LOW-COST-SILICON-PROCESS DEVELOPMENT

Phase IV: Process Improvement

SECOND QUARTERLY
TECHNICAL PROGRESS REPORT

R. V. Giraudi
C. G. Newman

April 1 9 8 1

MASTER

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

AC02-77CH00178

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use of the results of such use of any information, apparatus, product, or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

J. C. SCHUMACHER COMPANY

580 Airport Road, Oceanside, CA 92054

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
	TABLE OF CONTENTS	i
	LIST OF TABLES	iii
	LIST OF ILLUSTRATIONS	iv
	ABSTRACT	v
	PROJECT DESCRIPTION	vi
1	INTRODUCTION	1
	1.1 Process Description	1
	1.2 Project Objective	1
	1.3 Technical Approach	2
2	EXPERIMENTAL CHEMISTRY	3
	2.1 Reactor Calibration: Decomposition of t-butyl chloride	3
	2.1.1 Introduction	3
	2.1.2 Experimental Procedures	4
	2.1.3 Order Determination Results and Discussion	6
	2.1.4 Kinetic Results and Discussion	12
	2.2 Tribromosilane Thermal Disproportion- ation Kinetic Study	16
	2.2.1 Introduction	16
	2.2.2 Experimental Procedures	19
	2.2.3 Tribromosilane Control Reactions	20
	2.2.4 Order Determination Results and Discussion	21
	2.3 Tribromosilane Decomposition in a Free Space Reactor	29
	2.3.1 Introduction	29
	2.3.2 Experimental Procedures	29
	2.3.3 Results and Discussion	29
	2.4 Synthesis of Tribromosilane by the Hydrogenation of Tetrabromosilane	32

TABLE OF CONTENTS (contd.)

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
3	PROCESS DEVELOPMENT TESTS	35
	3.1 Tribromosilane Synthesis Reaction Unit	35
	3.1.1 Synthesis Reaction Unit Operational Performance - Bromination Mode	35
	3.1.2 Synthesis Reaction Unit Operational Performance - Tribromosilane Mode	36
	3.2 Synthesis Reactor Alloy Corrosion Studies Preliminary	38
	3.3 Distillation Unit	41
	3.3.1 Distillation Unit Operational Performance	41
	3.4 Silicon Product Reaction Unit	42
	3.4.1 Product Reaction Unit Operational Performance	42
	3.5 Engineering Support Activities	44
4	CONCLUSIONS	45
	4.1 Experimental Chemistry Studies	45
	4.2 Process Development Tasks	45
5	PLANNED ACTIVITIES	46
	5.1 Experimental Chemistry Tasks	46
	5.2 Process Development Tasks	46
6	REFERENCES	47
	APPENDIX	49

TABLES

<u>TABLE NO.</u>	<u>TITLE</u>	<u>PAGE</u>
1	Rate constants for the unimolecular decomposition of t-butyl chloride to 2-methy propene and hydrogen chloride.	3
2	The effect of t-butyl chloride concentration on the decomposition rate of t-butyl chloride.	9
3	The effect of reaction time on the decomposition of t-butyl chloride at 568.2 °K	11
4	The effect of temperature on the decomposition rate of t-butyl chloride.	14
5	Correlation results versus reaction order for tribromosilane.	23
6	The effect of tribromosilane decomposition versus argon dilution.	33
7	Free Space Reactor Mass Balance Results	34
8	Synthesis Reactor Corrosion Coupon Test Results (Preliminary)	40

ILLUSTRATIONS

<u>FIGURE NO.</u>	<u>TITLE</u>	<u>PAGE</u>
1	Experimental Rate Study Vacuum System	5
2	Log Rate versus log t-butyl Chloride Concentration Plot	8
3	Reactant t-butyl Chloride Concentration versus Reaction Time Plot	10
4	Integrated First Order Rate Expression versus Reaction Time	13
5	Log Rate Constant versus Reciprocal Temperature t-butyl Chloride Arrhenius Plot	15
6	Comparative Arrhenius Plot of Our Results versus Results of Previous Investigators	17
7	Reactant Tribromosilane Concentration versus Reaction Time Plot	22
8	Integrated First Order Rate Expression versus Reaction Time for Tribromosilane	24
9	Integrated 3/2 Order Rate Expression versus Reaction Time for Tribromosilane	25
10	Integrated Second Order Rate Expression versus Reaction Time for Tribromosilane	26
11	Experimental Free Space Reactor System	30

ABSTRACT

The J. C. Schumacher Company is investigating a number of promising techniques for improving the overall yield and economics of the tribromosilane based process to produce solar cell grade silicon. The current work is aimed at the identification of an optimum process and the characterization of that process through mini-plant operation and analysis. The three project tasks include process improvement studies, kinetic studies, and process economic studies.

During this second quarter reporting period process improvement studies continued in the mini-plant, focusing on the correlation of current mini-plant yield results with prior laboratory scale work. Silicon bromination in the synthesis unit and tribromosilane purification in the distillation unit proceeded efficiently and without complication during this reporting period. Tribromosilane yields in the synthesis unit were low due to unobtainable higher reaction temperatures. Initial polycrystalline silicon production studies have indicated consistent yields of 85%.

The laboratory scale static bulb reactor system was calibrated by observing the decomposition of t-butyl chloride. These results compared very well to results obtained by previous investigators for the same decomposition. Upon the conclusion of the calibration tests, the tribromosilane decomposition rate study was initiated. Two decompositions were completed and it was concluded that the reaction order can not be determined at this time. A free space reactor apparatus was assembled and tribromosilane decompositions, as a function of dilution in argon, was studied.

PROJECT DESCRIPTION

The goal of the Low Cost Silicon Process Development Project's Process Improvement Phase is three-fold. First, the mini-plant process systems will be utilized to further study various laboratory developments which show good promise of improving overall process economics. The most notable of these developments are the various catalytic agents which have been found to promote the hydrogenation of tetrabromosilane in the synthesis reactor unit. Secondly, an experimental chemistry task is focused on the determination of the tribromosilane decomposition rate. The results of this rate determination task will be integrated into the mini-plant through design improvements in the product reactor. Lastly, through economic analysis of the various process schemes the most viable production process will be chosen for full process characterization by way of extended mini-plant operations.

SECTION 1

INTRODUCTION

Low cost silicon process development work began in 1977 in the J. C. Schumacher Research Laboratory. The experimental process improvement work described in this report is sponsored by the Solar Energy Research Institute under DOE/SERI Contract XS-9-8279-1. The contract period is June 1979 through February 1981.

1.1 Process Description

The J. C. Schumacher Company's low cost silicon process is based on the silicon-bromine-hydrogen chemical system whose favorable characteristics make possible the generation of a high purity, granular polycrystalline silicon product from metallurgical grade silicon in a closed-loop process. The process chemistry was described in detail in the progress report ⁽¹⁾ issued in October 1979.

1.2 Project Objective

The project goal of this process improvement phase is the characterization and analysis of various process alternatives indicating possibilities for overall yield improvement and cost reductions.

Earlier phases of this work focused on the basic process chemistry and the integration of the various processing units into a closed-loop system. The comprehensive examination of the basic chemistry in the mini-plant operations, however, has been delayed. Modifications now being made are expected to allow completion of this work so that new "catalytic" reaction chemistry, which has shown improved yields of tribromosilane in experimental work, can be investigated in the mini-plant. Product reactor design improvements as indicated by rate determination studies will be incorporated into the mini-plant reactor for verification. Overall, the most viable process, both from technical and economic considerations will be identified for further study in the mini-plant.

1.3 Technical Approach

As described above, the three main areas of technical effort include experimental rate determination studies, the study of the basic process chemistry and catalysts in the mini-plant, and the selection of the most technically sound and economically viable process for further characterization in the mini-plant.

