Constant k_1
sec.	$SiHCl_3$	$SiCl_4$	H_2	$SiHCl_3$	$SiCl_4$	a	x_e		x 10^{-3}sec.$^{-1}$
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.

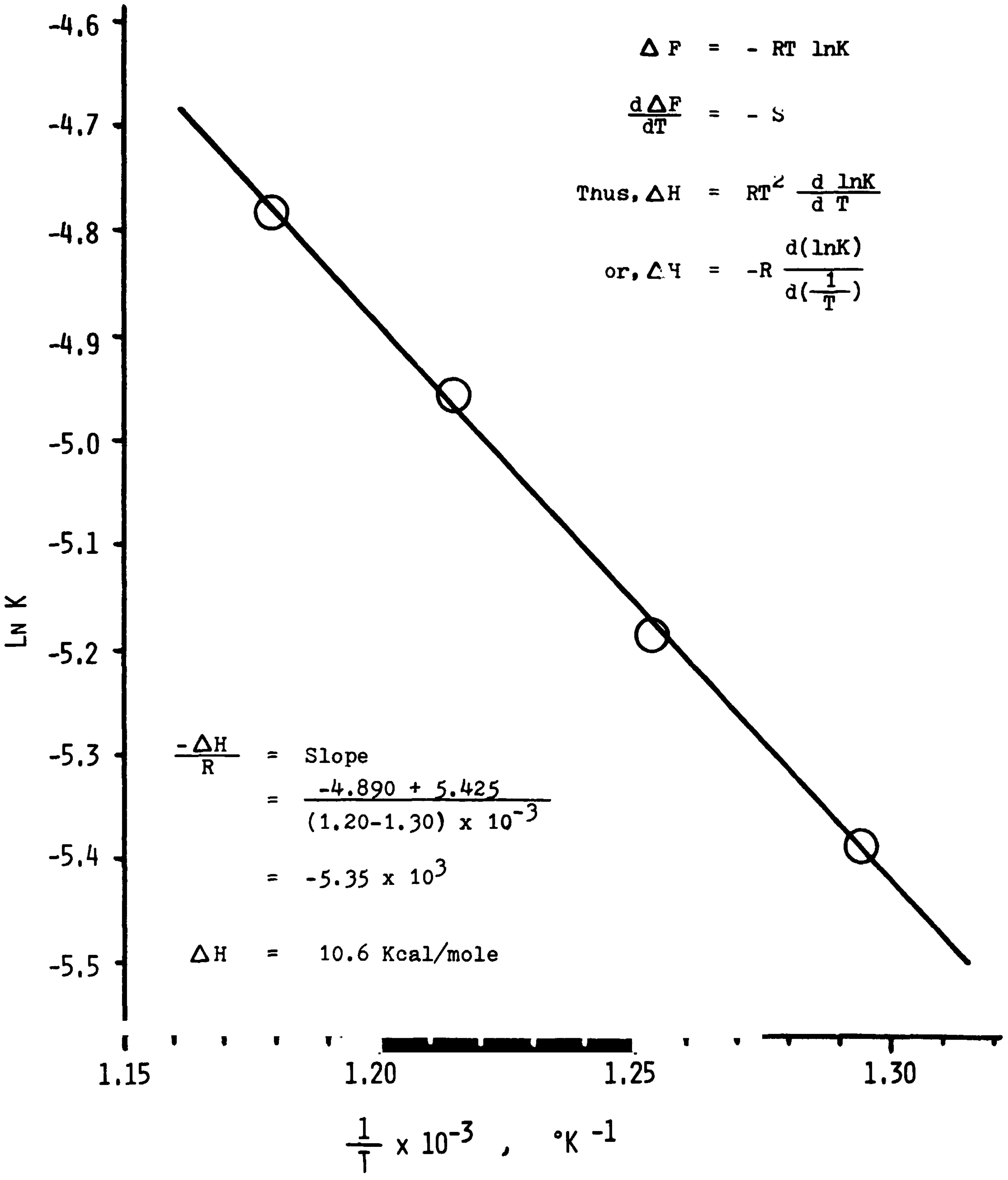
Time t	Composition Mole %		Composition at Time t (psia)/Mole Fraction			Initial Partial Press. $SiCl_4$	Equil. Partial Press. $SiHCl_3$	$\ln \frac{x_e}{x_e - x}$	Rate Constant k_1
sec.	$SiHCl_3$	$SiCl_4$	H_2	$SiHCl_3$	$SiCl_4$	a	x_e		$\times 10^{-3} sec.^{-1}$
20	14.7	85.3	(139.4) 0.6495	(11.06) 0.05152	(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 psig.	Reactor Pressure Atm.	$H_2/SiCl_4$ Ratio	Equilibrium Mole % $SiHCl_3$	Equilibrium Mole % $SiCl_4$	Rate Constant k_1 $\times 10^{-3}$ sec.$^{-1}$
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



