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**DEVELOPMENT OF A MODEL AND COMPUTER CODE TO DESCRIBE  
SOLAR GRADE SILICON PRODUCTION PROCESSES**

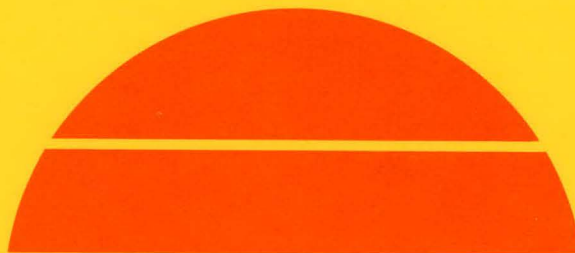
**Fourth Quarterly Report, July 1 to September 30, 1978**

**By  
R. K. Gould**

**November 1978**

**Work Performed Under Contract No. NAS-7-100-954862**

**AeroChem Research Laboratories, Inc.  
Princeton, New Jersey**



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# DEVELOPMENT OF A MODEL AND COMPUTER CODE TO DESCRIBE SOLAR GRADE SILICON PRODUCTION PROCESSES

FOURTH QUARTERLY REPORT

R. K. GOULD

NOVEMBER 1978

JPL Contract No. 954862  
DRL Item No. 4, DRD No. QR  
LSSA Silicon Material Task

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## FOREWORD AND ACKNOWLEDGMENTS

This report covers the period 1 July 1978 to 30 September 1978. During this period D.B. Olson and R. Srivastava contributed to the program.

## ABSTRACT

This program aims at developing a mathematical model, and a computer code based on this model, which will allow prediction of the product distribution in chemical reactors in which gaseous silicon compounds are converted to condensed-phase silicon. The reactors to be modeled are flow reactors in which silane or one of the halogenated silanes is thermally decomposed or reacted with an alkali metal,  $H_2$  or H atoms. Because the product of interest is particulate silicon, processes which must be modeled, in addition to mixing and reaction of gas-phase reactants, include the nucleation and growth of condensed Si via coagulation, condensation, and heterogeneous reaction.

During this report period mechanisms for the  $SiCl_4/Na$  and  $SiF_4/Na$  reaction systems were examined. Reaction schemes which include 25 elementary reactions were formulated for each system and run to test the sensitivity of the computed concentration and temperature profiles to the values given estimated rate coefficients. It was found that, for  $SiCl_4/Na$ , the rate of production of free Si is largely mixing-limited for reasonable rate coefficient estimates. For the  $SiF_4/Na$  system the results indicate that the endothermicities of many of the reactions involved in producing Si from  $SiF_4/Na$  cause this system to be chemistry-limited rather than mixing-limited.

Work is continuing on the problems of inserting particle nucleation and coagulation models into the code and is started on obtaining a suitable boundary layer code.

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## I. INTRODUCTION

This program aims at developing a mathematical model, and a computer code based on this model, which will allow prediction of the product distribution, as a function of time, in chemical reactors in which gaseous silicon compounds are converted to condensed-phase silicon. The reactors to be modeled are flow reactors in which silane or one of the halogenated silanes is thermally decomposed or reacted with an alkali metal,  $H_2$  or H atoms. Because the product of major interest is condensed-phase silicon, the model is being augmented to allow calculation of particle formation (via chemical reaction followed by nucleation), and the growth rate of the particulate Si via coagulation, condensation, and heterogeneous reaction. Since the efficiency of the particulate Si collection process will depend on the particle size distribution of the Si, this must also be computed.

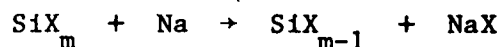
The basic model and computer code used as a starting point in developing this model is an axisymmetric, nonequilibrium, parallel stream mixing code which has been used for a number of years to treat systems in which parallel laminar or turbulent flows mix and undergo chemical reactions. This code, the Low Altitude Plume Program<sup>1</sup> (the LAPP code), treats only gas-phase chemistry; one of the major tasks is therefore the inclusion of "particle chemistry", i.e., nucleation and particle growth.<sup>2,3</sup> The code, as is implied by its name, treats the fluid dynamics of an open system. Thus modifications will also be required to account for the presence of reactor walls. We have obtained a version of a boundary layer code,<sup>4</sup> similar to LAPP in many of its details, and will be examining this code carefully in the next report period to see if it can be made to include particles so that it can be either coupled to the LAPP code or used by itself to compute phenomena occurring near reactor walls.