The results of the rate determination work will be used specifically to assist in the development of a silicon product reactor design. Depending upon the true nature of the decomposition reaction, this may include physical changes to the reactor and/or modifications to the operating scheme.

Initially, the basic process chemistry will be investigated and compared to prior experimental work. Next, various catalytic agents which have been shown to promote the production of tribromosilane by the hydrogenation of tetrabromosilane will be studied in the mini-plant. These studies are designed to verify the suitability of a given catalyst system both from the standpoint of the yield of suitable products and by-products as well as from the potential introduction of difficult to remove contaminants in the reactor effluent. Economic analysis of all technically viable processes will enable selection of the "best" silicon production process. This process will be subjected to extensive heat and material balance testing in the mini-plant for the purpose of fully characterizing all significant parameters.

SECTION 2

EXPERIMENTAL CHEMISTRY

2.1 Reactor Calibration: Decomposition of t-butyl Chloride

2.1.1 Introduction

When a new chemical apparatus is constructed it must be calibrated. The calibration process must include tests to determine reliability, accuracy and precision for producing and analyzing chemical data. When the apparatus has been calibrated, reliable chemical data can be obtained.

A newly built kinetic decomposition reactor system was tested for accuracy and precision by monitoring the decomposition of t-butyl chloride to form 2-methyl propene and hydrogen chloride, according to

This reaction (equation 1) has been studied by several investigators with very comparable results (Table 1). Since all experimentally determined rate constants are in excellent agreement, the decomposition of t-butyl chloride was chosen as a reactor calibrating standard.

TABLE 1

Rate constants for the unimolecular decomposition of t-butyl chloride to 2-methyl propene and hydrogen chloride.

	RATE CONSTANT (Sec^{-1})	TEMPERATURE RANGE ($^\circ\text{K}$)	REFERENCE
10	$12.4 \pm 0.2 \quad e^{-41,400 \pm 600/\text{RT}}$	563-614	2
10	$13.9 \pm 0.7 \quad e^{-45,000 \pm 1900/\text{RT}}$	547-624	3
10	$13.77 \pm 0.2 \quad e^{-45,000 \pm 600/\text{RT}}$	563-603	4
10	$13.9 \pm 0.4 \quad e^{-46,200 \pm 1200/\text{RT}}$	750-950	5
10	$13.74 \quad e^{-44,690/\text{RT}}$	715-845	6

2.1.2 Experimental Procedures

Vacuum System

All separations and chemical transfers were performed in a vacuum system using the techniques outlined by Jolly⁽⁷⁾. A diagram of the vacuum system is presented in Figure 1.

The vacuum system routinely operated at internal pressures of 10^{-4} mm Hg. These pressures were achieved by using a Duo-Seal, Model 1376B forepump and a single stage mercury diffusion pump. Pressure measurements were made with a McLeod gauge attached to the main manifold of the vacuum system. Four overhead storage bulbs and four liquid storage bulbs were also attached to the main manifold.

Analytical System

Reactant and product samples were measured quantitatively by gas chromatography (Carle Inst., ACG-111 equipped with a thermal conductivity detector). Using a 6' x 1/8", 8% OV101 on chromosorb W HP 80/100 mesh stainless steel column operating at 23°C. With a helium flow rate of about 21cc/min., retention times for t-butyl chloride, 2-methyl propene and hydrogen chloride were 1.75, 0.72 and 0.53 minutes, respectively.

The use of thermal conductivity detectors for quantitative analysis requires relative sensitivity calibrations for each component analyzed. Thus, known mixtures of product and reactant gases were periodically analyzed by the g.c. to insure stable and reproducible results. Four standardized known mixtures of t-butyl chloride and 2-methyl propene were prepared and analyzed. The sensitivity factor relationship between t-butyl chloride and 2-methyl propene was 1.23 ± 0.01 . In all cases, the extent of reaction was determined by the appearance of 2-methyl propene.

Decomposition Reactor

The kinetic reactions were carried out in a quartz static bulb reactor similar to that of Paquin⁽⁸⁾ and Vanderwielen⁽⁹⁾. The quartz reactor (954 ± 25 cc) was heated with an electric resistance heater and was well insulated. Reactor

FIGURE 1
EXPERIMENTAL RATE STUDY VACUUM SYSTEM

temperatures were measured to the nearest tenth degree (0.1 K) by a thermocouple connected to a millivolt potentiometer (Leeds and Northrup, Model 8686-3).

When the decomposition reactions were first started, it was found that with no reactor pretreatment, consistent results could not be obtained. The reaction proceeded at a rate greater than expected. This was believed to be the result of a heterogeneous reaction occurring on the walls of the reactor. It was necessary to "burn-in" some of the chloride as a reactor pretreatment in which 50cc of the chloride was decomposed at temperatures between 750 and 800°K to form a carbonaceous wall deposit. This treatment was sufficient to eliminate the assumed heterogeneous reactions. It was also found that long periods of reactor evacuation destroyed the wall deposits and caused the reappearance of the assumed heterogeneous reactions. Thus the reactor was not evacuated until just prior to an experiment to prevent the destruction of these deposits. Using this technique of material handling, consistent rate data was obtained.

2.1.3 Order Determination Results and Discussion

The overall reaction order for the t-butyl chloride (chloride or +Cl) decomposition was determined by three independent methods. They were the Vant Hoff method, the half-life method, and a graphical integrated rate equation method. These methods all yielded first order results.

The Vant Hoff method is derived from the basic rate equation for any reaction,

$$\text{Rate} = k (\text{chloride})^n$$

(where k is the rate constant and n is the order of the reaction). Taking the logarithm of both sides results in the following expression.

$$\log \text{rate} = \log k + n \log (\text{chloride})$$

This expression obeys the equation for a straight line ($y = b + mx$) and if "log rate" is plotted versus "log chloride concentration", for several different chloride concentrations, a straight line of slope n with a y intercept of log k results.

Table 2 presents the experimental results obtained in this study. In Figure 2, a Vant Hoff plot, the slope is 0.977 ± 0.012 with a certainty of better than 99% (correlation coefficient = 0.999). This result clearly demonstrates that the t-butyl chloride decomposition is first order.

The half-life method of determining reaction order is based on the relationship between reaction rate, reactant concentration, and reaction time. The rate of a first order reaction is independent of reactant concentration while the rate of a second order reaction is dependent on the square of reactant concentration. Thus, in a first order reaction, the first and second half-life times are equal while in a second order reaction, successive half-lives are twice as long. In the case of a zero order reaction, the reaction is complete at the end of the second half-life.

A plot (Figure 3) of percent reactant remaining as a function of reaction time was used to determine the various half-lives for t-butyl chloride decomposition. The experimental data is presented in Table 3. In Figure 3 the first and second half-lives are 4412 and 5400 seconds, respectively. These results are in fair agreement (within 22%) for a first order reaction. If second order is assumed, on the other hand, the results are in 61% error. The half-life results are more consistent with the first order result than zero or second order results.

The integrated rate equation method involves plotting the integrated rate expressions (for various reaction orders) versus time with the slope being equal to the rate constant. In the case of plotting the first order integrated rate equation versus time from zero to sixty (60) percent decomposition (Table 3) a straight line (correlation coefficient 0.999) was obtained. This is shown in Figure 4. The rate constant obtained from Figure 4 was within 4% of that determined by the standard first order equation ($\log k_{\text{slope}} = -3.829$, $\log k_{\text{exp}} = -3.812$). Plotting the same data (Table 3) using the zero order and second order integrated rate equations gave less linear agreement and rate constant values in greater error than the first order result.

FIGURE 2

Log Rate versus Log t-butyl Chloride Concentration Plot

TABLE 2

The Effect of t-butyl chloride Concentration on the Decomposition Rate of t-butyl chloride.