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

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

Thus, $\Delta H = RT^2 \frac{d \ln K}{d T}$

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

$$\frac{-\Delta H}{R} = \text{Slope}$$

$$= \frac{-4.890 + 5.425}{(1.20-1.30) \times 10^{-3}}$$

$$= -5.35 \times 10^{3}$$

$$\Delta H = 10.6 \text{ Kcal/mole}$$

FIGURE II HYDROCHLORINATION OF $SiCl_4$ AT 100 PSIG, 500°C AND AT VARIOUS MOLAR RATIOS OF $H_2 : SiCl_4$

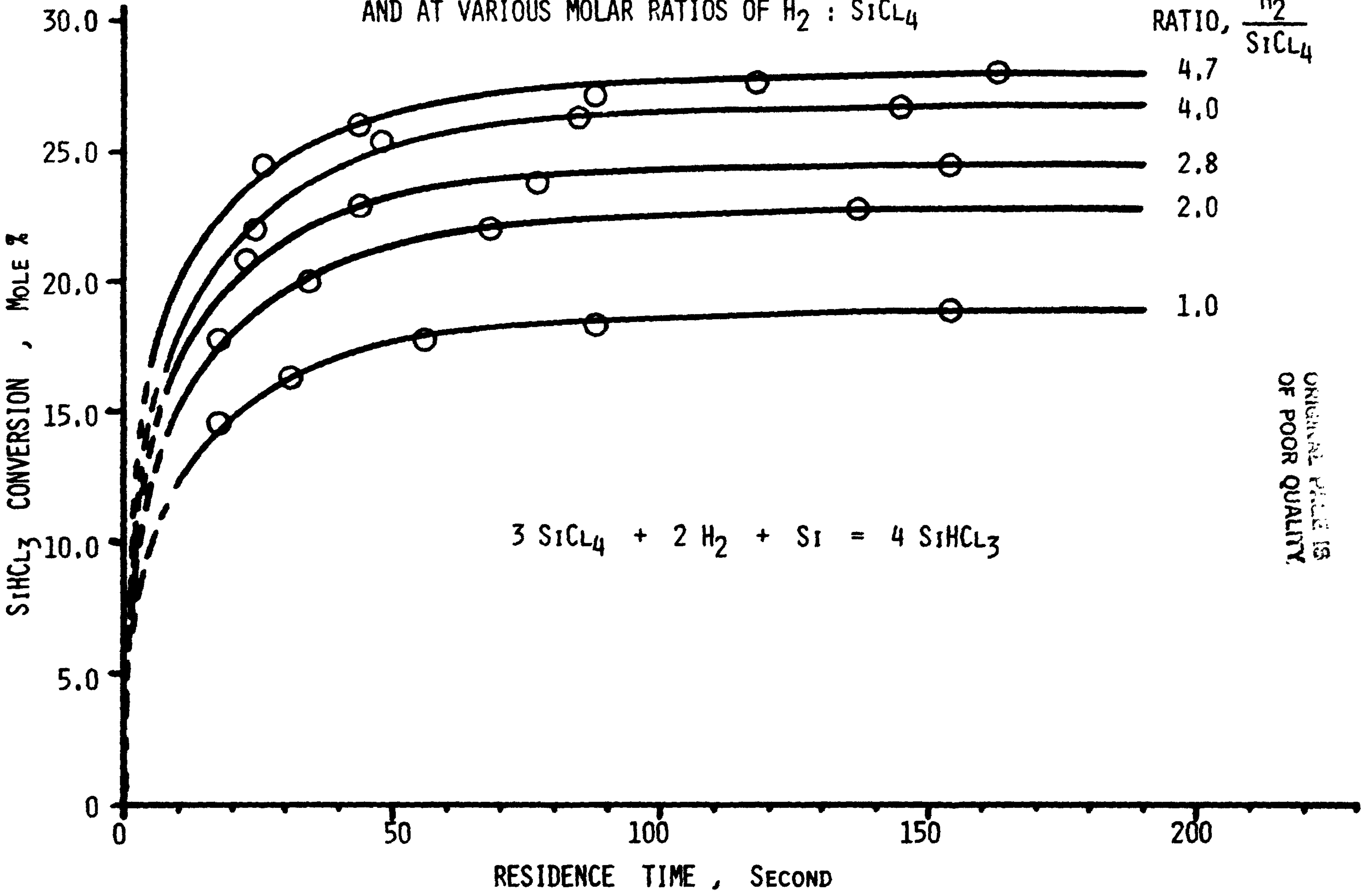


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FIGURE III PLOT OF THE PSUEDO-FIRST ORDER RATE EQUATION FOR THE HYDROCHLORINATION OF $SiCl_4$ AT 100 PSIG, 500 °C AND $H_2/SiCl_4$ RATIO 4.7

