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SEMICONDUCTOR GRADE, SOLAR SILICON PURIFICATION PROJECT

Technical Quarterly Report No. 10, April 1—June 30, 1978

By
William M. Ingle
Robert Chaney
Stephen Thompson
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July 25, 1978
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SEMICONDUCTOR GRADE, SOLAR SILICON PURIFICATION PROJECT

Motorola Report No. 2257/10

Technical Quarterly Report No. 10

JPL CONTRACT NO. 954442

by

William M. Ingle

Principal Investigator

Robert Chaney, Stephen Thompson, Dick Rosler, and John Jackson

Period Covered: 1 April 1978 - 30 June 1978

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ABSTRACT

The technical progress reported in the current quarterly report can be divided into seven task areas. They are as follows:

THERMAL DISPROPORTIONATION OF Si_xF_y HOMOLOGUES ON Si PACKED BEDS

Effort has been directed toward the study of the thermal disproportionation of Si_xF_y homologues on Si packed beds at 850°C and 500°C. A kinetic analysis of the data in terms of a steady state integral plug flow reactor has been conducted. The reaction was found to be consistent with a reaction third order in the reactant.

REVIEW OF EXPERIMENTAL RESULTS ON THE NEAR-CONTINUOUS REACTOR

The silicon transport data from forty runs conducted on the near-continuous reactor are summarized and discussed. It is particularly interesting to note that silicon transport rates increased an order of magnitude (from 5 to 50 gm/hr) during these runs without increasing the size of the mg silicon charge or Step I reactor. Additional increases are anticipated during the next quarter.

THERMAL ANALYSIS OF $(\text{SiF}_2)_x$ POLYMER

At 276 - 286°C a strong exothermic transition occurs in the $(\text{SiF}_2)_x$ polymer. The enthalpy (ΔH) measured by D.S.C. was -44.37 cal/gm. Other smaller endotherms were observed at 96°C and 363°C.

MOTOROLA PURIFICATION THERMODYNAMICS

In the Appendix can be found thermodynamic calculations for the predicted SiF_4 to SiF_2 conversion efficiencies for Step I in the SiF_4 transport purification process.

POLYMER CONDENSATION

It was concluded from the polymer condensation experiments at 0°C that substrates and higher pressures in the polymer condensation unit increase condensation efficiency. However, the higher pressure occurring in these experiments markedly reduced the Step I reaction efficiency.

CRYSTAL GROWTH

Single crystal silicon grown from silicon powder from the near-continuous reactor was shown to be 0.95 ohm cm "P" type at the seed end and 2 to 7 ohm cm "N" type at the tang.

PROCESS PLANT COSTING

Revised process plant costing estimates for a 1000 metric ton/year plant projects a \$7.71/kg total product cost. This is based on a fixed capital investment of \$9.1 MM in January 1975 dollars.

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I. INTRODUCTION

The tenth quarterly report covers the work at Motorola's Process Technology Laboratories for DOE/JPL on low cost semiconductor grade silicon for solar cells. In the first phase of the work, the transport purification of metallurgical grade silicon (mg Si) via silicon tetrafluoride was shown to be feasible by producing semiconductor grade silicon from mg Si at a rate of ≥ 50 gm/hr. Furthermore the economic analysis on a 1000 metric ton/year plant projects a final product cost of \$7.71 per kilogram, (January 1975 dollars). Accordingly, Phase II of the program has been initiated and will concentrate on the design and engineering of a 1000 gm/hr miniplant to be operational by May 1979.

II. EXPERIMENTAL RESULTS AND DISCUSSION

THERMAL DISPROPORTIONATION OF Si_xF_y HOMOLOGUES ON SI PACKED BEDS

The goal of this aspect of the Si/SiF_4 transport process investigation is to study factors affecting the thermal disproportionation of Si_xF_y ($x \geq 2$ to 11) into silicon on silicon packed beds. Reaction conditions have been quantified so that a constant fraction of homologues enter the bed per unit of time throughout the course of conversion. Under specified reaction conditions SiF_2 is condensed to form $(\text{SiF}_2)_x$ polymer. The polymer is heated at a uniform rate and gaseous homologues are driven through a heated Si-packed bed.

Figure 1 is a graph of % polymer conversion efficiency based on polymer input to the conversion bed versus conversion bed length.

Effort has been directed toward subjecting the data obtained during thermal disproportionation of homologues on Si packed beds at 850°C and 500°C to a kinetic analysis in terms of a steady state integral plug flow reactor.

In a plug flow reactor the composition of the reactant varies from position to position along a flow path; consequently the material balance for a reaction component must be made for a differential element of volume dV . Therefore we obtain

$$\text{input} = \text{out} + \text{disappearance by reaction} \quad (1)$$

$$\text{input of A moles/time} = F_A \quad (2)$$

$$\text{output of A moles/time} = F_A + dF_A \quad (3)$$

$$\begin{array}{l} \text{disappearance of A by reaction} \\ \text{moles/time} \end{array} = (-r_A)dV \quad (4)$$

ε

Figure 1. Conversion efficiency vs. bed length

Substitution in equation 1 yields:

$$F_A = (F_A + dF_A) + (-r_A)dV \quad (5)$$

if $F_A = F_{A0} - F_{A0} X_A \quad (6)$

where X_A = fraction of A converted to product
differentiating F_A with respect to X_A

$$dF_A = d(F_{A0}(1-X_A)) = -F_{A0} dX_A \quad (7)$$

Substituting into equation 5, we obtain:

$$F_A = F_A + -F_{A0} dX_A + (-r_A)dV \quad (8)$$

$$F_{A0} dX_A = (-r_A)dV \quad (9)$$

where $F_{A0} \frac{\text{moles A fed}}{\text{hr}} \quad dX_A \frac{\text{moles A reacted}}{\text{moles A fed}} = (-r_A)dV \quad (10)$

Equation 10 is the differential equation for the rate of disappearance of A at steady state in a plug flow reactor.^{1,2}

Upon rearrangement of equation 10 the expression for the rate of reaction in an integral reactor is obtained

$$(-r_A) = \frac{dX_A}{d(V/F_{A0})} \quad (11)$$

thus a plot of X_A vs. V/F_{A0} will have a slope at X_{Ai}

$$\text{slope } X_{Ai} = (-r_{Ai}) = \left[\frac{dX_A}{d(V/F_{A0})} \right]_{X_{Ai}} \quad (12)$$

$$\text{and since } C_A = C_{A0} (1 - X_A) \quad (13)$$

where C_A = concentration of A in moles ℓ^{-1} , a graph of $(-r_{Ai})$ vs. C_{Ai} can be plotted and the order of reaction with respect to A obtained via

$$(-r_A) = - \frac{dC_A}{dt} = k C_A^n \quad (14)$$

where k is the rate constant, C_A is the molar concentration of A, and n is the order.

Finally

$$\log (-r_A) = \log k + n \log C_A \quad (15)$$

a plot of $\log (-r_A)$ vs. $\log C_A$ has a slope equal to n, the order of reaction, and an intercept equal to $\log k$, the log of the rate constant.

The following is a kinetic analysis of the data collected on thermal disproportionation of homologues liberated from the $(\text{SiF}_2)_x$ polymer. The methods and techniques used to obtain this data have been reported in previous monthly reports.³

TABLE I

Data correlating Si bed length and conversion efficiency.