<u>t-butyl chloride concentration (moles/liter)</u>	<u>-log t-butyl chloride concentration (-log (moles/liter))</u>	<u>-log k</u>	<u>-log rate (-log moles/lsec)</u>
3.14×10^{-3}	2.50	3.31	5.87
2.04×10^{-3}	2.69	3.31	6.06
1.36×10^{-3}	2.87	3.33	6.25
7.56×10^{-4}	3.12	3.31	6.49
6.12×10^{-4}	3.21	3.31	6.55
4.40×10^{-4}	3.36	3.30	6.72

FIGURE 3

Reactant t-butyl Chloride Concentration versus Reaction Time

TABLE 3

The Effect of Reaction Time on the Decomposition of t-butyl chloride at 568.2°K⁺

$\ln \frac{[+Cl]_0}{[+Cl]_t}$	Reaction Time (τ) (Seconds)	Percent Decomposition (%)	$-\log k \text{ sec}^{-1}$
0.043	216	4.2	(3.698)
0.124	706	11.7	3.755
0.178	1017	16.3	3.779
0.245	1497	21.7	3.786
0.314	1942	26.7	3.791
0.385	2390	32.0	3.800
0.446	2811	36.0	3.800
0.662	4410	48.4	3.823
0.746	4909	52.6	3.818
0.892	5930	59.0	3.825
0.995	6874	63.0	3.839
1.162	7900	68.7	3.832
1.271	9861	71.9	3.890
2.608	19348		

+ Initial Reaction Pressure 87mm Hg

As a result of the consistent agreement found here with the order results of previous investigations, it can be concluded that the experimental reactor used in these studies can determine reaction order with reasonable certainty.

2.1.4 Kinetic Results and Discussion

The thermal decomposition reaction stoichiometry for the t-butyl chloride was

During chloride decompositions between 4 and 96%, 2-methyl propene and hydrogen chloride were the only reaction products detected. No minor decomposition products were observed.

All decompositions proceeded at rates proportional to k, where

$$k = A e^{-E/RT}, \text{sec}^{-1}.$$

Using the rate constant obtained from the standard first order rate expression

$$k = \frac{1}{\tau} \ln \frac{A_0}{A_\tau}$$

with τ defined as the reaction time, A_0 as the initial concentration of the chloride and A_τ as the concentration of the chloride at time τ .

Table 4 summarizes the rate data obtained from the chloride decomposition system. The usual Arrhenius plot obtained from this data is shown in Figure 5.

FIGURE 4

Integrated First Order Rate Expression versus Reaction Time

TABLE 4

The Effect of Temperature on the Decomposition Rate of t-butyl chloride

$\frac{10^3}{T(^{\circ}\text{K})}$	Initial Reactant pressure (mm Hg)	Temperature ($^{\circ}\text{K}$)	$-\log k \text{ (sec}^{-1}\text{)}$
1.813	115	551.6	4.369
1.784	111	560.5	4.060
1.776	77	563.1	3.984
1.771	116	564.7	3.919
1.759	87	568.5	3.812
1.743	168	573.7	3.648
1.734	118	576.7	2.568
1.729	103	578.4	3.490
1.706	143	586.2	3.282
1.702	110	587.5	3.229
1.679	148	595.6	2.999
1.679	134	595.6	2.997
1.675	145	597.0	2.971
1.667	140	599.9	2.904

FIGURE 5

Log Rate Constant versus Reciprocal Temperature
t-butyl Chloride Arrhenius Plot

The rate constant obtained from this plot was

$$k_{+Cl} = 10^{13.9} e^{-46,000/RT}, \text{sec}^{-1}.$$

The results obtained from our static reactor agree well with those obtained by previous investigators. Figure 6 shows the comparison of our Arrhenius results in relationship to those of previous investigations. As a rough estimate, our rate constants agree within 7% of the best average value (Table 1). Applying reasonable error limits on Arrhenius parameters would yield the following results

$$k_{+Cl} = 10^{13.9 \pm 0.4} e^{-46,000 \pm 1,500/RT} \text{sec}^{-1}.$$

With such good agreement between experimental rate results and those of previous investigators, it is felt safe to place a high degree of confidence in the reactor system, the analytical tools and data reduction techniques used in these studies.

2.2 Tribromosilane Thermal Disproportionation Kinetic Study

2.2.1 Introduction

The silicon product reactor produces high purity silicon by the thermal decomposition of tribromosilane.

In prior laboratory scale fluidized bed studies of this silicon production reaction, 85% of the theoretical conversion was attained. Pilot plant fluidized bed test runs routinely produce 75% to 85% of the theoretical yield. Among the potential reasons why these tests have not produced silicon at higher efficiencies are that less than optimum processing conditions were used and/or that a back reaction may be operating. The existence of a back reaction could suggest that the overall reaction is at an equilibrium state and the observed HSiBr_3 in the effluent is the equilibrium product of a hydrogenation of SiBr_4 reaction. To determine the true nature of the basic yield limiting factors for this system a well controlled kinetic study is essential.

FIGURE 6

Comparative Arrhenius Plot of Our Results versus Results
of Previous Investigators

Understanding the analogous trichlorosilane (HSiCl_3) decomposition may help interpret some of the complexities that arise in the HSiBr_3 decomposition. The decomposition of HSiCl_3 produces SiCl_4 , H_2 and Si.

During a study of the decomposition of alkylchlorosilanes by Eaborn et al⁽¹⁰⁾, the decomposition of HSiCl_3 was briefly investigated. They concluded that during the early stages of decomposition, dichlorosilane (H_2SiCl_2) was produced as a minor product. Its concentration went through a maximum as the reaction progressed. Its disappearance is probably due to a secondary decomposition process that is not the rate determining step.

A kinetic investigation of the thermal decomposition of HSiCl_3 by Bykovchenko et al⁽¹¹⁾, concluded that the rate determining step was first order. They claim that at temperatures between 873 to 933°K the rate constant can be described as:

$$k = 10^{11.76 \pm 0.29} e^{\frac{-57,000 \pm 1,200}{RT}} \text{ sec}^{-1}.$$

Bykovchenko also documents the formation of H_2SiCl_2 as a reaction by-product.

Since the formation of H_2SiCl_2 was observed by both Eaborn and Bykovchenko we will attempt to determine if dibromosilane is produced in the decomposition of HSiBr_3 . If dibromosilane (H_2SiBr_2) is formed and decomposed, as in the H_2SiCl_2 case, mechanistic similarities can be proposed for both decompositions. Since the HSiCl_3 decomposition was found to be first order, special attention will also be given to determine if the HSiBr_3 decomposition reaction is first order.

2.2.2 Experimental Procedures

The experimental apparatus used to observe the decomposition of tribromosilane was similar to the apparatus used for the t-butyl chloride, with a few modifications. A magnetically driven mixing tank was added to the main manifold, (Figure 1), close to the reactor. The purpose of this tank was to mechanically mix gaseous standards for chromatographic analysis and for reactor feed materials.

Reactants and product samples were measured quantitatively by gas chromatography (g.c.). The g.c. set up for the tribromosilane decomposition study was similar to that used for the calibration tests with the only difference being the column length (two feet versus six feet). A 2' x 1/8 x, 8% OV101 on chromosorb W HP 80/100 mesh stainless steel column operating at 23°C was used. With a He flow rate of 37 cc/min, retention times of tribromosilane, tetrabromosilane and what we believe is dibromosilane, from a boiling point and retention time relationship, were 0.94, 4.59 and 0.24 minutes, respectively. Four known mixtures of HSiBr_3 and SiBr_4 were prepared and analyzed. These results showed that the sensitivity factor between HSiBr_3 and SiBr_4 is 1.036. Thus the g.c. peak area of SiBr_4 must be multiplied by this factor to give the corresponding molar amount of HSiBr_3 .

The materials used in this study were doubly distilled HSiBr_3 at 99.5% assay and doubly distilled SiBr_4 at 99.9% assay. These materials were used without further purification. All rate measurements reported were corrected with respect to impurities.