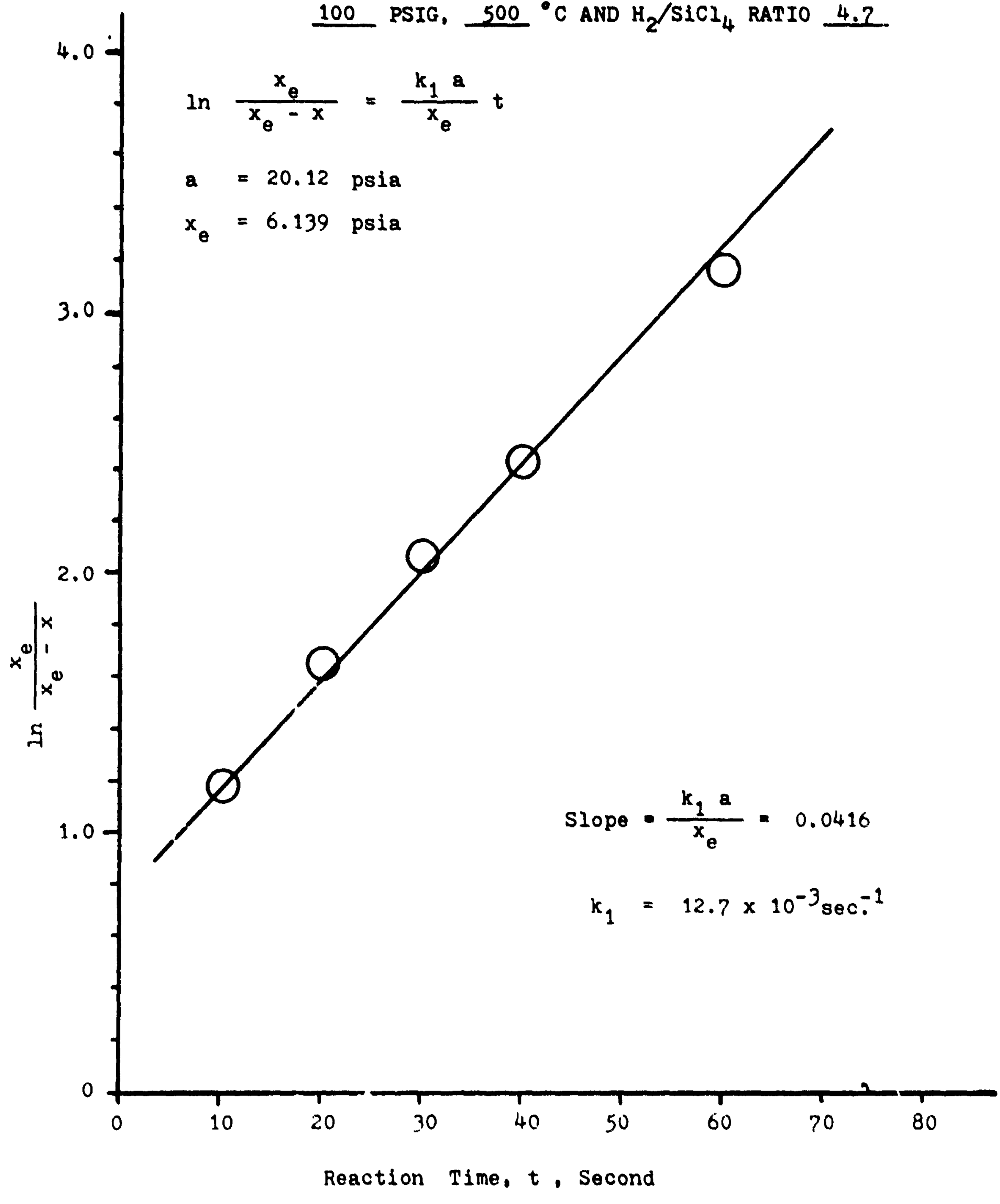


FIGURE IV PLOT OF THE PSUEDO-FIRST ORDER RATE EQUATION FOR THE HYDROCHLORINATION OF $SiCl_4$ AT 100 PSIG, 500 °C AND $H_2/SiCl_4$ RATIO 4.0

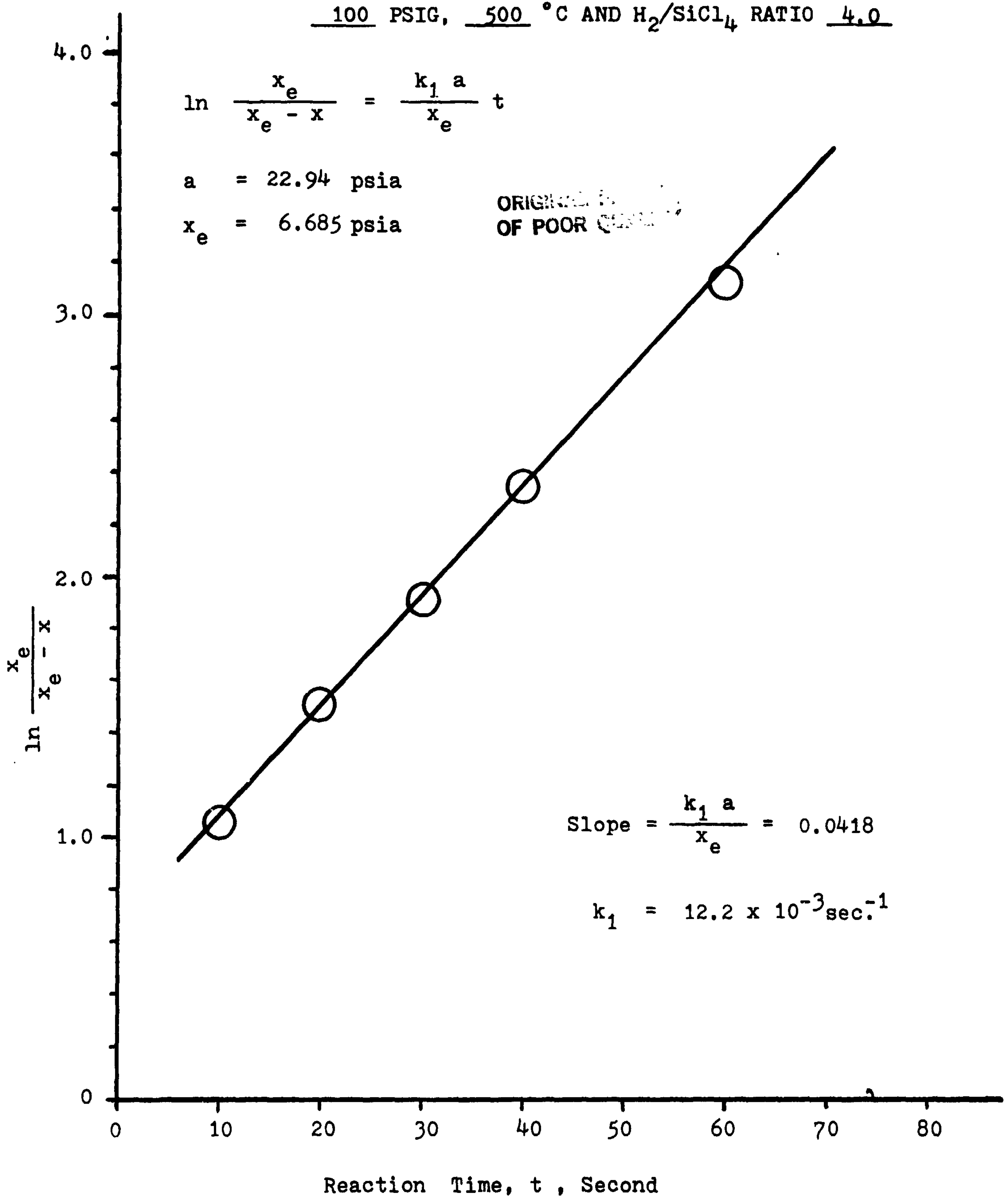


FIGURE V PLOT OF THE PSUEDO-FIRST ORDER RATE EQUATION FOR THE HYDROCHLORINATION OF $SiCl_4$ AT 100 PSIG, 500 °C AND $H_2/SiCl_4$ RATIO 2.8