## II. TECHNICAL DISCUSSION

### A. TEST CALCULATIONS ON $SiF_4/Na$ AND $SiCl_4/Na$

Some of the major uncertainties in computing the rate of formation of free silicon ( $Si(g)$ , ...,  $Si(l)$ ) are the values of rate coefficients for the

primary stripping reactions, e.g.,



These reactions, some of which are endothermic, will largely determine whether the diffusion flame reactions being used to produce silicon will be rate limited by mixing or chemical kinetics. To test (i) the importance of accuracy in the values given for these rate coefficients (which must be estimated) and (ii) to see if the computed results agree at all with qualitative observation of these flames, a number of calculations have been made in which the values given these rate coefficients have been varied. It has been found that, for the configuration used (which corresponds roughly to the Westinghouse geometry<sup>5</sup> and is similar to, but about an order of magnitude larger than the AeroChem experiments now being conducted<sup>6</sup>) the  $\text{SiF}_4/\text{Na}$  reaction system is quite slow and chemistry-limited; the  $\text{SiCl}_4/\text{Na}$  is very fast and largely mixing-limited.

In Table I the mechanisms investigated are shown. The sets of rate coefficients listed for the first four reactions have been used in order to test for sensitivity to rate coefficient inaccuracies.

#### 1. $\text{SiF}_4/\text{Na}$

In Table II concentration profiles are listed for  $\text{NaF}(\text{g})$  and  $\text{Si}(\text{g})$  which were obtained using the two sets of rate coefficients for Reactions 1 through 4 of Table I. In these cases a jet of Na-containing gas at 1400 K (initial Na mole fraction = 0.5) mixes with gas at 2000 K containing  $\text{SiF}_4$  (initial  $\text{SiF}_4$  mole fraction = 0.5). In both flows the balance of the input gas is an  $\text{H}_2/\text{Ar}$  mixture at a volume (molar) ratio of 4/1. In the case listed "fast chemistry" in Table II, the pre-exponential factor for the Reactions 1-4 was  $2 \times 10^{-11}$ ; for "slow chemistry" these factors were  $2 \times 10^{-13}$ . The amount of free Si being formed is down a factor  $\geq 100$  in the slow chemistry case. Thus, for this case, the production of the major product of interest is chemistry-limited. The buildup of the product NaF is different by a factor  $\approx 10$  in these cases. (For the slow chemistry case our examination of  $\text{SiF}_3$  profiles shows this radical to be present in large amounts. The entire chain of reactions is held up by the highly endothermic Reaction 3.) The pre-exponentials used in the fast chemistry case are about as large as they can reasonably be. Thus in practice this system should (i) form free Si rather late, after considerable mixing has occurred, and (ii) release heat slowly since only those reactions occurring late in the scheme are exothermic. In regard to this last point, it

is noteworthy that in the fast chemistry case, temperatures are actually reduced at  $X/R = 10$ . At this stage in the reaction process endothermic reactions are dominant; temperature increases due to exothermic reactions will occur later in the flow, once condensation of  $Si(l)$  is well under way.

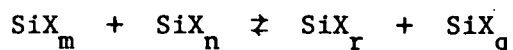
## 2. $SiCl_4/Na$

In Table III similar information is shown for the  $SiCl_4/Na$  system. In this case the rate coefficients for Reactions 1-4 has been varied a factor of 5 (rather than the factor of 100 used in the  $SiF_4/Na$  cases). It is clear that in this system the reactions forming  $NaCl(g)$  and  $Si(g)$  are mixing limited. The concentrations of these product species agree to within a factor of two. In fact the fast chemistry system has produced slightly less  $Si(g)$  and  $NaCl(g)$  because of higher temperatures which slow mixing a bit.\*

Thus in this case, as one expects from observations of these flames, mixing-limited chemistry and large heat release are encountered.