Before serious rate data was obtained, the reactor internals were passivated. By heating the reactor to 600°C under a dynamic vacuum, to remove any carbonaceous deposits left by the decomposition of the chloride, and decomposing seven small samples of tribromosilane at 460 to 600°C, the reactor's internals were coated with silicon to insure that any heterogeneous reactions were reacting with a silicon surface and not the quartz reactor itself.

2.2.3 Tribromosilane Control Reactions

The reaction stoichiometry for the conversion of tribromosilane to tetrabromosilane is generally accepted to be:

To experimentally verify the decomposition stoichiometry in our reactor, an inert material is used as an internal standard. This material serves as a reference in determining the quantity of tribromosilane decomposed per unit of tetrabromosilane produced. By determining the number of decomposed tribromosilane molecules required to produce one tetrabromosilane molecule, the reaction stoichiometry can be established.

The criteria for such a standard are that it be stable at reaction temperatures, easily chromatographed with the other components, and inert with respect to reactions with HSiBr_3 at HSiBr_3 decomposition temperatures. Sulfur hexafluoride was chosen for the internal standard because it is generally inert with respect to chemical reactions and decomposition at moderate temperatures. When SF_6 was exposed to our reactor at 843°K for 5 hours no by-products were detected by the g.c., and it was therefore assumed stable in the system. The SF_6 was also easily separated chromatographically from all other bromosilane reactant and products.

However, when equal amounts of SF_6 and HSiBr_3 were held in the reactor at 803°K for 3 hours, three (3) new peaks were observed that had retention times different from every bromosilane material previously produced in these studies. Also, all of the HSiBr_3 had been consumed and much less than the expected amount of SiBr_4 was produced. In a different control reaction, pure HSiBr_3 was exposed to the reactor at 803°K for 18 hrs. with only about 42% decomposition. These control reactions show that SF_6 is not a good internal standard for studying the decomposition stoichiometry of HSiBr_3 . Therefore, the stoichiometric studies have been postponed until a stable internal standard

can be found. Currently silicon tetrafluoride (SiF_4) is being considered as a possible internal standard.

Without knowing the experimental reaction stoichiometry in the system used in these studies, further rate measurements and control reactions are somewhat complicated. Until the reaction stoichiometry can be experimentally determined, the generally accepted stoichiometric equation will be used. Thus, for rate measurement calculations for every one molecule (1) SiBr_4 produced, 1.33 molecules of HSiBr_3 will be considered to be consumed.

During the process of determining the rate of HSiBr_3 decomposition to SiBr_4 , control experiments were performed to determine if a significant back reaction (the hydrogenation of SiBr_4) was operating. Two control experiments were performed, one attempting to force the hydrogenation reaction to occur by using an excess of H_2 and in the other using conditions that were comparable to actual HSiBr_3 decomposition conditions. The first allowed H_2 and SiBr_4 (H_2 : SiBr_4 molar ratio of 120:1.0) to react at 853°K for 20 hours. The product analysis results showed an $\text{HSiBr}_3/\text{SiBr}_4$ ratio of 0.30. When a 1.5:1.0 molar ratio was reacted at 853°K for 20 hours, the $\text{HSiBr}_3/\text{SiBr}_4$ product ratio was 0.046. Since HSiBr_3 is produced even under conditions not forcing the back reaction, special consideration of the back reaction must be made when calculating reaction rates.

2.2.4 Order Determination Results and Discussion

Two HSiBr_3 decompositions have been completed to date, at reaction temperatures of 890.6°K and at 861.9°K . Figure 7 shows a plot of HSiBr_3 remaining versus reaction time for these two experiments.

FIGURE 7

The data in Figure 7 was used to evaluate the various half-lives for the tribromosilane decomposition. Using the 861.9°K reaction as a preliminary base case, the time for the first and second half-lives were 400 seconds and 850 seconds, respectively. (A third half-life was not considered because of back reaction complications described in Section 2.2.2.) These half-life results suggest the HSiBr_3 decomposition may be second order; however, one should consider that this agreement is based solely on preliminary data and may be fortuitous. Thus no error analysis will be reported at this time.

For both decomposition runs the integrated rate equation method, described earlier, was used for first order, 3/2 order and second order systems. A plot of the integrated rate equation versus reaction time for these systems is shown in Figures 8-10. Linear correlations could be reasonably made and certainties were above 80% for all reaction orders analyzed. A zero order integrated rate equation plot was constructed and the resultant line was definitely non-linear. Table 5 shows the correlation results versus reaction order for both runs.

TABLE 5

Correlation Results versus Reaction Order for Tribromosilane

Reaction Temperature	First Order (Corr. Coef./% Agreement)	3/2 Order (Corr. Coef./% Agreement)	Second Order (Corr. Coef./% Agreement)
890.6°K	0.991/91 %	0.996/94 %	0.990/95 %
861.9°K	0.998/95 %	0.994/93 %	0.967/85 %

The data appear to be reasonably consistent with all three reaction order possibilities. However, these results can not be resolved any further using existing data. Further work is planned to conclusively resolve this order determination question.

FIGURE 8

Integrated First Order Rate Expression versus Reaction Time for Tribromosilane

FIGURE 9

Integrated 3/2 Order Rate Expression versus Reaction Time for Tribromosilane

FIGURE 10

Integrated Second Order Rate Expression versus Reaction Time for Tribromosilane

From these three reaction order results, many mechanistic possibilities arise. In the case of a first order reaction, our energetic results may be very comparable with those of Bykovchenko⁽¹¹⁾ and the most probable unimolecular primary decomposition mode would be HBr elimination.

The dibromosilylene (SiBr_2) species could dimerize and decompose to ultimately produce a Si atom and a SiBr_4 molecule as product materials. One conceivable overall mechanism for a first order HSiBr_3 decomposition that is consistent with the overall stoichiometry appears as follows:

Thus the possibility of the HSiBr_3 decomposition being first order appears reasonable.

In the case of the 3/2 order reaction (Figure 9), two possibilities exist. The first is a radical reaction with a unique termination step, while the second is a first order reaction occurring in its' pressure fall-off regime. The radical reaction possibility would not be the best choice to explain this 3/2 order result because of the unique termination step required. The pressure fall-off complication possibility, however, seems more likely. Fall-off effects are found in decompositions of small molecules at high temperatures. The phenomena is caused by the inability of the reactant molecule to properly distribute vibrational energy prior to decomposition⁽¹²⁾. This 3/2 order phenomena has been previously documented by Purnell and Walsh in their decomposition of silane (SiH_4)⁽¹³⁾. Recent calculations and experimentation by Newman et al demonstrated that the 3/2 order dependence on SiH_4 was due solely to fall-off complications and not a radical reaction⁽¹⁴⁾. In the SiH_4 case the reaction was first order and

appeared to be 3/2 order due to fall-off complications. Since both SiH_4 and HSiBr_3 are five atom molecules, similar fall-off effects may be operating in the HSiBr_3 decomposition case. Future experiments will be designed to distinguish between these two reaction order conclusions.

The preliminary HSiBr_3 decomposition experimental results also agree with a second order mechanism. Speculating on this mode of decomposition suggests disproportionation as a possible initiating step.

Subsequent reaction steps require the production of silicon, hydrogen, and additional SiBr_4 to account for the overall stoichiometry. These materials can be produced by the secondary decomposition of H_2SiBr_2 to produce H_2 and SiBr_2 , followed by SiBr_2 dimerization and subsequent decomposition, as follows.

This mechanism is also consistent with the overall stoichiometry.

A second order decomposition should thus initially produce H_2SiBr_2 in high concentrations when the concentration of HSiBr_3 is high, and while the reaction proceeds, the concentration of H_2SiBr_2 should decrease faster than that of the decomposition of HSiBr_3 ⁽¹⁰⁾.