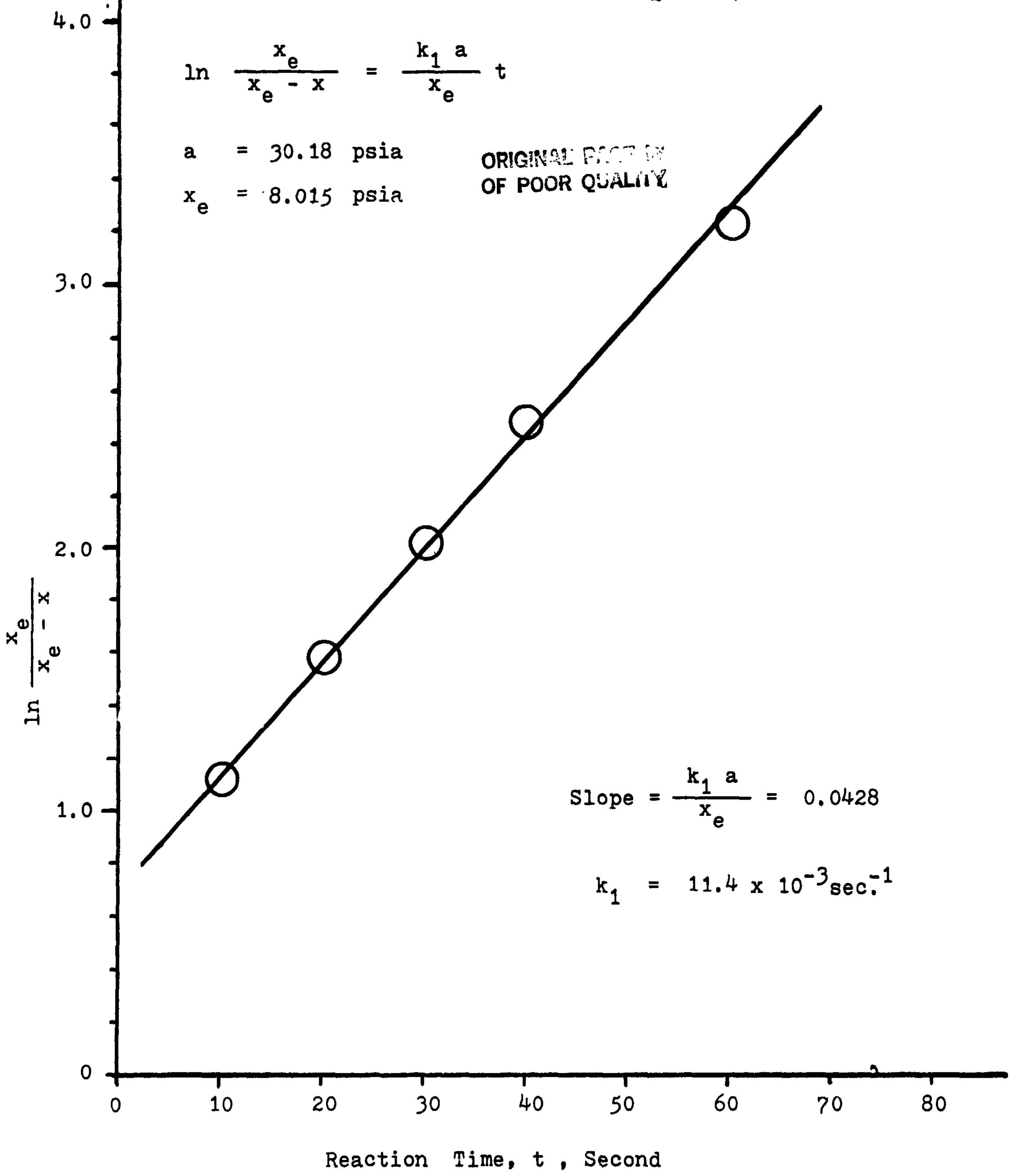


FIGURE VI PLOT OF THE PSUEDO-FIRST ORDER RATE EQUATION FOR THE HYDROCHLORINATION OF $SiCl_4$ AT 100 PSIG, 500 °C AND $H_2/SiCl_4$ RATIO 2.0