<u>Bed Length (in)</u>	<u>Conversion Efficiency</u>	<u>Conversion Efficiency</u>
	<u>850°C</u>	<u>500°C</u>
0.5	0.50	
2.0	0.70	
4.0	0.74	0.65
8.0	0.85	0.80
16.0	0.95	0.87

The mean value of the pressure measured at a point midway between the disproportionation bed and the condensation/liberation trap is

$$\begin{aligned} \bar{P} &= 0.87 \text{ torr} \quad \sigma = 0.16 \text{ torr} \\ \bar{P} &= 1.14 \times 10^{-3} \text{ ats.} \end{aligned}$$

A. Calculation of F_{A0}

$$C_{A0} = \frac{N_{A0}}{V} = \frac{P_{A0}}{RT} = \frac{1.14 \times 10^{-3} \text{ ats}}{0.082 \text{ l ats deg}^{-1} \text{ mol}^{-1} \times T} \quad (16)$$

$$C_{A0}^{500} = 1.80 \times 10^{-5} \text{ moles A l}^{-1}$$

$$C_{A0}^{850} = 1.24 \times 10^{-5} \text{ moles A l}^{-1}$$

if v = volumetric flow rate

$$F_{A0}^{950} = C_{A0}^{850} v = (1.24 \times 10^{-5} \text{ moles l}^{-1})(v) \quad (17)$$

$$F_{A0}^{500} = C_{A0}^{500} v = (1.80 \times 10^{-5} \text{ moles l}^{-1})(v)$$

B. Calculation of v

Table II presents data showing the liberation rate (gms/min) for several runs calculated on the mass of polymer liberated divided by the time for liberation.

TABLE II
Mean liberation rate.

Run	Liberation Rate (gms min ⁻¹)	Run	Liberation Rate (gms min ⁻¹)
1	0.33	10	0.43
2	0.14	11	0.41
3	0.23	12	0.40
4	0.22	13	0.35
5	0.29	14	0.36
6	0.30	15	0.25
7	0.13	16	0.30
8	0.46	17	0.37
9	0.36		

$$\bar{v} = 0.313 \text{ gms min}^{-1} \quad \sigma = 0.095$$

Table III presents data showing the mean weight of polymer formed during the course of fourteen runs.

TABLE III

Mean liberation rate.

mean weight polymer formed (14 runs)	= 24.34 gms
standard deviation	= 4.86 gms
liberation time	= 84 mins.
$\bar{v}$	= 0.290 gms/min.

The mean weight of polymer formed equals 24.34 gms polymer ($\sigma = 4.86$ gms). Since the liberation time was 84 minutes, the value of $\bar{v}$ (the volumetric flow rate) equals

$$\bar{v} = \frac{24.34 \text{ gms}}{84 \text{ mins}} = 0.290 \text{ gms min}^{-1}$$

Taking the mean value of $\bar{v}$ arrived at by the two methods of analysis, we arrive at

$$\bar{v} = 0.3015 \text{ gms/min} \equiv 18.09 \text{ gms/hr}$$

In order to calculate $\bar{v}$ in terms of moles hr^{-1} we require the molecular weight of the homologues entering the conversion bed. GC/MS studies correlating pressure and species liberated versus temperature of liberation has indicated that Si_2F_6 is the major component in the gaseous mixture formed upon heating $(\text{SiF}_2)_x$ polymer.⁴ Therefore, if we assume that, based on the MS studies Si_2F_6 (mw = 170) is the major species entering the bed we obtain $\bar{v} = 0.106 \text{ moles hr}^{-1}$, hence $F_{\text{Ao}}^{850} = C_{\text{Ao}} \bar{v} = 2.84 \times 10^{-5} \text{ moles hr}^{-1}$, and $F_{\text{Ao}}^{500} = 4.27 \times 10^{-5} \text{ moles l}^{-1}$.

C. Calculation of volume occupied by Si particles

In order to calculate the true volume (V) of silicon contained within the conversion bed for different bed lengths we require the mean density of the Si charge within the bed. In order to obtain this value a graph of weight Si versus length of Si charge with the bed was plotted in Figure 2. From this graph a mean value of weight Si/length Si charge is obtained which, when multiplied by the required bed length, gives a mean weight of Si for a given bed length (Table IV). Calculation of the volume occupied

TABLE IV
Volume occupied by Si charge

Bed Length		Si Wgt.		V	Mean Density M/V g/cc	V	
radius	mm	actual	from graph			True Volume	95% Significance
						cc	ℓ
16	406.4	641.8 g	655 g	0.563 ℓ	1.163	567.6	0.5676
8	203.2	596.1	326	0.282	1.156	287.5	0.2825
4	101.6	163.1	165	0.1402	1.176	142.9	0.1429
2	50.8	102.8	80	0.0701	1.14	69.3	0.069
0.5	12.7	39.5/35.6	20	0.0176	1.136	17.3	0.017

$$V = \pi r^2 h = 1.38 \times 10^{-3} h$$

tube dimensions = 42 mm I.D.

$$\sigma_{Si}^{20^\circ C} = 2.42 \text{ gms/cc}$$

$$V = \frac{M}{1.154 \pm 0.03 \text{ gcc}^{-1}}$$

$$\begin{aligned}\sigma &= 0.0165 \\ \bar{x} &= 1.154 \\ \bar{x} \pm 1.96 \sigma &= 95\% \text{ level} \\ 95\% &= 1.154 \pm 0.03 \text{ gcc}^{-1}\end{aligned}$$

by the charge within the reactor tube allows a mean density calculation ($\bar{\rho} = 1.154 \pm 0.03 \text{ g cc}^{-1}$, 95% significance). Multiplication of $\bar{\rho}$ times the mean weight gives V, the true volume occupied by the Si charge for the bed lengths required (Table IV).

D. Calculation of $(-r_{Ai})$

Tables V & VI present X_A and V/F_{Ao} for various bed lengths leading to a graph of X_A vs. V/F_{Ao} as required by equation 11. Figures 3 and 4 are graphs of X_A vs. V/F_{Ao} for 850°C and 500°C conversions respectively. The slopes of the lines at X_{Ai} are equal to $(-r_{Ai})$ as expressed in equation 12.

Tables VII & VIII present values of $(-r_A)$ for various X_A for 850°C and 500°C conversions, making use of the expression $C_{Ai} = (1 - X_{Ai})$ we may obtain C_{Ai} at $(-r_{Ai})$ for X_{Ai} .

TABLE V

Data correlating bed length and V/F_{Ao} for conversions conducted at 850°C

Bed Length	$V(\ell) \pm 2.6\%$	V/F_{Ao} ($\ell \text{ hr mol}^{-1}$)	X_A
16	0.5676	19203.6	0.95
8	0.2825	9557	0.85
4	0.1429	4835	0.74
2	0.0693	2345	0.70
0.5	0.0173	585.3	0.50

Figure 3. X_A vs. V/F_{A0} (850°C)

Figure 4. x_A vs. V/F_{A0} (850°C & 500°C)

TABLE VI

Data correlating bed length and V/F_{A0} for conversions conducted at 500°C.