Preliminary laboratory results also show H_2SiBr_2 being formed in relatively high concentration in the initial stages of decomposition and decreasing rapidly as the reaction proceeds. This result indicates that the HSiBr_3 decomposition may be proceeding by a second order reaction.

Altogether, it is not possible to determine, at this time, the overall reaction order of the HSiBr_3 decomposition. Further experiments which should resolve this question are underway.

2.3 Tribromosilane Decomposition in a Free Space Reactor

2.3.1 Introduction

The thermal decomposition of tribromosilane is being studied kinetically in a free space reactor. The reactor study is helpful in comparing pilot facility fluidized bed reactor studies, in laboratory scale static bulb reactor studies and in determining the rate of gas phase tribromosilane decomposition that could be possible within entrained gas bubbles in a fluid bed reactor.

2.3.2 Experimental Procedures

The tribromosilane was decomposed in a cylindrical quartz reactor with a reaction zone of 150 mm x 36 mm (Figure 11). Three cold condensers in series were used to condense all bromosilane product and reactant material. A glass wool filter was used to capture the product of homogeneous nucleation. Experiments with three different HSiBr_3 concentrations were performed, using molar ratios of 6.1/1.0, 1.9/1.0 and 0.75/1.0 (argon to HSiBr_3). During all three reactions the reactor was maintained at 770°C with a residence time of 1.4 seconds.

2.3.3 Results and Discussion

Both homogeneously and heterogeneously nucleated reactions occurred in each experiment. The heterogeneous reaction produced a silver colored metallic plating on the reactor walls while the homogeneous reaction produced a silicon bearing product whose color seemed to depend on the concentration of charged HSiBr_3 . The 6.1/1.0 HSiBr_3 reaction produced a yellow silicon bearing product which slowly turned orange and then brown as the reaction proceeded. The 1.9/1.0 HSiBr_3 reaction produced a red silicon bearing product at first, which slowly turned brown as the reaction proceeded. The 0.75/1.0 HSiBr_3 reaction produced a purple silicon bearing product at first which again slowly became brown as the reaction proceeded. Product color difference may be a function of chemical or physical characteristics.

FIGURE 11

EXPERIMENTAL FREE SPACE REACTOR SYSTEM

Assuming that a minimal amount of HSiBr_3 is consumed in growth on homogeneously nucleated silicon particles, some interesting conclusions can be drawn. If the production of silicon follows the rate equation

$$\text{rate} = k (\text{HSiBr}_3)^n$$

so that

$$\log \text{rate} = \log k + n \log (\text{HSiBr}_3)$$

the order of the reaction can be computed. Knowing the amount of silicon produced (Table 6) and using the above equation, the overall reaction order n is found to be 0.72 (correlation coefficient = 0.996). This approximately first order result could be described as either the average of a mixture of orders or as a true first order reaction. From mass balance calculations (Table 7 and Appendix) there appears to be two independent reactions proceeding simultaneously.

Assuming that only these two reactions are occurring, and they can be separated, then from the mass balances the amount of charged material that reacts via equation (2) and (10) can be calculated. Of the HSiBr_3 charged to the reactor our results show that for the 6.1/1.0 reaction, 26% went by reaction 2 and 74% by reaction 10; with the 1.9/1.0 reaction, 76% went by reaction 2 and 24% by reaction 10; and with the 0.75/1.0 reaction, 70% went by reaction 2 and 30% by reaction 10. Reaction 2 appears to be second order, ($n = 1.7$, correlation coefficient = 0.975) and reaction 10 may be zero order ($n = 0.23$ correlation coefficient = 0.527).

For the overall reaction, however, which appears to be first order;

$$k = \frac{1}{\tau} \ln \frac{A_0}{A_\tau}$$

(where k is the first order rate constant), we can infer from the data,

in Table 6, that $k = 0.964 \text{ sec}^{-1}$ for the 6.1/1.0 dilution experiment, $k = 0.975 \text{ sec}^{-1}$ for the 1.9/1.0 dilution experiment, and $k = 0.820 \text{ sec}^{-1}$ for the 0.75/1.0 dilution experiment.

Further kinetic studies are required to resolve the questions raised by this preliminary data.

2.4 Synthesis of Tribromosilane by the Hydrogenation of Tetrabromosilane

This study was postponed until mid-April. No experimental studies were initiated.

TABLE 6

The Effect of Tribromosilane Decomposition versus Argon Dilution

<u>Date</u>	<u>Dilution</u> <u>(Ar/HSiBr₃)</u>	<u>Reaction</u> <u>Temperature</u>	<u>Residence</u> <u>Time (sec)</u>	<u>HSiBr₃ in</u> <u>Effluent (%)</u>	<u>Amorphous</u> <u>Silicon Produced (g)</u>	<u>Polycrystalline</u> <u>Silicon Produced (g)</u>
3/22	1.9 : 1.0	770	1.39	35	19.0	2.8
3/24	6.1 : 1.0	776	1.43	38	10.8	1.2
3/26	0.75: 1.0	770	1.29	48	29.4	4.1

TABLE 7

Free Space Reactor Mass Balance Results*

Substance	14% HSiBr ₃ Feed		35% HSiBr ₃ Feed		57% HSiBr ₃ Feed	
	Reactor Feed	Reactor Products and Effluents	Reactor Feed	Reactor Products and Effluents	Reactor Feed	Reactor Products and Effluents
HSiBr ₃	360.2	95.2	927.0	256.1	1621.0	635.3
SiBr ₄	7.2	201.0	18.4	615.3	32.2	891.0
Silicon homogeneous heterogeneous	Ø	12.0	Ø	21.8	Ø	33.5
		10.8		19.0		29.4
		1.2		2.8		4.1
HBr	Ø	59.1	Ø	50.4	Ø	90.8
H ₂	Ø	0.3	Ø	1.9	Ø	2.5
Total	367.4	367.6	945.4	945.4	1653.2	1653.1

* All quantities given in grams.

SECTION 3
PROCESS DEVELOPMENT TESTS

The goals for this quarter were to: 1) complete the investigation and correlation of current mini-plant yield results with prior laboratory scale work; 2) incorporate catalytic synthesis reaction experimental work into the mini-plant operation; and 3) to perform extended mini-plant tests of the integrated modular process units for purposes of technical and economic evaluation. Even though mechanical problems, equipment deliveries, and modifications have limited the extent to which these goals have been reached, operation of the various modular process units during the quarter has provided important information and direction for continued development work.

3.1 Tribromosilane Synthesis Reaction Unit

The production of tribromosilane in the synthesis reaction unit is based on the chemical reaction in which metallurgical grade silicon is consumed by reaction with hydrogen and tetrabromosilane, SiBr_4 , as shown by Equation 11 below.

In experimental work the effluent from the synthesis reactor contained 35-40 mole percent tribromosilane, SiHBr_3 , with the remainder consisting primarily of tetrabromosilane⁽¹⁵⁾. The reaction, both in the mini-plant and the laboratory, is carried out in quartz reactors packed with metallurgical grade silicon.

3.1.1 Synthesis Reaction Unit Operational Performance - Bromination Mode

In order to perform sustained mini-plant operations as well as experimental work in the laboratory, a quantity of SiBr_4 starting material is needed. Since the overall chemistry allows for a closed-loop process, this material need only be generated for start-up and system surge capacities, make-up for losses due to vent and waste streams, and any experimental work necessary. The modular mini-plant, therefore, was not set up with a separate silicon bromination unit. This reaction instead is carried out in the synthesis

reaction unit according to Equation 12 as reported previously⁽¹⁶⁾.

This reaction goes to completion leaving no bromine in the effluent.

Silicon brominations were carried out on three separate occasions during the quarter totalling roughly ten days of operational time. With no difficulties encountered, the operation of the synthesis reaction unit in this mode (bromination) was rapidly approaching a routine status.