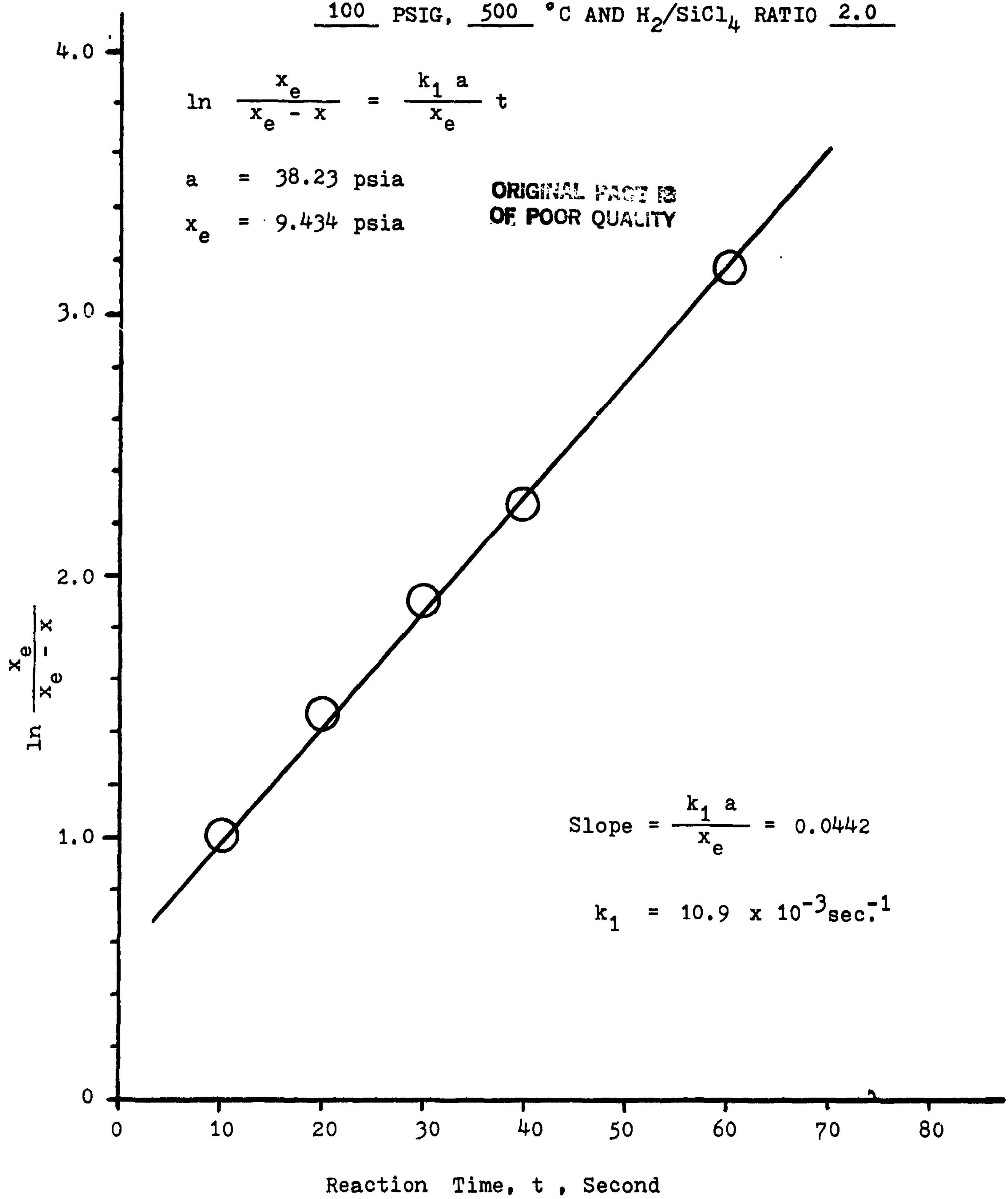
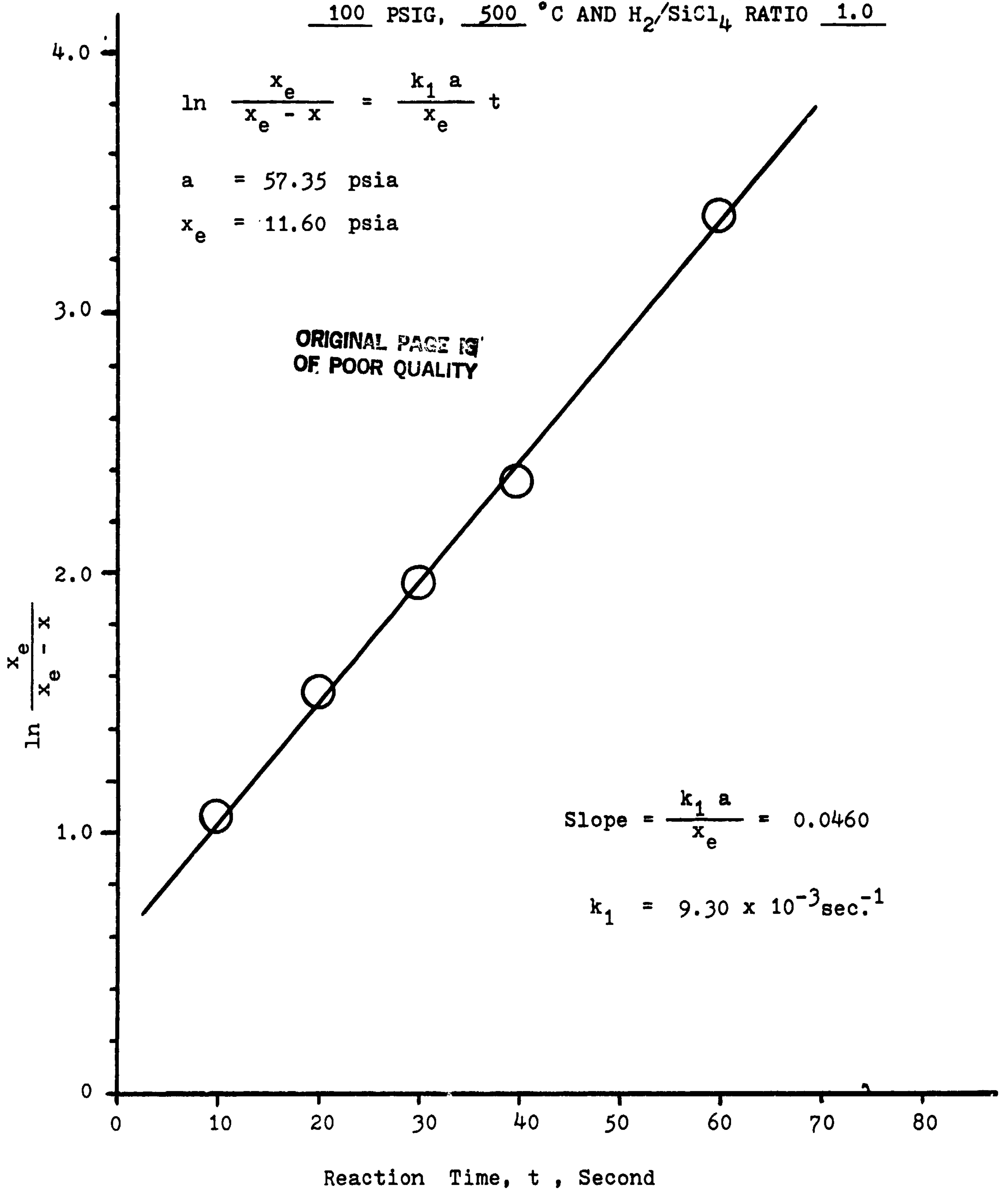


FIGURE VII PLOT OF THE PSUEDO-FIRST ORDER RATE EQUATION FOR THE HYDROCHLORINATION OF $SiCl_4$ AT 100 PSIG, 500 °C AND $H_2/SiCl_4$ RATIO 1.0