Bed Length (in)	$V(l) \pm 2.6\%$	V/F_{A0} (l hr mol ⁻¹)	x_A
16	0.5676	1.33×10^4	0.87
8	0.2825	6.62×10^3	0.80
4	0.1429	3.34×10^3	0.65

TABLE VII

Data correlating $1-x_A$ and C_A

x_A	slope = $(-r_A)$ = $dx_A/d(V/F_{A0})$ (moles l ⁻¹ hr ⁻¹)	$(1-x_A)$	C_A M hr ⁻¹
0.2	0.124	0.8	9.92×10^{-6}
0.3	0.065	0.7	8.68×10^{-6}
0.4	0.035	0.6	7.44×10^{-6}
0.5	0.0167	0.5	6.2×10^{-6}
0.6	0.0097	0.4	9.96×10^{-6}
0.7	0.0049	0.3	3.72×10^{-6}
0.74	0.0038	0.26	3.22×10^{-6}
0.79	0.00172	0.21	2.604×10^{-6}
0.8	0.00158	0.2	2.48×10^{-6}

TABLE VIII
Data correlating $1 - x_A$ and C_A (500°C)

x_A	$(-r_A)$ (moles l ⁻¹ hr ⁻¹)	$1 - x_A$	C_A M hr ⁻¹
0.4	0.0204	0.60	7.44×10^{-6}
0.5	0.0131	0.50	6.2×10^{-6}
0.6	0.0075	0.40	4.96×10^{-6}
0.70	0.0043	0.30	3.72×10^{-6}

E. Determination of reactor order

By making use of equations 14 and 15 it can be seen that a plot of $\log (-r_A)$ vs. $\log C_A$ should be a straight line of slope n ; where n is equal to the order of the reaction with respect to C_A . Figure 5 is a graph of $\log (-r_A)$ vs. $\log C_A$ for the 850°C conversion. The slope of the line for the 850°C conversion is:

$$n = \text{slope} = 2.98$$

$$\log_{10} k = \text{intercept} = 13.86$$

$$k = 1.67 \times 10^{14} \text{ M}^{-2} \text{ hr}^{-1}$$

$$\text{correlation coefficient} = 0.993$$

F. Calculation of k , the observed rate constant, and confirmation of units for the 850°C conversion.

Since

$$(-r_A) = kC^n \text{ and } n = 3$$

then

$$\frac{(-r_A)}{C^3} = k$$

$$\therefore \frac{(-r_A)}{C^3} = k$$

We obtain for $(-r_{Ai}) = 0.065 \text{ M hr}^{-1}$ and C_{Ai} at $(-r_{Ai}) = 8.68 \times 10^{-6} \text{ M}$.

$$-r_A = kC^n$$

$$\log_{10}(-r_A) = \log k + \log C^n$$

$$\log_{10}(-r_A) = \log k + n \log C_A$$

$$\text{Slope} = 2.98 \quad \text{Torr} = 0.993$$

Figure 5. $\log(-r_A)$ vs. $\log C_A$ (850°C)

We obtain

$$k = \frac{0.065 \text{ M hr}^{-1}}{(8.68 \times 10^{-6} \text{ M})^3} = 9.94 \times 10^{13} \text{ M}^{-2} \text{ hr}^{-1}$$

It is apparent however that this value of k will differ from the k value obtained from the log/log plot as the latter has been subjected to a least squares regression analysis and represents the statistical closer-fit value. It is concluded that the reaction is 3rd order in C_A which we have postulated to be Si_2F_6 based on GC/MS data and that the derived 3rd order rate constant k is the rate constant for Si_2F_6 disproportionation on the Si packed bed at 850°C . The data has been shown to be consistent with the analysis of steady state integral plug flow reactor.

Figure 6 is a graph of $\log(-r_A)$ vs. $\log C_A$ with a slope of 3 drawn through the data points for 850°C conversion and for 500°C conversion. It can be seen that there is agreement with the 850°C reaction in that the 500°C conversion data is also consistent with an order of $n = 3$. Future effort will be directed toward elucidation of homologue conversion by kinetic analysis and homologue conversions at pressures between 100 torr and atmospheric pressure.

REVIEW OF EXPERIMENTAL RESULTS ON THE NEAR-CONTINUOUS REACTOR

The purpose of the near-continuous reactor has been to demonstrate feasibility of the $(\text{SiF}_2)_x$ polymer transport purification process to produce semiconductor grade silicon at acceptable rates. It was constructed to incorporate current technology from all aspects of the project into one apparatus. Over the past six months the apparatus has undergone numerous modifications to facilitate higher transport rates and longer (more continuous) run times.

During the past quarter two modifications were incorporated into the apparatus design.

- i) The use of the ball valve was discontinued.
- ii) Three sets of 4" quartz flanges to facilitate removal of the high temperature reactor, low temperature coil and silicon harvester were incorporated. A sketch of the flange is shown in Figure 7. Each flange

Figure 6. $(-r_A)$ vs. C_A

TITLE: O. RING GROOVE (4.00)
QUARTZ FLANGE
SOLAR SILICON PUR.

SIZE	CODE IDENT. NO.	DRAWING NO.
B	04713	GJ-04

PARKER "O" RING - 158 REF

Figure 7. The sketch above depicts the o-ring grooves in the four inch conical quartz flanges supplied by Thermal American Fused Quartz Company.

assembly consists of two 4 inch quartz flanges (Thermal American Fuzed Quartz Co.) with o-ring grooves. To isolate the Viton o-rings from the Si_xF_y homologues, a quartz sleeve was attached to the upstream quartz flange and extends past the seal. Furthermore, a teflon seal (Gortex Teflon Joint Sealant, 1/8 inch) was placed inside the o-ring to further isolate the o-ring from Si_xF_y homologues. The Teflon Joint Sealant/Viton o-ring combination was chosen to provide a high vacuum seal with minimum contamination. The vacuum connection is formed with the o-ring seal while the teflon isolates the o-ring from the Si_xF_y homologues. This combination offers a high vacuum seal at a lower compression than a simple teflon seal. The compression for the seal is supplied by a Kimax conical pipe flange coupling assembly equipped with eight bolts tightened to about 30 inch pounds.

In Table IX can be found a summary of runs conducted to date on the near-continuous apparatus. It is interesting to note how the silicon transport rates (gm/hr) have increased over this time period and are presently at ~50 gm/hr. A sketch of the near-continuous apparatus is depicted in the previous quarterly report; a typical operational procedure was described in Appendix I of the October Quarterly.⁴

The high temperature furnace (~1350°C) was mounted in a horizontal configuration during runs NC-1 through NC-22. Thereafter a vertical furnace mounting was employed.

Runs NC-6, 9, 14, 22 and 27 represent Si_xF_y recycle runs. Si_xF_y recycle is accomplished by redistilling the Si_xF_y homologues through the silicon harvesting bed which is maintained at ~800°C. After run NC-27, Si_xF_y recycle was not deemed necessary because of the high observed polymer conversion efficiencies (>95% on the first pass). During the unitized polymer conversion Si_xF_y partial pressures increased above 5 torr which we have observed to lead to decomposition of the higher homologues into SiF_4 and silicon before reaching the harvestor bed. Furthermore, as the bed fills with silicon (less free void space through the bed) the Si_xF_y partial pressure increases above 10 torr