Based on these results, it does not appear that this process step will present any unusual problems in the overall process scheme. In a full scale commercial size facility this process step could be carried out in a separate reactor or in the synthesis reactor depending on the final design, materials of construction, and operational mode of the synthesis unit.

3.1.2 Synthesis Reaction Unit Operational Performance - Tribromosilane Mode

During the thirteen weeks of available operational time in this reporting period, the synthesis reaction unit was operated in the tribromosilane synthesis mode approximately twenty-seven days (non-continuous). The need to generate SiBr_4 as starting material reduced the operational time for SiHBr_3 production by about two to three weeks (additional time was consumed in removing waste bed material and repacking with fresh metallurgical grade silicon between bromination and tribromosilane runs in the synthesis reactor). Mechanical problem delays accounted for the balance of the available operation time.

Of the synthesis runs that were made, a variety of operating conditions and variables were investigated. Reactor wall temperatures were varied from as low as 600°C to as high as 950°C , the mole ratios of hydrogen to tetrabromosilane were adjusted from 1:1 up to 6:1, and residence times, based on superficial velocities, were varied from 4 to 17 seconds.

Initial evaluation of the run results were below expectations. Yields of tribromosilane (13-20 mole %) in the effluent from the reactor at the lower wall temperatures (600-770°C) tended to agree for the most part with yields obtained in earlier laboratory experimental work⁽¹⁵⁾. The yield results (15-25 mole %) at the higher wall temperatures (800-950°C), however, did not agree with the earlier experimental work. The maximum yields at these higher temperatures appeared to level off in the 20-25 mole percent range.

Closer examination of the system has revealed the fact that the true effective bed temperatures are not represented by wall temperature readings. This was shown in later runs in which a single temperature probe, installed vertically down into the silicon bed, indicated bed temperatures 75°C to 140°C lower than wall temperatures. This is to be expected from the endothermic nature of the reaction as previously reported⁽¹⁶⁾ which produces a temperature gradient within the bed. Thus, the effective temperatures at which the reactions occurred were probably much lower than wall temperature so that direct correlation with previous laboratory work can not be made.

Although the higher reaction temperatures necessary for increased yields were not obtained in the synthesis unit during the runs involved, general trends could be derived from the run data and results, and are as follows:

- a) higher operating temperatures resulted in increased yields
- b) shorter residence times increased yields
- c) higher mole ratios of hydrogen to tetrabromosilane increased yields.

These trends are consistent with prior experimental observations.

On some occasions during the runs, portions of the silicon bed were fused together with deposited silicon. Silicon deposition on the reactor walls also occurred at times. Both problems appeared to be the result of the synthesis unit being operated for periods of time at conditions which would favor SiHBr_3 decomposition. Later observations indicated that shorter residence times tended to alleviate the problems.

Modifications and mechanical problems both contributed to the long delays in operation of the synthesis unit during the quarter. Safety concerns and the inability to achieve higher reaction temperatures led to the modification of the feed inlet piping and the addition of a feed preheater section. A chronic mechanical problem was the failure of the quartz in a reducer section that serves as the reactor bottom head and feed inlet nozzle. This reducer section, connected to other quartz sections by the use of metal back-up flanges and bolts, was subjected to high operating temperatures and temperature cycling. Due to the large difference in the coefficient of thermal expansion between the metal flanges and bolts, and that of the quartz ($14.4 \times 10^{-6}/^{\circ}\text{C}$ versus $0.6 \times 10^{-6}/^{\circ}\text{C}$), leaking occurred at elevated temperatures, and mechanical failure took place on cool-down. The use of compression springs and spring washers on the bolts did not remedy the problem.

Faced with the continued problems of unobtainable higher reaction temperatures and the failure of hot quartz flanged joints, a new synthesis reactor was designed and fabricated. The new design eliminates hot quartz flanged joints and is expected to allow higher overall reaction temperatures. This unit will be installed and started up in the month of April. With the new reactor in operation, added runs will be made to correlate mini-plant results with those of prior laboratory work. After stable operation has been achieved at yields comparable to those of the laboratory work, efforts will begin on investigating new catalyzed synthesis reactions.

3.2 Synthesis Reactor Alloy Corrosion Studies (Preliminary)

The synthesis and product reactors in the present mini-plant process are constructed of quartz. This material was selected for its superior chemical and thermal properties. The J. C. Schumacher Company has employed the use of two types of quartz materials, fused quartz (transparent) and fused silica (translucent).

There are, however, certain difficulties associated with the use of quartz in the process. One problem described earlier was its' coefficient of thermal expansion which is over twenty-four times less than that of the typical metal components used with quartz to make connections. Another problem is the weaker mechanical properties of quartz compared to most metal alloys^(17,18). Even though devitrification* (crystallization) of fused quartz does not occur at perceptible rates below 1000°C under normal conditions, this also could become a problem upon prolonged operation in the present system.

Thus an alloys corrosion study was begun to investigate other possible materials of construction for use in the process. An initial selection of ten alloys and metals was made. Corrosion coupons fabricated from these materials were then placed in the synthesis reactor silicon bed. Table 8 gives the results of the corrosion tests after seventy-eight hours of tribromosilane production in the reactor. Different coupons, however, were placed in different positions in the bed and therefore may not have been subjected to the most severe operating conditions. Inconel 600 thermowells in the same service show a very pronounced corrosion rate increase along their lengths corresponding to lower and lower bed depths in the reactor. These results are considered preliminary and further tests are being conducted.

* Devitrification occurs by a process of nucleation and growth. Manufacturers and researchers list a number of promoters of nucleation such as alkaline solutions, salts, hydrogen, oxygen, certain metals, moisture, dirt and even fingerprints^(19,20). The product of devitrification is ~~is~~ cristobalite which manifests itself, as the fused quartz cools below 250°C, by a hazy film made up of a maze of micro-fine cracks.

TABLE 8

Synthesis Reactor Corrosion Coupon Test Results (Preliminary)

Coupon Material	Corrosion Rate (mils/yr)	Hours In Operation	Evaluation	Comments
Chlorimet 3	(wt. gain.)	78	Good	Hard, stable coating not removable by scraping; ~50 microns thick. Some minor chips.
Incolloy 800h	11.5	78	Good	No surface pitting. Very thin coating, easily removed.
Durco 20	79.2	78	Fair	Surface roughened by attack. Light coating removed by washing and light scraping.
Inconel	49.9	78	Fair	Surface attack, uneven scale, adhered in places.
Chlorimet 2	—	78	Poor	Attacked; thick chipped scale.
Nickel 200	—	78	Very Poor	Attacked; crusty scale easily removed.
Monel 400	—	78	Very Poor	Attacked; heavy removable scale.
Durimet 100	—	78	Very Poor	Attacked; heavy removable scale.
Zirconium	—	78	Reactive	Formed white powder.
Titanium - Pd	—	78	Reactive	Formed yellow liquid.

3.3 Distillation Unit

The mini-plant distillation unit as operated in the J. C. Schumacher polycrystalline silicon process provides for the separation and purification of tribromosilane from a composite feed stream of tribromosilane and tetrabromosilane. This feed stream is made up of the combined effluents from the synthesis reaction unit and the product reaction unit. Purified tribromosilane, the distillate, is collected and fed to the product reaction unit. Tetrabromosilane, contained in the distillation bottoms stream, is recycled back to the synthesis unit and thereby closes the process loop.

3.3.1 Distillation Unit Operational Performance

The distillation unit was operated in conjunction with the synthesis unit throughout the reporting period. The operations ran smoothly and without incident during this time. All of the effluent from the synthesis unit was processed with the resultant products, purified tribromosilane and tetrabromosilane bottoms, being transferred to their respective in-process storage vessels.

The main concern in the distillation step is the level of impurities in the separated streams. To determine the types of impurities and their relative amounts that exist in the distillate and bottoms streams, samples were taken and submitted to an independent laboratory for analysis. These samples were taken prior to the introduction of corrosion coupons into the synthesis reactor and therefore are not contaminated with coupon corrosion products.