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

$a = 57.35$ psia

$x_e = 11.60$ psia

$$\text{Slope} = \frac{k_1 a}{x_e} = 0.0460$$

$$k_1 = 9.30 \times 10^{-3} \text{sec.}^{-1}$$

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

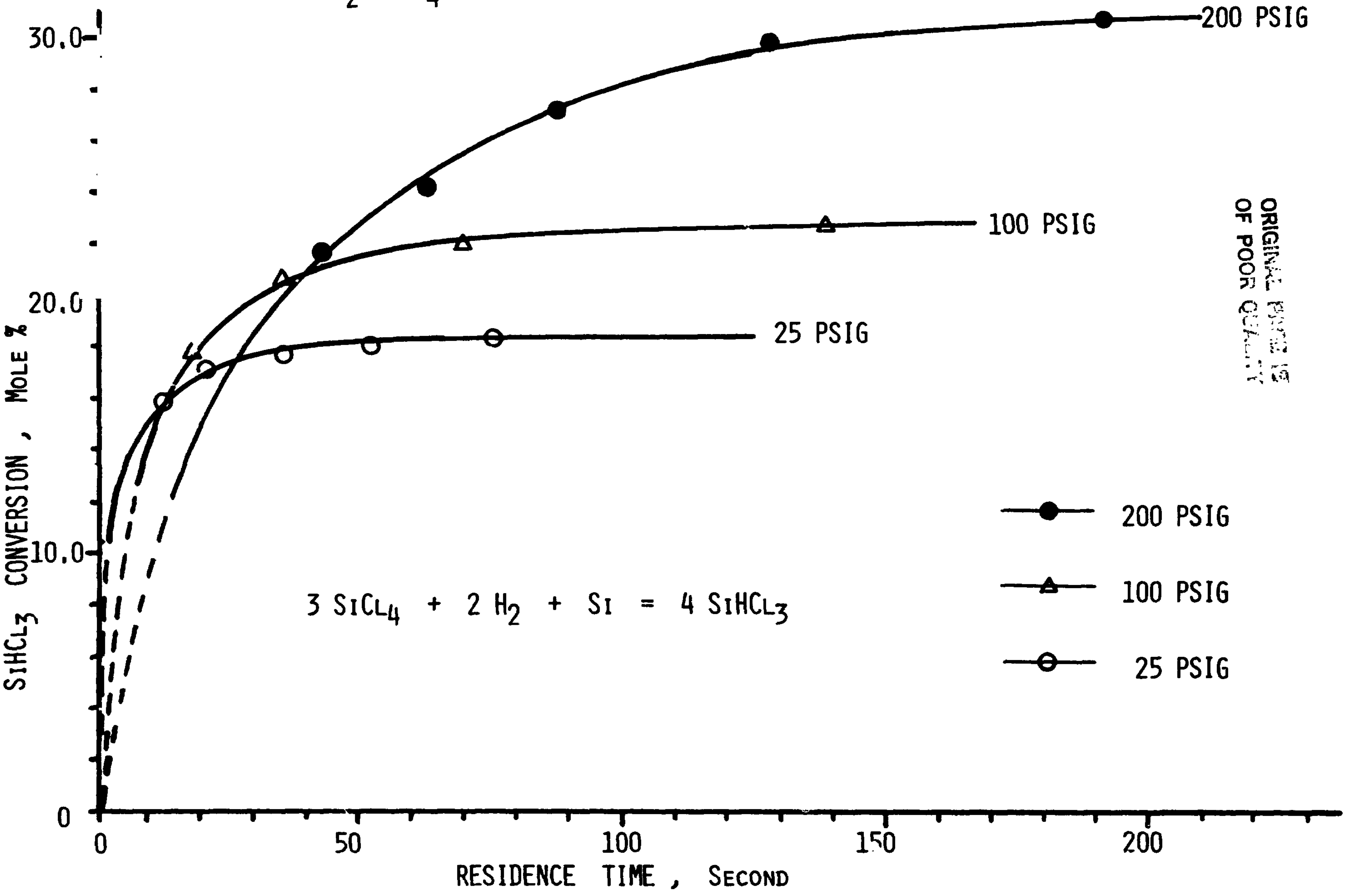
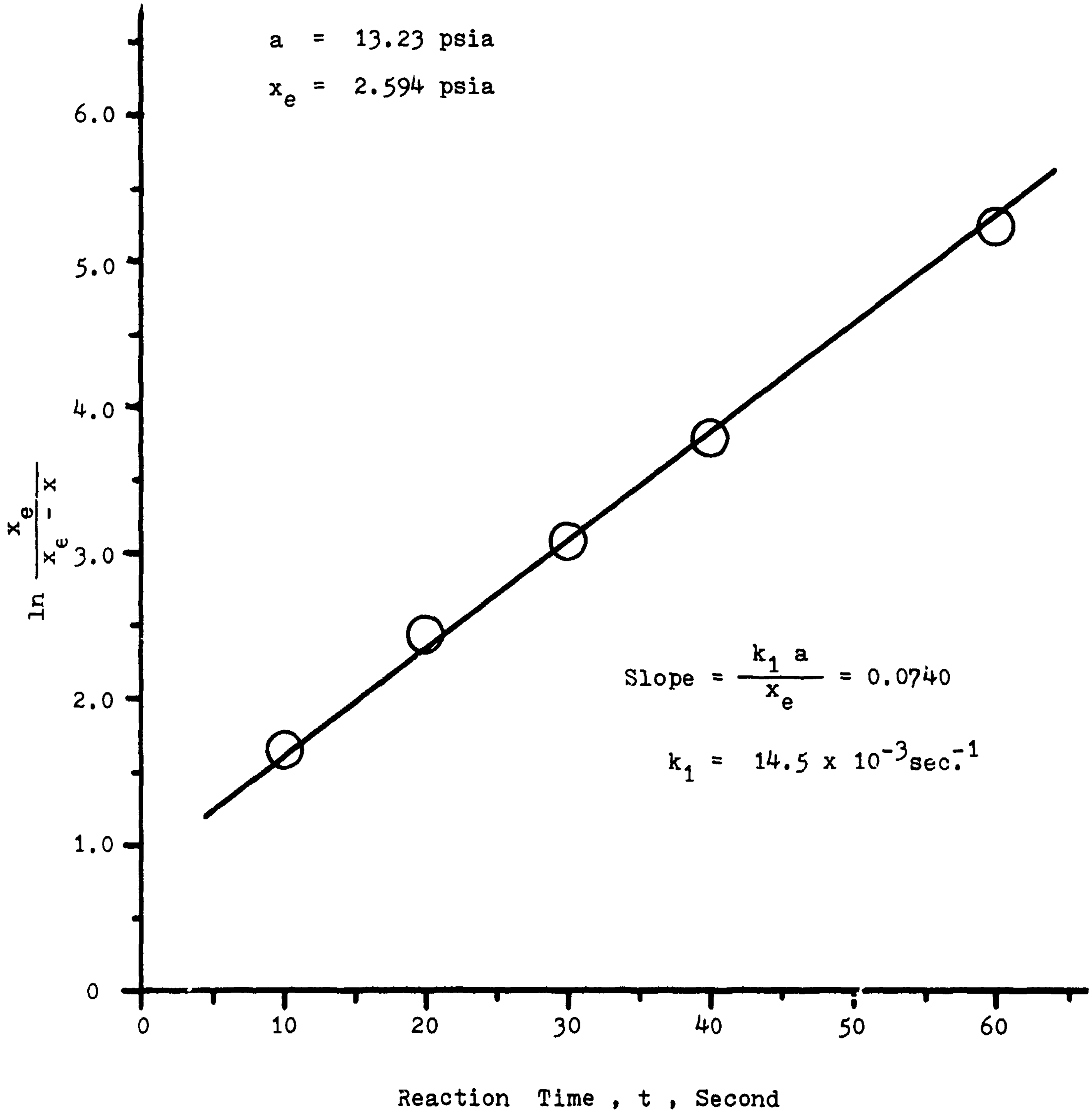


FIGURE IX PLOT OF THE PSUEDO-FIRST ORDER RATE EQUATION FOR THE HYDROCHLORINATION OF $SiCl_4$ AT 25 PSIG 500 °C AND $H_2/SiCl_4$ FEED RATIO OF 2.0