TABLE IX
SUMMARY OF DATA FROM ALL SILICON TRANSPORT RUNS
ON NEAR-CONTINUOUS APPARATUS TO DATE

Run No.	Run Date	Run Time (Min)	SiF ₄ Delivered (gm)	SiF ₄ Unreacted (gm)	Step 1(a) Conversion (%)	SiF ₄ from Conversion (gm)	Silicon (b) Purified (gm)	Transport Rate (gm/hr)	SiF ₄ (c) Recovery (%)
NC-1	9/9/77	60	31.7	10.4	67.2	6.9	1.86	1.86	54.3
NC-2	"	60	31.7	3.9	87.7	20.7	5.6	5.6	74.8
NC-3	10/6	60	129.6	26.4	79.6	41.6	11.2	11.2	52.5
NC-4	"	15	32.4	5.9	81.8	3.7	1.0	4.0	29.6
NC-5	"	15	32.4	20.5	36.7	9.8	2.6	10.6	93.5
NC-6	"	--	Si _x F _y recycle (from NC-3-5)			20.7	5.6	--	66.2 (overall)
NC-7	7	15	32.4	8.0	75.3	9.0	2.4	9.6	52.4
NC-8	"	60	129.6	38.8	69.4	59.5	16.0	16.0	75.8
NC-9	"	--	Si _x F _y recycle (from NC-7 & 8)			35.1	9.45	--	92.8 (overall)
NC-10	19	30	96.0	35.1	63.4	48.1	12.95	25.9	87.2
NC-11	20	30	96.0	35.9	62.6	37.8	10.18	20.4	76.8
NC-12	"	25	80.0	29.6	63.0	12.0	3.23	6.5	52.0
NC-13	21	30	96.0	45.9	52.2	43.3	11.66	23.3	92.9
NC-14	"	--	Si _x F _y recycle (from NC-13-13)			53.6	14.43	--	92.8 (overall)
NC-15	11/28	30	100	33.2	66.8	16.9	4.6	9.2	50.1
NC-16	"	30	100	29.0	71.0	16.7	4.5	9.0	45.7
NC-17	"	60	200	58.6	70.7	45.5	12.3	12.3	52.1
NC-18	"	60	200	53.3	70.9	89.8	24.2	24.2	71.6
NC-19	"	60	200	67.7	66.1	64.5	17.4	17.4	66.1
NC-20	29	120	400	130.9	67.1	157.2	42.3	21.2	72.0
NC-21	30	120	400	191.4	52.2	95.0	25.7	12.7	71.0
NC-22	12/1	--	Si _x F _y recycle (from NC-16-21)			172.8	46.6	--	76.8 (overall)
NC-23	1/23/78	30	101	50.3	50.2	27.0	7.3	14.3	76.5
NC-24	25	60	202	86.0	57.4	81.8	22.0	22.0	83.0
NC-25	26	60	202	71.2	64.8	126.2	34.0	34.0	97.7
NC-26	28	60	202	95.1	52.9	109.5	29.5	29.5	101
NC-27	28	--	Si _x F _y recycle (from NC-23-26)			47.2	12.7	--	98.2 (overall)
NC-28	3/30	30	133	94.3	29.1	12.7	3.4	13.6	80.5
NC-29	"	15	110	50.8	53.8	(COIL CRACKED UPON WARMING)			
NC-30	4/6	15	70.5	46.2	34.5	10.2	2.8	11.2	80.0
NC-31	7	15	41.0	13.0	68.2	24.7	6.7	13.3	92.0
NC-32	10	120	607	158.8	73.8	419.5	112.9	56.5	95.3 (e)
NC-33	11	120	562	(COIL CRACKED UPON WARMING)					
NC-34	5/10	15	50.0	21.3	57.4	96.7	26.0	34.7	93.1
NC-35	"	15	72.5	33.6	53.7				
NC-36	11	15	79.5	37.4	52.9				
NC-37	12	120	661	268.6	59.4	379.8	102.3	51.1	98.1
NC-38(f)	15	120	639.5	243.3	62.0	395.5	106.5	53.2	99.9(d)
NC-39(f)	24	120	611	212.7	65.2	362.2	97.5	48.8	94.0(e)
NC-40	25	120	632.5	(COIL CRACKED UPON WARMING)					

(a) Bed parameters (mg Si): Diameter 1"; Length 53.5 cm; Temperature 1330°C inlet, 1350 (center), 1300 outlet; particle size 5-20 mesh mg Si; Weight 396 gm mg Si + 4.0 gm SiO₂.

(b) Calculated value.

(c) Measured value.

(d) Includes Si_xF_y recycle.

(e) Si_xF_y recycle will increase this value 3-6%.

(f) Inlet pressure at start of run NC-38 was 155 torr, run NC-39 was 300 torr; inlet pressure at finish of run NC-38 equaled 98 torr, run #2 equaled 99 torr; downstream pressures of 0.50 and 0.55 torr were observed for runs NC-38 and 39 respectively.

which leads to higher homologue conversion efficiencies. For example, in runs NC-23 through 26, NC-30 through 33 and NC-34 through 38 the increasing conversion efficiency trend is readily apparent. After runs NC-26, 29, 33, 38, and 40, the silicon was harvested and the bed replaced. Run NC-38 includes a Si_xF_y recycle and demonstrates within the accuracy of the monitoring equipment ($\pm 0.1\%$) that all of the SiF_4 introduced into the reactor is recovered as SiF_4 .

The mass of SiF_4 delivered during runs NC-1 through 27 was monitored by a calibrated mass flow controller. The mass flow controller used in runs NC-23 through 26 was not functioning properly and may have led to erroneous results. The mass of SiF_4 delivered in runs 28 through 40 was determined by a precise balance to ± 0.5 gm.

A mechanical design problem, which has surfaced during the high volume runs, is the cracking of the low temperature quartz coil (runs NC-29, 33 and 40). In each case the coil cracked upon warming the polymer to ambient, during which time the polymer is expanding which could stress the quartz coil. This mechanical problem, though annoying, is not expected to present problems in the engineering demonstration runs because of the increased mechanical strength of the metallic construction materials proposed for the low temperature heat exchanger.

During this past quarter it was suspected that Step I of the transport reaction may be undergoing an induction period. Specifically the first runs (e.g., runs NC-23, 28, 30) on a fresh mg silicon charge have been observed to yield low SiF_4 to SiF_2 conversion efficiencies on Step I when high SiF_4 flow rates are employed. (≥ 300 gm SiF_4 /hr). The latter runs on the same charge would demonstrate typical conversion efficiencies under the same conditions. Prior to runs NC-34 and 39 argon was passed through the mg silicon bedheated to 1300°C . In these runs no induction period was observed.

The plans for the near-continuous reactor for the forthcoming quarter include increasing the SiF_4 flow rates from 300 gm/hr to 600 and 1000 gm/hr

through the 1 inch diameter reactor tube to observe kinetic or heat transport limitations. In light of the fact that during the course of experiments on the near-continuous reactor, flow rates (and transport rates) have increased over an order of magnitude, without affecting Step I conversion efficiency, considerably higher rates may well be within reach. Furthermore, as pointed out by Katzen Assoc., the current work being supported by the D.O.E. on coal gasification has demonstrated that heat fluxes much greater than we presently require are readily obtainable. One especially interesting design employs Si-C "glow bars" within the reactor. Even though this type of design most likely will not be used on the present near-continuous reactor, it will be considered for the engineering demonstration runs scheduled for the middle of next year.

POLYMER CONDENSATION

Parameters which affect the condensation of SiF_2 are of considerable interest for plant design considerations. Previous work⁵ has centered on the "conditioning" effect by predeposition on a substrate. The efficiency of a simple jacket condenser appeared to be increased by approximately 8% when depositing on polymer-coated glass. Preliminary condensation experiments indicated that the temperature of a substrate went through a maximum during a three hour run. This appeared to be related to a pressure change which occurred in the condenser.

These observations led to further work during which pressure emerged as an important variable.

A. Effect of Substrate (0°C)

To examine the effect of a substrate, two matched experiments were run consecutively to minimize observed variations in step 1 reactor conversion efficiency. Also, short run times (30 mins) were necessary to minimize the effect of pressure build-up.

Prior to the substrate run 97, glass spheres of average diameter 2.497 cm ($\hat{S} = 0.074$ cm) were loaded into the condenser. The temperature of these was monitored via a thermocouple well located at the approximate center. Details of the experimental method have been reported previously³. During both runs coolant temperature was maintained at 0°C and 42.4 g SiF₄ passed through mg Si within a period of 30 mins. Results are given in Table X, (experiments 1 and 2,) some conclusions are;

1. The presence of a substrate increases condenser efficiency and, in view of the relative surface areas of the inner lining (790 sq. cm) and the substrate (1898 sq. cm), condensation may be a function of surface area. However during the experiment condensation did appear to occur selectively on the walls of the condenser. This may be due to the lower temperature of the condenser wall. The maximum recorded temperature differential was 11°C. Also, once deposition was initiated, condensation of SiF₂ would occur faster on the predeposited polymer.
2. From Table X, experiments 1 and 2, reactor conversion efficiency is reduced by approximately 10%. Back pressure increase became significant during the last six minutes of the run.
3. The apparatus consists of three discrete units, (i) the hot reactor tube, which is not weighed, (ii) condenser and (iii) liquid N₂ trap, both of which are weighed. Any disparity between the expected weight of polymer and the amounts collected in the weighed units (Polymer Lost in System - Table X) can only be explained by assuming that this material is lost in the reactor. Incorporation of a second liquid N₂ trap (later experiment) confirmed that any polymer loss to the vacuum system is negligible.