## 3. Simplified Reaction Schemes

A small amount of effort has been expended in performing calculations with simplified reaction schemes to cut computer run time. It has been found that excluding Reactions 16-22



has little (less than a factor of 2) effect on the rate of  $NaX$  and free  $Si$  production. Also, temperature and velocity are not affected appreciably. Thus these reactions (and probably the stripping reactions involving H-atoms, Reactions 5-8) can generally be left out.

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\* Calculations in which rate coefficients were decreased by a factor of 100 from the values used in the slow chemistry case show that even unrealistically low rate coefficients result in less than a factor of 2 decrease in  $NaCl(g)$  concentration. A factor of 10 to 50 drop is observed in the  $Si(g)$  concentration in this case as the  $SiCl_2$  and  $SiCl_3$  concentrations increase as Reactions 3 and 4 become somewhat limiting.

## B. CODE DEVELOPMENT

Work has centered on obtaining working versions of the particle chemistry<sup>2,3</sup> (nucleation, coagulation, condensation/evaporation) models incorporated in the large gas-phase code<sup>1</sup> (LAPP). There remain coding problems involved in how to make the transition from large "molecules" (i.e., small particles) which do not slip or maintain temperature differences with the gas phase and large particles which do. Also the nucleation model has been found to involve a very stiff set of equations which make this routine very costly to run. We will be obtaining different integration subroutines in the near future which are designed specially for such problems which, if need be, can be incorporated into the code to deal with this problem.

We have obtained a card deck of the GENMIX<sup>4</sup> boundary layer code which we are examining with the view of using it to attack the boundary layer problem for flow near reactor walls. The first problem will be to debug this code (which does not run at present). We plan to either (i) add parts of this code to LAPP to make it applicable for boundary layer problems or (ii) add two phase flow routines to GENMIX so that it can be used in conjunction with LAPP to describe the flow reactions of interest.

We have also obtained a listing of an elliptic code<sup>7</sup> which, while it contains provisions for only a single global gas-phase chemical reaction, can be used to obtain descriptions of recirculating interior flow fields. The code has been card-punched and will be tried during the next quarter.

## III. CONCLUSIONS

From test cases run during this report period it appears that in the  $\text{SiCl}_4/\text{Na}$  system, the rate of reaction will generally be limited by mixing. The mechanism formulated for this system gives rapid heat release and formation of free Si. For  $\text{SiF}_4/\text{Na}$ , on the other hand, the rate of free Si formation appears limited by the rate of Reactions 1-4 of Table I. Heat release is slow to occur and, in early parts of this flame, the temperature actually decreases as radicals ( $\text{SiF}_x$ ,  $\leq x \leq 3$ ) build up. Qualitative observations on these flames tend to support these calculations. The  $\text{SiCl}_4/\text{Na}$  flame is very vigorous and appears as a very hot diffusion flame. The  $\text{SiF}_4/\text{Na}$  flame is a very diffuse, nearly invisible flame.

#### IV. PLANS

During the next quarter we plan to (i) formulate a mechanism for  $\text{SiH}_4$  decomposition and run test cases, (ii) continue efforts to obtain working particle chemistry routines in LAPP, (iii) debug the GENMIX<sup>4</sup> and elliptic<sup>7</sup> codes so that boundary layer and recirculating flows can be examined and (iv) continue our examination of the  $\text{SiF}_4/\text{Na}$  and  $\text{SiCl}_4/\text{Na}$  systems to determine which of the reactions in Table I can be ignored in cases of interest to this program.