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



$a = 13.23$ psia

$x_e = 2.594$ psia

$$\text{Slope} = \frac{k_1 a}{x_e} = 0.0740$$

$$k_1 = 14.5 \times 10^{-3} \text{sec.}^{-1}$$

FIGURE X 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

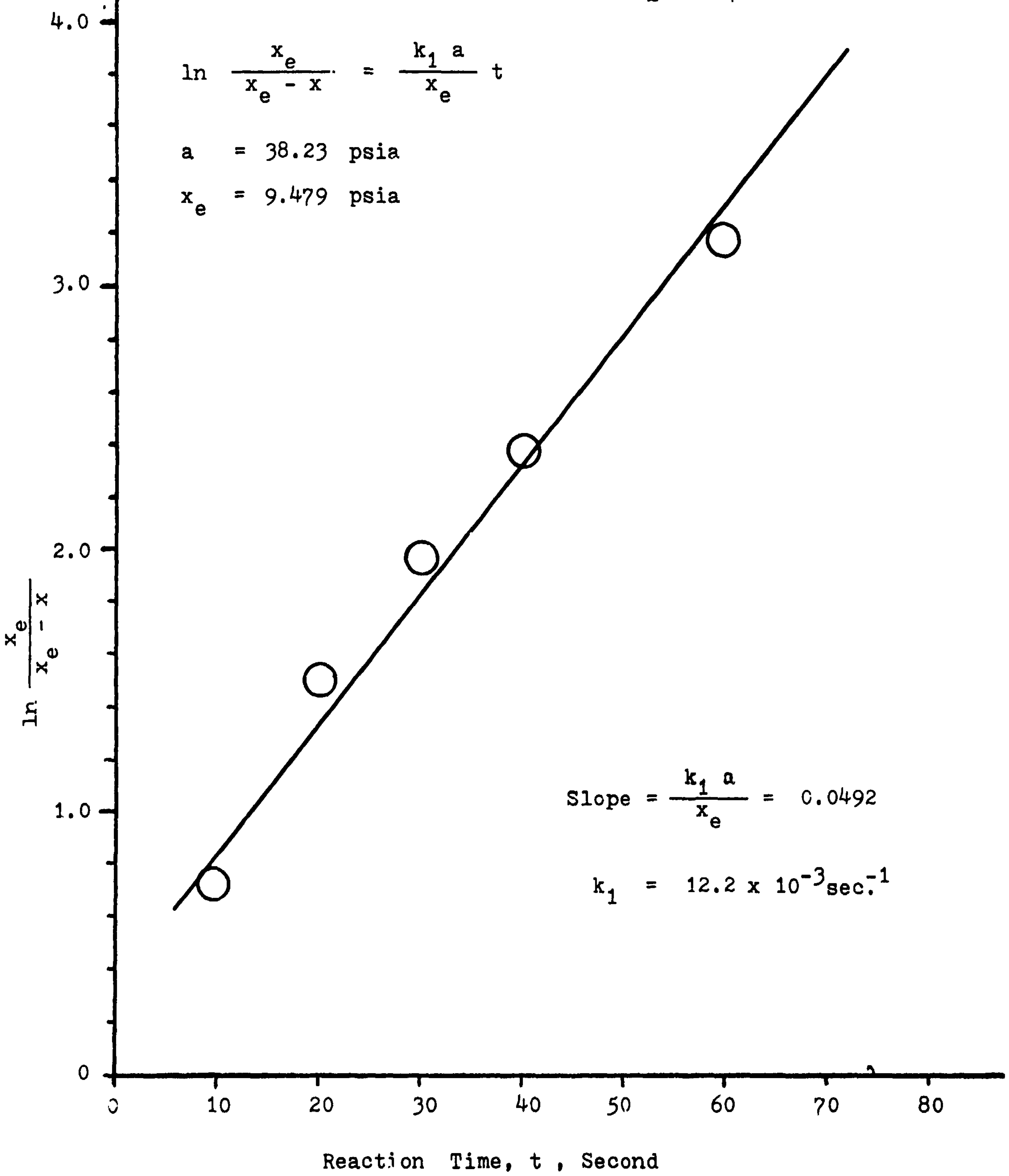
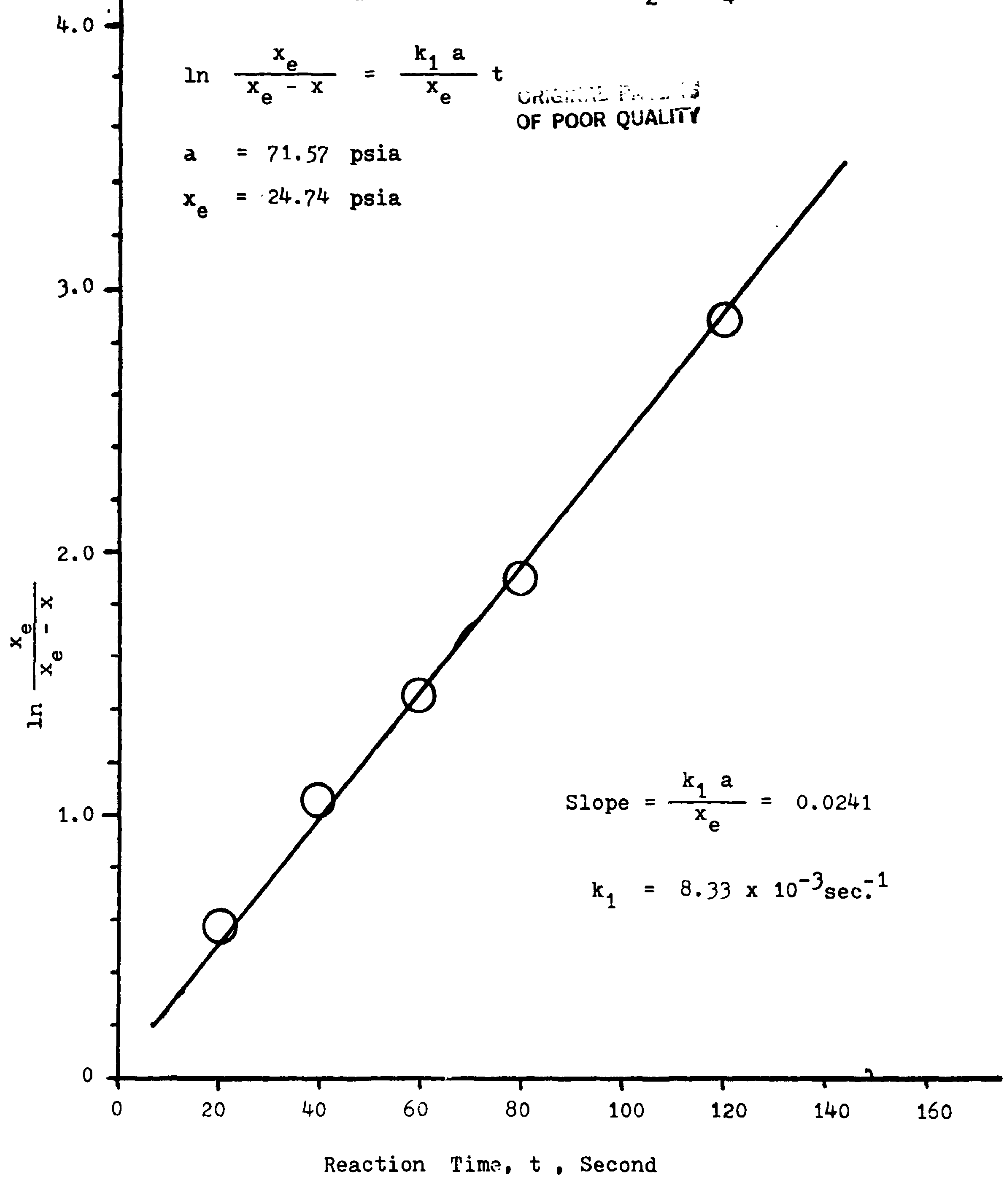