During this experiment the relative difference between the amount of material lost in the system with and without substrate (2.4 g) may not be relevant. However this loss factor becomes significant when high pressures (>2 torr) prevail in the condenser for a substantial fraction of the run time. Polymer is forced to condense in the cool areas of the reactor. Visual examination of the cold SiF₄ reactor tube has revealed build up of a material which varied in appearance from a grey powder to metallic plates and nodules in the hot zone.

TABLE X
Effect of substrate 0°C on condensation efficiency

	1	Experiment 2	3
	No Substrate	Substrate	No Substrate
Unreacted SiF ₄ collected in liquid N ₂ trap (g)	4.1	7.1	17.0
Stage 1 conversion (%)	92.3	83.2	59.9
Calculated weight of polymer formed (g)	49.4	44.5	32.2
Gain in condenser weight (g)	10.9	26.2	5.3
Condenser efficiency (%)	22.1	58.9	16.5
Polymer collected in liquid N ₂ trap (g)	25.0	2.4	3.8
Polymer lost in system (g)	13.5	15.9	23.1
Condenser pressure (torr)	1.2	see below	4.0
Coolant temperature (°C)	0	0	0

Run Time (mins)	0	5	10	15	20	24	25	25	27	28	29
Condenser Pressure (torr)	0.95	1.0	1.1	1.2	1.2	2.0	2.0	2.5	3.0	4.0	5.0
Substrate Temperature (°C)	0	2	5	7	10	11	11	10	9	8	7

B. Effect of Pressure

The results suggest that substrate-induced pressure can materially affect the efficiency of the $\text{SiF}_4 \rightarrow \text{SiF}_2$ conversion.⁵ To investigate this in more detail, and to estimate the effect of surface area, a 200 minute run was planned with a smaller substrate. The coolant was set at 0°C , (25°C higher than the previous "long" run) because of the desire to work at intermediate efficiencies (30-90%).

200 glass spheres of mean diameter 1.572 cm ($S = 0.055$) were loaded into the condenser and SiF_4 (2.82.7 g) passed over a period of 200 mins. The reactor conversion was measured by stopping the gas flow and directly weighing the amount of polymer and SiF_4 captured by the liquid N_2 trap. Trap removal after the first 30 minutes is registered as a fall in the substrate exotherm (Figure 8). To preserve continuity the condenser was weighed only at the end of the run. The results are shown in both Table XI and Figure 8. Some general comments are:

1. Pressure and temperature behaved similarly to the previous 180 minute run. After an induction period the pressure of SiF_2 + unreacted SiF_4 rises to an approximately constant value. Also the substrate temperature peaks before the pressure changes, then falls to an equilibrium value which is a few degrees above that of the coolant.

2. The effect on substrate temperature of weighing the SiF_4 during the second conversion determination is not measurable. This is due to the small temperature differential between the condenser and substrate.

3. The general shape of the curves can be explained by the observed changes in stage 1 conversion. Substrate temperature increases as the exothermic condensation proceeds. However, the deposited polymer impedes the flow of SiF_4 and product SiF_2 , causing the partial pressure of SiF_2 to rise which in turn may either (i) favor the reverse reaction or (ii) cause

FIGURE 8.

TABLE XI

	Run	Period (mins)	
	0-30	30-170	170-200
1. Unreacted SiF ₄ collected in liquid N ₂ trap(g)	4.3	106.9	35.0
2. Polymer " " " " " (g)	12.3	9.5	0.2
3. Stage 1 conversion (%)	89.8	55.5	17.4
4. Calculated weight of polymer formed (g)	38.2	115.5	9.4
5. " " " " in condenser & reactor (g)	25.9	106	9.2
6. Overall gain in condenser weight (g)		55.7	
7. Overall condenser efficiency (%)		39.6	
8. Total polymer lost in system		101.1	
9. Temperature and pressure variation	See Figure 8		

polymer to precondense in the reactor. The latter explanation is favored, in view of the calculated amount of polymer lost in the reactor. The substrate temperature falls because the exothermic deposition of SiF_2 is no longer occurring in the condenser or occurs to a lesser extent than at lower pressures.

4. Assuming the above to be correct, then the overall condenser efficiency will depend on the ratio of time spent at high and low pressure. However the previously reported 180 min run suggests that, if the condenser is run at -25°C , the efficiency is increased by a factor of approximately 2. Hence, temperature remains a significant parameter.

5. If relatively large smooth spheres induce a deleterious pressure change within 90 minutes, then it is likely that a bed of irregular shaped silicon chunks would accelerate such a change, as in a packed Si condenser bed.

6. For this run the overall amount of polymer lost in the reactor is significant. The amount of material deposited between the hot zone and the condenser represents 28% of the theoretically obtainable weight of polymer.

THERMAL ANALYSIS OF $(\text{SiF}_2)_x$ POLYMER

Differential Scanning Calorimetry (DSC) is an instrumental method which measures the enthalpic changes of a system occurring over a desired temperature range. The underlying principle, which has been outlined in a previous report,⁷ is that temperature changes of the material under study are measured by a thermocouple in contact with the material. This is com-

pared to the output of a thermocouple in contact with reference material. The reference material should have no change in heat capacity over the temperature range that is to be studied. Data output consists of a graph of heat evolved or taken in by the sample as a function of temperature. Any peaks on the baseline correspond to exothermic or endothermic transitions. The position of the peak indicates the temperature of such a transition. The area is directly related to the magnitude of the transition.

The polymer was handled in a nitrogen-purged glove box due to its pyrophoric character. A cold weld press was loaded into the glove box and the polymer sealed in gold pans. During the initial stages of this work the pans ruptured when the temperature reached the range 290° to 310°C. Cleaning in inorganic acids and organic solvents and reducing the sample amounts to 1 to 3 mg (close to the detection limits of the instrument (DuPont 900)) ensured that the sealed pans did not rupture.

To obtain quantitative data a calibration coefficient (E) was determined, using known standards, over the temperature range of interest.

$$E = \frac{[\Delta H \text{ sample (m cal/mg)}] [\text{sample mass (mg)}] [\text{Heating Rate} (^{\circ}\text{C)/min}]}{[\text{Peak Area (sq.in)}] [\text{Y-axis sensitivity} (^{\circ}\text{C})] [\text{X-axis sensitivity } ^{\circ}\text{C/in}]}$$

Plotting E vs. peak temperature allows an estimate of the value of E for a specific temperature. Using this value of E in the relationship below:

$$\Delta H(\text{mcal/mg}) = \frac{[E] [\text{Peak Area (sq.in.)}] [\text{Y-axis sensitivity, } (^{\circ}\text{C/in})] [\text{X-axis } + \frac{\text{sensitivity} (^{\circ}\text{C/in})]}{[\text{Sample Mass (mg.)}] [\text{Heating Rate} (^{\circ}\text{C)/min}]}]$$

will give a quantitative estimate of the ΔH value for each significant peak. The area of the peaks was measured using Simpsons Rule. Overall precision was estimated to be within 15% of what the true values should be, which is quite reasonable considering the technique and material handling problems encountered.

To determine if a peak was due to a phase change, the sample was cooled and the region in which the peak appeared was again scanned. Reappearance of the peak indicated a phase change had occurred as opposed to an irreversible chemical reaction.