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TABLE I

MECHANISM AND REACTION RATES USED FOR  $\text{SiCl}_4/\text{Na}$  AND  $\text{SiF}_4/\text{Na}$  CALCULATIONS

Reaction	Rate Coefficient <sup>a,c</sup>	
	X = Cl	X = F
1. $\text{Na} + \text{SiX}_4 \rightleftharpoons \text{NaX} + \text{SiX}_3$	$3 \times 10^{-13}$ $1.5 \times 10^{-12}$	$2 \times 10^{-13} \exp(-31400/\text{RT})$ $2 \times 10^{-11} \exp(-31400/\text{RT})$
2. $\text{Na} + \text{SiX}_3 \rightleftharpoons \text{NaX} + \text{SiX}_2$	$7 \times 10^{-13}$ $3.5 \times 10^{-12}$	$2 \times 10^{-13} \exp(-23900/\text{RT})$ $2 \times 10^{-11} \exp(-23900/\text{RT})$
3. $\text{Na} + \text{SiX}_2 \rightleftharpoons \text{NaX} + \text{SiX}$	$7 \times 10^{-13} \exp(-19000/\text{RT})$ $3.5 \times 10^{-12} \exp(-19000/\text{RT})$	$2 \times 10^{-13} \exp(-40600/\text{RT})$ $2 \times 10^{-11} \exp(-40600/\text{RT})$
4. $\text{Na} + \text{SiX} \rightleftharpoons \text{NaX} + \text{Si}$	$7 \times 10^{-13}$ $3.5 \times 10^{-12}$	$2 \times 10^{-13} \exp(-17400/\text{RT})$ $2 \times 10^{-11} \exp(-17400/\text{RT})$
5. $\text{H} + \text{SiX}_4 \rightleftharpoons \text{HX} + \text{SiX}_3$	$8 \times 10^{-12}$	$2 \times 10^{-13} \exp(-9300/\text{RT})$
6. $\text{H} + \text{SiX}_3 \rightleftharpoons \text{HX} + \text{SiX}_2$	$8 \times 10^{-12}$	$2 \times 10^{-13} \exp(-1800/\text{RT})$
7. $\text{H} + \text{SiX}_2 \rightleftharpoons \text{HX} + \text{SiX}$	$8 \times 10^{-12} \exp(-14000/\text{RT})$	$2 \times 10^{-13} \exp(-19000/\text{RT})$
8. $\text{H} + \text{SiX} \rightleftharpoons \text{HX} + \text{Si}$	$8 \times 10^{-12}$	$2 \times 10^{-13}$
9. $\text{Si} + \text{Si} + \text{M} \rightleftharpoons \text{Si}_2 + \text{M}$	$1 \times 10^{-32}$	$1 \times 10^{-32}$
10. $\text{Si}_2 + \text{Si} + \text{M} \rightleftharpoons \text{Si}_3 + \text{M}$	$1 \times 10^{-32}$	$1 \times 10^{-32}$
11. $\text{Na} + \text{HX} \rightleftharpoons \text{NaX} + \text{H}$	$4 \times 10^{-13} \exp(-6000/\text{RT})$	$4 \times 10^{-13} \exp(-22000/\text{RT})$
12. $\text{X} + \text{X} + \text{M} \rightleftharpoons \text{X}_2 + \text{M}$	$4 \times 10^{-33}$	$3 \times 10^{-33}$
13. $\text{X}_2 + \text{H} \rightleftharpoons \text{HX} + \text{X}$	$3 \times 10^{-10} \exp(-4800/\text{RT})$	$2 \times 10^{-10} \exp(-2400/\text{RT})$
14. $\text{Na} + \text{X}_2 \rightleftharpoons \text{NaX} + \text{X}$	$2 \times 10^{-10}$	$8 \times 10^{-10}$
15. $\text{H} + \text{X} + \text{M} \rightleftharpoons \text{HX} + \text{M}$	$5 \times 10^{-33}$	$1 \times 10^{-32} \exp(-3000/\text{RT})$
16. $\text{SiX}_2 + \text{SiX}_4 \rightleftharpoons 2\text{SiX}_3$	$1 \times 10^{-13}^b$	$1 \times 10^{-13}$
17. $\text{SiX}_4 + \text{SiX} \rightleftharpoons \text{SiX}_3 + \text{SiX}_2$	$1 \times 10^{-13}$	$1 \times 10^{-13}$
18. $2\text{SiX}_2 \rightleftharpoons \text{SiX}_3 + \text{SiX}$	$1 \times 10^{-13}^b$	$1 \times 10^{-13}$
19. $\text{SiX}_4 + \text{Si} \rightleftharpoons \text{SiX}_3 + \text{SiX}$	$1 \times 10^{-13}$	$1 \times 10^{-13}$
20. $\text{SiX}_4 + \text{Si} \rightleftharpoons 2\text{SiX}_2$	$1 \times 10^{-13}$	$1 \times 10^{-13}$
21. $\text{SiX}_2 + \text{SiX} \rightleftharpoons \text{SiX}_3 + \text{Si}$	$1 \times 10^{-13}$	$1 \times 10^{-13}$
22. $2\text{SiX} \rightleftharpoons \text{SiX}_2 + \text{Si}$	$1 \times 10^{-13}$	$1 \times 10^{-13}$
23. $\text{Si}_2 + \text{X} \rightleftharpoons \text{SiX} + \text{Si}$	$1 \times 10^{-13}$	$1 \times 10^{-13}$
24. $\text{H} + \text{H} + \text{M} \rightleftharpoons \text{H}_2 + \text{M}$	$3 \times 10^{-33}$	$3 \times 10^{-33}$
25. $\text{X} + \text{H}_2 \rightleftharpoons \text{HX} + \text{H}$	$7 \times 10^{-11} \exp(-4500/\text{RT})$	$2 \times 10^{-11} \exp(-3800/\text{RT})$