FIGURE XI PLOT OF THE PSUEDO-FIRST ORDER RATE EQUATION FOR THE HYDROCHLORINATION OF $SiCl_4$ AT 200 PSIG, 500 °C AND $H_2/SiCl_4$ RATIO 2.0



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

$a = 71.57$ psia

$x_e = 24.74$ psia

$$\text{Slope} = \frac{k_1 a}{x_e} = 0.0241$$

$k_1 = 8.33 \times 10^{-3} \text{sec.}^{-1}$

FIGURE XII PLOT OF THE PSUEDO-FIRST ORDER RATE CONSTANT κ_1 VERSUS PRESSURE

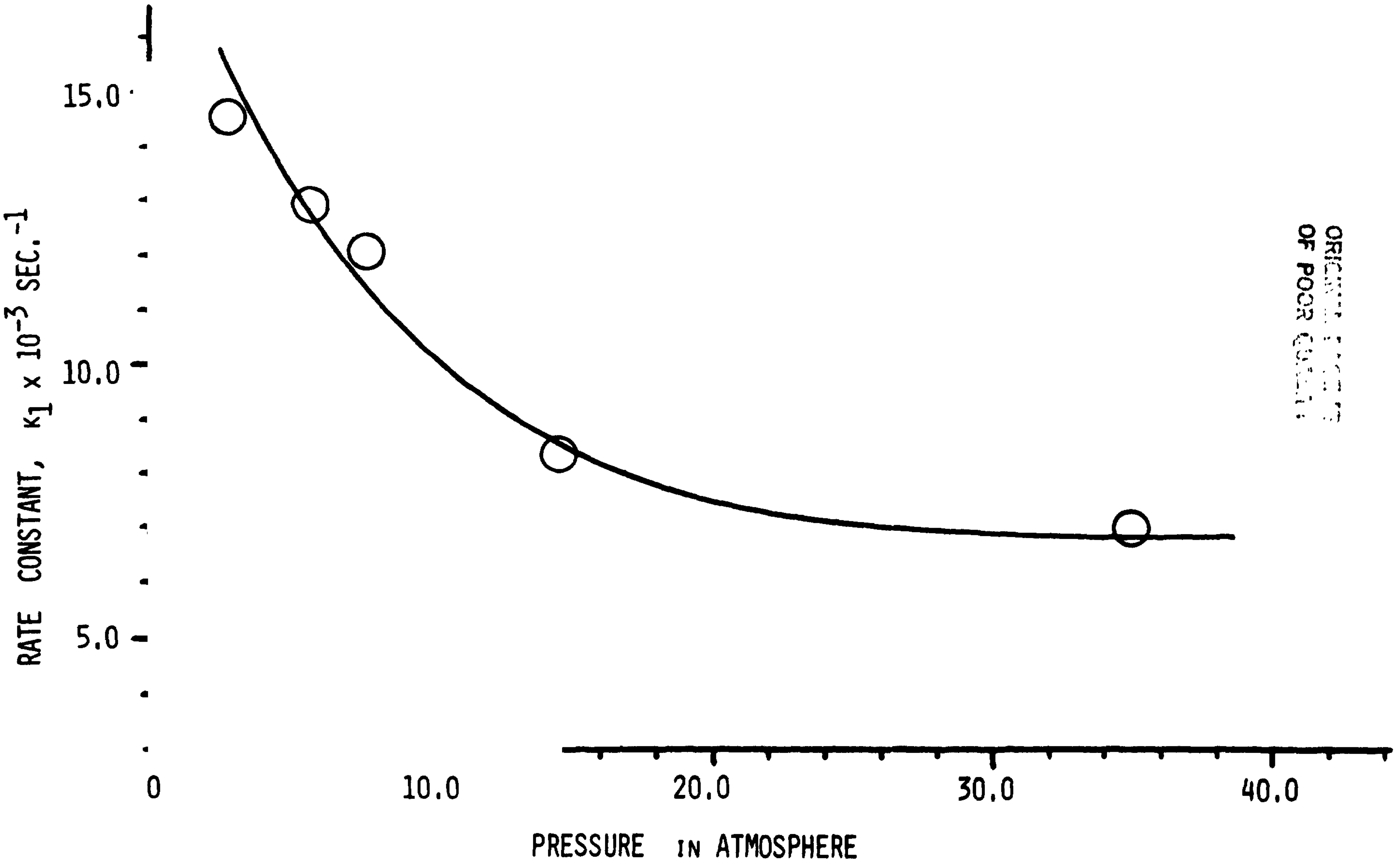


FIGURE XIII SCHEMATIC OF THE QUARTZ HYDROCHLORINATION REACTOR