Results

A total of ten runs were performed on the polymer, during six of these runs the experiment had to be terminated due to can rupture. One variable of interest was heating rate. Sharper peaks result from faster rates. For this reason, the results in Table XI reported below are given for 10°C/min. and 20°C/min. Where no value for ΔH is reported, this was due to high noise levels at that temperature range. During the conversion of one gram of homologues to silicon and silicon tetrafluoride approximately 44 cal are released. Because the molecular weight of the polymer is unknown it was not possible to estimate a molar heat of formation of the homologues.

The reversible endotherm observed at 97°C may correspond to the heat required to melt the "polymer," i.e., to form liquid homologues. As the temperature is raised to the critical range 276° - 286°C, a strongly exothermic transition occurs. This correlates with the decomposition temperature under nitrogen measured by T.G.A.⁷ At this point the can may rupture. During experiments when rupture did occur, silicon (in the form of brown powder) was forced out of the can into the adjacent region. Enthalpy measured for this peak corresponds to

At this temperature the homologue mixture is likely to be in the gaseous state. ΔH for the liquid $\rightarrow$ gas transition was not observable. No doubt homologue rearrangements occurring above the melting point preclude a well-defined vaporization transition temperature.

$$\begin{aligned} \text{Now, } \Delta H_F \text{ SiF}_4 &= -386.1 \text{ Kcal mole}^{-1} \quad (\text{JANAF, 1965}) \\ &= 3.71 \text{ Kcal gm}^{-1} \end{aligned}$$

TABLE XII
DSC data at 1 atmosphere

Sample	Weight(mg)	Heating Rate °C/min	Type	Peaks Position °C	ΔH (mcal/mg)
1	0.804	10	Endo	98	High Noise
			Exo	276	42.8
			Endo	363	91.3
2	1.565	20	Endo	96	2.25
			Exo	282	44.17
			Endo	363	8.47
3	1.347	20	Endo	98	2.04
			Exo	286	50.3
			Endo	363	High Noise
4	2.333	10	Endo	98	2.28
			Exo	276	40.21
			Endo	363	8.89

Summary

Range Peak Temperature	Type	Mean ΔH (std. deviation)
96-98°C	Endotherm	2.19 ± (0.13) cal/gm
	Irreversible	
276-286°C	Exotherm	-44.37 ± (4.28) "
363°C (sharp)	Endotherm	8.83 ± (0.33) "

Assuming the homologues can be represented by $n(\text{SiF}_2)_x$

$$\Delta H_F^X = \frac{\Delta H_F^{\text{SiF}_4} - \Delta H(\text{measured})}{n} = \frac{-3.71 - (-0.045)}{n}$$

$$\therefore \Delta H_F^X = -3.665 \frac{1}{n} \text{ Kcal gm}$$

Because the value of n is unknown it is not possible to calculate the heat of formation of the homologues.

The effect of pressure on the reaction mechanism has yet to be determined. However, assuming the pathway is identical to that under vacuum, it would be of considerable interest to determine the exact composition of the homologues prior to harvesting.

Origin of the well-defined endotherm at 363°C remains unknown. A peak at this temperature did not appear in the previous³ mass spectrum vs. temperature work. A possible explanation would be release of silicon tetrafluoride from the silicon. However, this is unlikely in view of the small amounts included in the lattice.

CRYSTAL GROWTH

A small ingot was grown from the gray to brown powder material produced from Run NC-38 on the near continuous reactor. The procedure used was similar to the previously reported experiments⁴.

Two batches of powder (46g and 24.9g) were partially melted in an rf induction-heated crystal furnace. Since melting was not complete due to the problems of melting powders and the presence of a glassy material in the melt, these batches were etched, after cooling, and combined for the third experiment. Etching was required to removed quartz adhering to the silicon from the crucibles. The ingot pulled from the combined charge was 0.95 Ωcm , "P" type at the seed end. The tang was 2 to 7 Ωcm "N" type.

The glassy material mentioned above contained only oxide as determined by Auger spectroscopy. The source was probably adsorbed oxygen on the surface of the fine powder used as feed. The etching process may well have removed some impurities; however, since the whole silicon sample was recharged in the third experiment, purification by segregation is not expected. Emission spec. analysis of the samples will further clarify this.

PROCESS PLANT COSTING

The projected process flow diagram, mass balance, energy balance, and reactor and harvester sizing for a 1000 metric ton per year plant were given on pages 26 to 31 of the Technical Quarterly Report No. 9 in April, 1978. The process flow diagram is shown again in Figure 9. Based on this information and energy losses of 150% in the step 1 reactor rather than the previously assumed 30%, an estimate of the purchased cost of the major pieces of equipment has been made as shown in Table XIII.

The costs for the reactor are based on conversations with Mr. George Johnston of Astro Industries in Santa Barbara regarding the furnace and Mr. Robert Pijaszek of Ultracarbon in Bay City, Michigan. regarding the graphite reactor tube.

SiF₄ PURIFICATION OF MG Si

Figure 9.

TABLE XIII

MAJOR PROCESS EQUIPMENT - 1000 MTON/YR

<u>TYPE/FUNCTION/MTLS OF CONST.</u>	<u>DUTY</u>	<u>SIZE</u>	<u>COST, \$1000</u>
mg Si storage hopper	2 wks	1.3×10^4 gal	12
Si product storage	2 "	1.1×10^4 "	10
SiF ₄ storage @ -90°C	3 "	3×10^3 "	5
Reactor (11)/graphite +		16" IDx48"	660
Inlet mg Si hopper (11)	2½ hrs	8" IDx24"	17
Outlet slag hopper (11)	12 "	8" IDx24 "	15
Baffle (11)		16" IDx48" (42 gal)	22
Polymerization pre-cooler	5.5×10^5 Btu/hr (U = 80)	14 ft ²	3
Main polymerization-scraper condenser	1.9×10^6 " (U = 20)	951 ft ²	119
Recycle polymerization pre-cooler	3×10^5 " (U = 80)	12 ft ²	3
Recycle polymerization-scraper condenser	1.1×10^5 " (U = 20)	54 ft ²	8
Harvester (11)		16" IDx48"	462
Inlet seed hopper (11)		8" IDx24"	15
Outlet sg Si hopper/cooler (11)		8" IDx24"	22
SiF ₄ condenser-scraper condenser	2.1×10^5 Btu/hr	123 ft ²	18
SiF ₄ storage for recycle @ -90°C	1 day	3×10^3 gal	5
SiF ₄ vaporizer	1.5×10^5 "	52 ft ²	4
Compressors		100 hp	60
TOTAL PURCHASED COST			1460

The costs and overall U of 20 Btu/(ft²-°F-hr) for the scraper condensers are based on discussions with Mr. Louis Kuhl of the Vogt Machine Co. in Louisville, Ky.

The total purchased cost of process equipment is seen in Table XIII to be \$1.46 MM based on 1975 dollars. This, when used per the standard format that is used by Lamar is seen in Table XIV to give a fixed capital investment of just under \$9.1 MM for a 1000 metric ton per year plant. Using this capital together with materials and operating costs as shown in Table XV gives a total product cost of \$7.71/kg Si.

The effect of a higher or lower than estimated capital investment on the product cost is shown in Figure 10. It would take \$15 MM (65% more than the \$9.1 MM capital estimate) to bring the product cost up to \$10/kg. Doubling the SiF₄ cost would add \$0.54/kg. Doubling the electricity usage would add \$0.41/kg.