The results indicated a number of metal impurities in both the tribromosilane stream and the tetrabromosilane stream. The types of metals present were typical of those found as impurities in the metallurgical grade silicon used in the synthesis reactor. The tribromosilane stream contained relatively low amounts of these impurities (ppb) except for one, titanium, which was analyzed at 1500 ppb. The titanium is believed to be evolved in the synthesis reactor in the form of titanium tetrabromide (b.p. = 230°C) and carried out in the effluent stream. It would therefore be contained in the feed stream to the distillation unit. Titanium is of extreme importance because of its adverse effects as an impurity in the polycrystalline silicon used in

the fabrication of solar cells and semiconductor devices (reports indicate levels less than one part per billion may be a problem⁽²¹⁾). Preliminary calculations, however, indicate that even at a 1500 ppb level in the tribromosilane feed stream to the product reactor, the amount of titanium deposited by decomposition mechanisms would be far below the one part per billion levels.

Further sampling of the distillation streams will continue along with laboratory experimental work in which deposited silicon will be analyzed for titanium and compared to inlet stream concentrations. It should also be pointed out that up to this point in time no effort has been made to purge or selectively remove impurity build-ups in the tetrabromosilane stream coming from the distillation unit. Also, the distillation unit has not been operated in such a manner as to optimize the reduction of impurities in the overhead. With the improvement methods available in this area of operation, it is believed that titanium and other impurities can be readily purged from the system.

3.4 Silicon Product Reaction Unit

The production of polycrystalline silicon in the product reaction unit is accomplished by the thermal decomposition of purified tribromosilane according to Equation 2 below.

This reaction is carried out in a fluid bed reactor containing silicon seed material. The silicon deposits on the seed material by the mechanism of chemical vapor deposition (CVD). Product is removed in the form of granular particles. Conversions of 85 to 90 percent have been achieved based on analysis of tetrabromosilane contained in the reactor effluent.

3.4.1 Product Reaction Unit Operational Performance

Several weeks were spent at the beginning of this reporting period making modifications to the product reaction unit. Resistance heating problems required the rewiring of some control unit circuits. The need to collect and sample the effluent from the product reactor separately from that of the synthesis reactor required the installation of a dedicated effluent

condenser, a gas/liquid separator, and a sample piping system. A feed injection system was also installed to enable routine calibrations to be made of the feed pump output. Modifications were completed in mid-February.

During the last week in February a product reaction run was made of 30 hours duration. In this run the tribromosilane feed to the reactor was diluted with hydrogen in a molar ratio of from 1.5:1 to 4.5:1 ($H_2:SiHBr_3$) and the feed stream preheaters were set at approximately 550°C. Reactor wall temperatures were varied from 650 to 800°C while the fluid bed temperatures were monitored with an internal probe and ranged from 650 to 750°C. A total of 32.4 kilograms of tribromosilane were fed to the reactor and an overall conversion about 41 percent was obtained based on molar percentages of tetrabromosilane in the effluent stream. The reactor, however, failed when cracks developed shortly after an incremental reaction temperature increase had been initiated.

Examination of the reactor after cool-down indicated that the cause of failure was silicon deposited on the reactor walls. A coating from 1 to 3 millimeters thick had formed on the walls in the bed region. Eventually, after several temperature increases, the thermal expansion of the deposited silicon exerted enough force on the quartz to cause its failure. Wall deposition was apparently due to the low reaction temperatures (650 - 750°C) and poor bed fluidization, both of which allowed the tribromosilane to reach the walls before decomposing. The low reaction temperatures are also reflected in the poor conversions (~41%). In order to correct these problems, a reactor of new design has been fabricated. Installation and testing of the reactor is planned for April.

Another product run was made during the last week in March using a reactor design very similar to that of the newly designed reactor. The main difference was that the reactor used had top and bottom flanged connections (the new unit would be of a one-piece design). An inert gas was first passed through the bed to characterize fluidization flow rates. The tribromosilane was then fed

to the reactor in a 1:1 molar dilution with argon. The run lasted three hours during which the wall temperature was maintained at 900°C. Although the run was short, the results were promising. A conversion of 85% was obtained based on the mole percent tetrabromosilane in the effluent. Homogeneous silicon nucleation was small as reported by observation. Wall deposits of silicon were also small and appeared to have formed only where poor inlet gas distribution occurred. On cool-down, however, the quartz reactor body flange failed in a manner similar to hot quartz joints in the synthesis unit.

3.5 Engineering Support Activities

In support of the mini-plant development efforts, several other areas of work have been undertaken. In the distillation and product reaction unit areas, a literature search on the types of impurities in polycrystalline silicon and their effects on the manufacture of solar cells and semiconductor devices is underway. Case studies on different distillation arrangements will also begin in order to examine the most economic way of obtaining the required tribromosilane purity while purging impurities from the system. Work is also continuing in the areas of fluid bed technology and quartz equipment manufacture.

SECTION 4

CONCLUSIONS

4.1 Experimental Chemistry Studies

- The study of the tribromosilane thermal decomposition kinetics was initiated using 1) the calibration of the static bulb reactor, 2) preliminary rate measurement observations and 3) free space reactor experiments.
- A laboratory scale experimental synthesis reactor was designed and construction begun.

4.2 Process Development Tasks

- Silicon bromination reactions proceeded smoothly and without incident.
- Laboratory scale tribromosilane yields were not realized in the mini-plant due to unobtainable higher reaction temperatures.
- Metal alloy corrosion studies were initiated.
- The distillation unit performed very well under current operating conditions. Titanium, which has accumulated in the system, has been detected in the tribromosilane fraction.
- Initial product reaction runs have given good yields but reactor failures have delayed comprehensive testing.

SECTION 5

PLANNED ACTIVITIES

5.1 Experimental Chemistry Tasks

- Continue tribromosilane decomposition study to determine the stoichiometry and reaction order.
- Conclude free space reactor dilution studies.
- Initiate tribromosilane dilution experiments in a fluidized bed reactor.
- Initiate neat tribromosilane decomposition in a fluidized bed reactor.
- Initiate material balance tests and scale-up tests using laboratory synthesis reactors.

5.2 Process Development Tasks

- Operate synthesis unit in the effective temperature range to gain maximum conversion.
- Examine catalytic synthesis reaction mode.
- Continue corrosion study tests and evaluations.
- Continue tests and evaluations on impurities in tribromosilane distillate and product silicon.
- Test new product reactor for fluidization characteristics and high-temperature operation.

SECTION 6

REFERENCES

1. E. Moore, et al, First Quarterly Technical Progress Report, Contract DOE/SERI XS-9-8279-1, October 1979.
2. D. H. R. Barton and P. F. Onyon, Trans. Faraday Soc. 46, 114 (1950).
3. D. Brearly, G. B. Kistiakowsky, and C. H. Stauffer, J. Am. Chem. Soc. 58, 43 (1936).
4. S. C. Wong, Ph.D. Thesis, University of London (1958).
5. W. Tsang, J. Chem. Phys. 40, 1498 (1964).
6. W. Tsang, J. Chem. Phys. 40, 1171 (1964).
7. W. L. Jolly, The Synthesis and Characterization of Inorganic Compounds, Prentice-Hall, New Jersey (1970).
8. D. P. Paquin, Ph.D. Thesis, University of California, San Diego (1976).
9. A. J. Vanderwielen, Ph.D. Thesis, University of California, San Diego (1974).
10. C. Eaborn, J. M. Simmie and I.M.T. Davidson, J. Organometallic Chemistry, 47, 45 (1973)
11. V. G. Bykovchenko, V. I. Pchelintsev and E. A. Chernyshev, Kinetics and Catalysis, (English Translation) 14, 1162 (1973)
12. W. C. Gardiner, Jr., Rates and Mechanisms of Chemical Reactions, W. A. Benjamin, Inc. (1972) p 112.
13. J. H. Purnell and R. Walsh, Proc. R. Soc., 293 543 (1966)