TABLE XIV

ESTIMATION OF PLANT INVESTMENT FOR SiF_4 PURIFICATION PROCESS

		Investment \$1000
1.0	DIRECT PLANT INVESTMENT COSTS	
1.	Major Process Equipment Cost	\$1460.00
2.	Installation of Major Process Equipment	43% 627.80
3.	Process Piping, Installed	74% 1080.40
4.	Instrumentation, Installed	19% 277.40
5.	Electrical, Installed	10% 146.00
6.	Process Buildings, Installed	10% 146.00
1.1	SUBTOTAL FOR DIRECT PLANT INVESTMENT COSTS (PRIMARILY BATTERY LIMIT FACILITIES)	3737.60
2.0	OTHER DIRECT PLANT INVESTMENT COSTS	
1.	Utilities, Installed	48% 700.80
2.	General Services, Site Development, Fire Protection, etc.	12% 175.20
3.	General Buildings, Offices, Shops, etc.	14% 204.40
4.	Receiving, Shipping Facilities	21% 306.60
2.1	SUBTOTAL FOR OTHER DIRECT PLANT INVESTMENT COSTS (PRIMARILY OFFSITE FACILITIES OUTSIDE BATTERY LIMITS)	1387.00
3.0	TOTAL DIRECT PLANT INVESTMENT COST, 1.1 + 2.1	5124.60
4.0	INDIRECT PLANT INVESTMENT COSTS	
1.	Engineering, Overhead, etc.	55% 803.00
2.	Normal Cont. for Floods, Strikes, etc.	71% 1036.60
4.1	TOTAL INDIRECT PLANT INVESTMENT COST	1839.60
5.0	TOTAL DIRECT AND INDIRECT PLANT INVESTMENT COST, 3.0 + 4.1	6964.20
6.0	OVERALL CONTINGENCY	30% 2089.30
7.0	FIXED CAPITAL INVESTMENT FOR PLANT, 5.0 + 6.0	9053.50

TABLE XV

ESTIMATION OF TOTAL PRODUCT COST WITH Si_xF_y RECYCLE
(\$ PER KG SG SI PRODUCED)

1. DIRECT MANUFACTURING

1. RAW MATLS MG SI 1.09 KG X \$1.00/KG	1.09
SiF ₄ 0.24 KG X \$1.00/LB X 2.2 LB/KG	0.54
2. DIRECT OP. LABOR 10 MEN/SHIFT	
5 SKILLED @ 6.90/HR X .0372 = .26	0.44
5 SEMI-SK @ 4.90/HR X .0372 = .18	
3. UTILITIES ELECTRICITY 13.8 KW-HR X \$.03/KW-HR	0.41
REFRIGERANT 0.00155 MM BTU X \$85/MM BTU	0.13
0.015 MM BTU X \$24.4/MM BTU	0.37
4. SUPERVISION/CLERICAL 15% OF 1.2	0.07
5. MAINT. & REPAIRS 10% OF FIXED CAPITAL (\$9.1 MM)	0.91
6. OPERATING SUPPLIES 20% OF 1.5	0.18
7. LABORATORY CHARGE 15% OF 1.2	0.07

2. INDIRECT MANUFACTURING

1. DEPREC./LOCAL TAXES/INSURANCE/INTEREST, 21% OF FIXED CAP.	1.91
(10%) (2%) (1%) (8%)	
3. PLANT OVERHEAD, 60% OF (1.2 + 1.4 + 1/2 1.5)	0.58
4. TOTAL MANUFACTURING COST	6.70
5. GENERAL EXPENSES, ADMIN/DIST. & SALES/R & D 15% OF MAN. COST	1.01
(6%) (6%) (3%)	
6. TOTAL COST OF PRODUCT	7.71

SiF_4 PURIFICATION PROCESS

Figure 10. SG SILICON PRODUCTION COST VS. FIXED CAPITAL INVESTMENT FOR SiF_4 COST OF \$1 AND \$2/LB.

III. CONCLUSIONS AND RECOMMENDATIONS

Motorola's $(\text{SiF}_2)_x$ polymer transport purification program has demonstrated chemical process feasibility (Phase I) at transport rates ≥ 50 gms/hr on consecutive multi-hour runs. Furthermore, single crystal Czochralski type ingots pulled from metallurgical grade silicon purified by the $(\text{SiF}_2)_x$ polymer transport purification process revealed that the silicon purity exceeds the requirement of "solar grade" silicon. The total cost of semiconductor grade silicon purified in this fashion is estimated to be \$7.71/Kg (January 1976 dollars).

An aggressive program plan has been adopted to demonstrate engineering feasibility (Phase II) on a 1000 gm/hr mini-plant by July 1979. The mini-plant will provide necessary engineering data for design and scaleup to larger sizes.

Therefore it is recommended that the project proceed through Phase II with the design, construction and demonstration of the 1000 gm/hr mini-plant. The successful demonstration of the mini-plant and the economic considerations derived from its operation will clearly define the production potential for the $(\text{SiF}_2)_x$ polymer process.

IV. NEW TECHNOLOGY

The following new technology items have been uncovered during this program.

I. Description - Bakeable, Double Action, Quartz Ball Valve

Innovators - William M. Ingle

Carl Goetz

Progress Reports - Technical Progress Report No. 18 - July 1977

Pages - Report No. 18, Pages 8, 9, and 10

Date Reported - December 9, 1977

II. Description - Purification of Mg Silican Via Atmosphere Control II

Innovators - William M. Ingle

Stephen W. Thompson

Robert E. Chaney

Progress Reports - Technical Quarterly Report No. 6

Pages - Report No. 6 Page 11 - 17 and Appendix I

Date Reported - December 9, 1977

V. PLANS

As of mid-June, agreement was reached between JPL and Motorola as to the work objectives for proceeding to Phase II (initial six months) of the program. The major purpose of the first six months of Phase II is to design an experimental facility capable of demonstrating the engineering feasibility of producing silicon at a rate equivalent to 1000 grams per hour in each cycle of the process. The detail design of the equipment to conduct this engineering demonstration will be carried out by an outside engineering design/consultant firm. As recommended by JPL, we made initial contact with Katzen Associates on May 31. Since then, we have sent them background information and had our first formal meeting with them on June 23. Katzen Associates has said that they have manpower available for our design as soon as we complete the necessary formalities to a contract.

Although only the first six months are agreed to at this point, Figure 11 shows the complete year to give a perspective as to the objectives. Note the October completion of the system design and review by JPL prior to going ahead with the fabrication and assembly of the system. Due to the increased emphasis on the engineering aspects of the program, Chemist John Jackson is transferring to another position within Motorola while Chemical Engineer Manu Patel will join us the first week in July.

Parallel to the engineering design effort, design support and R & D work will continue with the emphasis being on obtaining information related to engineering scale-up needs as shown in section 3 and 4 on Figure 10.

Figure 11.

TITLE

SiF₄ PURIFICATION - JPL CONTRACT No. 954442

6/2/78

LEGEND

△ SCHEDULE EVENT
ONE TIME

▲ COMPLETED EVENT

△ RESCHEDULED EVENT
NUMBER INDICATES
RESCHEDULING SEQUENCE

△-△ SCHEDULED EVENT TIME
DATE

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APPENDIX

MOTOROLA SiF_4 PURIFICATION THERMODYNAMICS

(authored by S. Thompson & R. Chaney)

I. INTRODUCTION

The purpose of this communication is to address the questions which arose at our May 2, 1978 meeting concerning the use of the JANAF Tables (1967 and 1976) in making thermodynamic calculations and engineering predictions.

The following are a series of calculations intended to illustrate the problems and underscore the necessity of care in using tabulated values for these functions. The following assumptions were made:

- 1) Ideality of the gases was assumed
- 2) The silicon bed contains a large excess of Si
- 3) The vapor pressure of Si at the temperatures in question is negligible
- 4) Symbols used are the same as the JANAF Tables

II. CALCULATION OF ΔG OF REACTION

In Table I are listed the values of ΔG° for SiF_2 and SiF_4 at three different temperatures used by Motorola (1623°K), Margrave (1423°K) and Pease (1473°K). These values were interpolated from the 1967 and the 1976 JANAF Tables.

Based on the table values and standard free energy relationships,

$$\Delta G_{\text{reaction}} = \Delta G^\circ + RT \ln K_p$$

$$\Delta G = 2 \Delta G_{\text{f}(\text{SiF}_2)}^\circ - \Delta G_{\text{f}(\text{SiF}_4)}^\circ + RT \ln \frac{P_{(\text{SiF}_2)}^2}{P_{(\text{SiF}_4)}},$$

the $\Delta G_{\text{reaction}}$ was calculated from several Motorola experimental runs and for the stated conditions of Pease and Margrave. The

TABLE I
 ΔG_f° Values from JANAF Tables

TEMPERATURE	$\Delta G_f^\circ(\text{SiF}_2)$ (Kcal/mole)		$\Delta G_f^\circ(\text{SiF}_4)$ (Kcal/mole)	
1423°K		<u>Difference</u>		<u>Difference</u>
(1967)	-157.706		-336.913	
(1976)	-150.591	4.5	-337.127	.064
1473°K				
(1967)	-157.940		-335.188	
(1976)	-150.873	4.5	-335.408	.065
1623°K				
(1967)	-158.597		-329.990	
(1976)	-151.677	4.4	-330.229	.072

results are listed in Table II. Use of the 1967 tables yields negative free energies under all conditions, while the 1976 table produces positive free energies of reaction. This indicates that, in all cases, using the new JANAF Tables under the stated conditions, no reaction would have been observed. Figure 1 graphically illustrates these results. The parallelograms for the work of Margrave and of Pease illustrate the reported pressure ranges under which they conducted their experiments.

These results show the effects that a small change in a large value (such as <5% in $\Delta G_f^O(\text{SiF}_2)$) can have, when small differences in large numbers are used in calculations. If the latest JANAF values for ΔG_f^O are in question then the enthalpy values must also be suspect.

If we were to assume that the system described on line 1 from Table II were at equilibrium, then $\Delta G_{\text{reaction}} = 0$. Further using the $\Delta G_f^O(\text{SiF}_4) = -330.229$ Kcal/mole from the 1976 Table would give a calculated value for $\Delta G_f^O(\text{SiF}_2)$ of -154.746, which lies between the two (1967 and 1976) JANAF values. The % difference is 2% from the 1976 JANAF value.

III. CALCULATION OF % CONVERSION (α)

In the reaction,

let α be the degree of reaction or percent conversion of SiF_4 to SiF_2 . Thus, the concentration of $\text{SiF}_2 = 2\alpha$, $\text{SiF}_4 = 1-\alpha$ and $\text{Si} = 1-\alpha$. Again, assuming Si is in excess and the vapor pressure negligible, the total number of moles in the gas stream is $(1+\alpha)$ times the original content of SiF_4 and

TABLE II

	Summary of $\Delta G_{\text{reaction}}$					Calculations	Calc. $\Delta G_{\text{reaction}}$	
	P	T	% Eff.	P_{SiF_2}	P_{SiF_4}	$RT \ln \frac{P_{\text{SiF}_2}^2}{P_{\text{SiF}_4}}$	Tables Used	
	(Torr)	(°K)	(%)	(Torr)	(Torr)	(Kcal/mole)	1967	1976
							(Kcal/mole)	
1) Motorola ⁽²⁾	0.2	1623	77	.175	.025	-20.737	-7.941	+6.138
2) Motorola ⁽³⁾	0.7	1623	74.0	.518	.182	-20.14	-7.344	+6.735
3) Motorola	20	1623	34.9	6.98	13.02	-17.136	-4.34	+9.739
4) Motorola	2.2	1623	53.8	1.184	1.016	-20.354	-7.558	+6.521
5) Margrave ⁽⁴⁾	0.2	1423	65	0.13	0.07	-22.774	-1.273	+13.171
6) Margrave	0.1	1423	65	.065	.035	-24.734	-3.233	+11.211
7) Pease ⁽⁵⁾ (inlet)	3	1473	40	1.2	1.8	-20.088	-0.78	+13.574
8) Pease (trap)	0.05	1473	40	.02	.03	-32.051	-12.743	+1.611

(1) Pressures in atmospheres

(2) Motorola Quarterly Report No. 6 - batch reactor

(3) Motorola Monthly Report #25, Table II - near continuous reactor

(4) J. Amer. Chem. Soc. 37, 3819 (65); reported pressure from 0.2 to 0.1 torr

(5) U.S. Patent #2,840,538, 1958; reported pressure from 3 to 0.05 torr

Figure 2. Graphical representation of the $\Delta G_{\text{reaction}}$ from Table II based on values from both the 1967 and 1976 JANAF values for ΔG_f° of SiF_2 and SiF_4 .

$$K_p = \frac{p^2_{(\text{SiF}_2)}}{P_{(\text{SiF}_4)}}$$

where p is the partial pressure of the gas and P_t is the total pressure.

$$p_{(\text{SiF}_2)} = \left(\frac{2\alpha}{1+\alpha}\right) P_t; \quad p_{(\text{SiF}_4)} = \left(\frac{1-\alpha}{1+\alpha}\right) P_t$$

$$K_p = \frac{4\alpha^2 P_t}{1-\alpha^2}$$

or

$$\alpha = \left(\frac{K_p}{K_p + 4P_t}\right)^{\frac{1}{2}}$$

At equilibrium, $\Delta G_{\text{reaction}} = 0$ and

$$\Delta G^0 = -RT \ln K_p$$

$$\ln K_p = \frac{\Delta G^0}{-RT}$$

Using the two JANAF Tables in question, the values for K_p were calculated for the three temperatures discussed above. This allowed the relationship between α and total pressure to be calculated. Figure 2 shows the curves for 1423°K. The bar illustrates the results of Margrave's work. Similarly in Figure 3, Pease's results are superimposed on the curve for 1473°K. In Figure 4 are shown the theoretical curves for 1623°K. The large difference in the curves for each case arise from taking the small differences between large numbers and then raising them to an exponent.

The 1623°K results are particularly interesting. If we take several examples of our experimental data taken under a variety of conditions and equipment as shown in Figure 4, we see that they fall near a curve between those predicted by

Figure 2. Plot of α vs. $\log P_t$ for 1423°K calculated from ΔG_f^0 values from JANAF Tables

A) 1967 Tables

B) 1976 Tables

C) Mangrove

Figure 3. Plot of α vs. $\log P_t$ for 1473°K calculated

From JANAF Tables

A) 1967 Tables

B) 1976 Tables

C) Pease's data

Figure 4. Plot of α vs. $\log P_t$ for 1623°K calculated from ΔG_f^0 values from JANAF Tables

A) 1967 Tables

B) 1976 Tables

C) Based on experimental data

1) batch reactor, Quarterly Report No. 7
(95% confidence interval for P_t and % conversion; 15 data values)

2) batch reactor, Quarterly Report No. 6

3) near-continuous reactor, Monthly Report No. 25, Table II

4) batch reactor, Monthly Report No. 25

1967 and 1976 JANAF Tables. Again, calculation of $\Delta G_f^\circ(\text{SiF}_2)$ using the curve C), and using the 1976 value for $\Delta G_f^\circ(\text{SiF}_4)$ yields -153,621 Kcal/mole, intermediately between the reported values and 1.3 % different than the 1976 value.

IV. CONCLUSIONS

These results lead to the inescapable conclusion that the values listed in the JANAF Table (particularly 1976) are suspect. We submit that Motorola's reported experimental conversion efficiencies are consistent with theoretical calculations and the independent work of Pease and Margrave.

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