14. C. G. Newman, H. E. O'Neal, M. A. Ring, F. Leska and N. Shipley, International Journal of Chemical Kinetics, XI, 1167 (1979)
15. E. Moore and C. Newman, Final Technical Progress Report, Contract DOE/SERI XS-9-8279-1, October 1980.
16. J. C. Schumacher, et al, Final Report, Contract DOE/JPL 954914-78/2, January 1979.
17. R. H. Perry, "Chemical Engineers' Handbook", 4th ed., McGraw-Hill Book Company, Inc., New York, 1969.
18. R. C. Weast, "Handbook of Chemistry and Physics", 51st. ed., The Chemical Rubber Co., Cleveland, Ohio, 1970-1971.
19. N. G. Ainslie, C. R. Morelock, and D. Turnbull, "Devitrification Kinetics of Fused Silica", reprint from Symposium of Nucleation and Crystallization in Glasses and Melts, The American Ceramic Society, 1962.
20. "Fused Quartz", Catalog 878, Quartz Scientific Inc. Fairport Harbor, Ohio, Aug. 1978.
21. J. H. Wohlgemuth and M. N. Giuliano, "Analysis of the Effects of Impurities in Silicon - Final Report" Contract DOE/JPL 955307-4, Solarex Corporation, Rockville, Maryland, January 1979 - January 1980.

A P P E N D I X

Mass Balance Calculations

The measured quantities in this experiment were: the composition and weight of the feed to the reactor, the percent HSiBr_3 and SiBr_4 in the effluent (using a gas chromatograph), and the combined weight of silicon, HSiBr_3 , and SiBr_4 leaving the reactor. The weights of the HBr and H_2 were not measured.

The first step in calculating the mass balance is to make a silicon balance. In this calculation it is assumed that only the following reactions are occurring in any appreciable amount.

The reaction with a 1.9 to 1.0 HSiBr_3 feed will be used as an example.

Silicon Balance

Feed: 927g HSiBr_3 , 3.45 moles
18.4g SiBr_4 , 0.05 moles

Silicon in feed:

HSiBr_3	$(927\text{g})(28\text{g Si}/269\text{g HSiBr}_3) = 96.5\text{g}$
SiBr_4	$(18.4\text{g})(28\text{g Si}/348\text{g SiBr}_4) = \underline{1.5\text{g}}$
TOTAL	98.0g

Products and Effluents

Let S = grams of silicon produced in the reaction

X = mole % of HSiBr_3 in effluent

Total weight of silicon + HSiBr_3 + SiBr_4 = 893.1g

X = 35.0% HSiBr_3

HSiBr₃

$$\text{grams Si} = (893.1 - S) \left(\frac{X \cdot 269 \text{g/mol HSiBr}_3}{X \cdot 269 \text{g/mol HSiBr}_3 + (1-X) \cdot 348 \text{g/mol SiBr}_4} \right) \left(\frac{28 \text{g Si}}{269 \text{g HSiBr}_3} \right)$$

$$\text{grams Si} = (893.1 - S) \left(\frac{(.35)(26)(.35)(26)}{(.35)(269) + (.65)(348)} \right) \left(\frac{28}{269} \right)$$

$$\text{grams Si} = 27.3 - .031S$$

SiBr₄

$$\text{grams Si} = (893.1 - S) \left(\frac{(.65)(348 \text{g/mol SiBr}_4)}{(.35)(269 \text{g/mol HSiBr}_3) + (.65)(348 \text{g/mol SiBr}_4)} \right) \left(\frac{28 \text{g Si}}{348 \text{g SiBr}_4} \right)$$

$$\text{grams Si} = 50.8 - .057S$$

Si

$$\text{grams Si} = S$$

Silicon in feed = Silicon in effluents + products

$$98.0 = (27.3 - .031S) + (50.8 - 0.57S) + S$$

$$\text{solving for S: } 0.912S = 19.9$$

$$\therefore S = 21.8 \text{g} = \text{grams Silicon produced}$$

$$\text{gHSiBr}_3 = (893.1 - 21.8) \left(\frac{.35 \cdot 269}{.35 \cdot 269 + .65 \cdot 348} \right) = 256.1 \text{g}$$

$$\text{gSiBr}_4 = (893.1 - 21.8) \left(\frac{.65 \cdot 348}{.35 \cdot 269 + .65 \cdot 348} \right) = 615.3 \text{g}$$

Summary:	<u>Feed</u>	<u>Effluent and Products</u>
HSiBr ₃	927g	256.1g
SiBr ₄	18.4g	615.3g
Si	0	21.8g

Now the amount of HBr and H₂ produced by the reactions must be calculated. To accomplish this the amount of HSiBr₃ reacted in each of the reactions (1) and (2) must be determined.

Let F = the number of moles of HSiBr₃ fed to the reactor
 R = the number of moles of HSiBr₃ reacted
 f = the number of moles of SiBr₄ fed to the reactor
 S = the number of moles of Si produced
 Z = the fraction of R reacted by reaction (1).
 X = mole % of HSiBr₃ in effluent

Z is the variable which needs to be determined. From the stoichiometry of reactions (1) and (2),

$$X = \frac{(F-R)}{(F-R) + [(f + RZ(3/4)) + R(1-Z)(1/2)]} \quad (3)$$

$$S = RZ(1/4) + R(1-Z)(1/2) \quad (4)$$

solving (4) for R:

$$R = \frac{4S}{2-Z} \quad (5)$$

substituting (5) into (3),

$$X = \frac{F-4S/(2-Z)}{F-4S/(2-Z) + f + Z(4S/(2-Z))(3/4) + (4S/(2-Z))(1-Z)(1/2)} \quad (6)$$

multiplying (6) by (2-Z)

$$X = \frac{F(2-Z)-4S}{F(2-Z)-4S + f(2-Z) + 3SZ + 2S-2SZ} \quad (7)$$

simplifying,

$$X = \frac{2F - ZF - 4S}{S(F + f - S) - Z(F + f - S)} \quad (8)$$

$$Z(X(F + f - S) - F) = 2X(F + f - S) + 4S - 2F$$

$$Z = \frac{2X(F + f - S) + 4S - 2F}{X(F + f - S) - F} \quad (9)$$

Using equation (9), Z can now be calculated.

$$X = 0.35$$

$$F = 3.45$$

$$f = 5.29 \times 10^{-2}$$

$$S = 7.79 \times 10^{-1}$$

substituting these values into (9),

$$Z = .751$$

Thus 75.1% of the HSiBr_3 which reacted did so by reaction 1, and 24.9% by reaction 2.

substituting S and Z into equation (5),

$$R = \frac{4(.779)}{2 - .751} = 2.49 \text{ moles (671g) } \text{HSiBr}_3 \text{ reacted.}$$

Now the amount of HBr and H_2 produced by the reaction can be calculated.

HBr: by reaction (2),

$$\text{grams HBr} = (2.49 \text{ moles } \text{HSiBr}_3)(1 - .751)(2\text{HSiBr}_3/2\text{HBr})(81\text{g HBr/mole}) = 50.3\text{g}$$

H₂: by reaction (1),

$$\text{grams H}_2 = (2.49 \text{ moles HSiBr}_3)(.751)(4\text{HSiBr}_3/2\text{H}_2)(2\text{g H}_2/\text{mole})$$

$$\text{H}_2 = 1.9\text{g}$$

Summary:

	<u>Feed</u>	<u>Effluent and Products</u>
HSiBr ₃	927.0g	256.1g
SiBr ₄	18.4g	615.3g
Si	0	21.8g
HBr	0	50.3g
H ₂	0	1.9g

RECEIVED BY TIC MAY 4 - 1981