<sup>a</sup> Rate coefficients in  $\text{cm}^3$ , molecule, s, and kcal/mol units.<sup>b</sup> Rate coefficient for backward reaction.<sup>c</sup> For the first four reactions a slow set of rate coefficients (the first coefficient listed) and a fast set (the second one listed) have been examined.

TABLE II

## CONCENTRATION PROFILES FOR Si(g) AND NaF(g)

Initial jet velocity = 3960 cm sec<sup>-1</sup>Outer flow velocity = 2400 cm sec<sup>-1</sup>

Initial jet temperature = 1400 K

Outer flow temperature = 2000 K

X/R = 10

S l o w   C h e m i s t r y				F a s t   C h e m i s t r y		
<u>Y/R</u>	<u>T,K</u>	<u>Si(g) mole fraction</u>	<u>NaF(g) mole fraction</u>	<u>T,K</u>	<u>Si(g) mole fraction</u>	<u>NaF(g) mole fraction</u>
0.0	1400	2.0(-10)	8.8(-7)	1400	6.9(-7)	3.4(-5)
0.2	1400	2.2(-10)	4.9(-6)	1400	2.9(-6)	1.67(-4)
0.4	1403	3.4(-10)	5.6(-5)	1395	5.8(-6)	1.42(-3)
0.6	1421	5.1(-10)	5.1(-4)	1396	9.8(-7)	7.1(-3)
0.8	1496	1.08(-9)	3.2(-3)	1437	3.4(-7)	2.1(-2)
1.0	1640	2.7(-9)	1.17(-2)	1545	2.6(-7)	4.5(-2)
1.2	1793	8.2(-10)	1.20(-2)	1739	9.1(-8)	7.1(-2)
1.4	1944	3.2(-11)	1.10(-2)	1866	1.0(-8)	5.1(-2)

TABLE III

## CONCENTRATION PROFILES FOR Si(g) AND NaCl(g)

Initial jet velocity = 3960 cm sec<sup>-1</sup>Outer flow velocity = 2440 cm sec<sup>-1</sup>

Initial jet temperature = 1100 K

Outer flow temperature = 2000 K

$$X/R = 7.5$$

S l o w    C h e m i s t r y				F a s t    C h e m i s t r y		
<u>Y/R</u>	<u>T,K</u>	<u>Si(g) mole fraction</u>	<u>NaCl(g) mole fraction</u>	<u>T,K</u>	<u>Si(g) mole fraction</u>	<u>NaCl(g) mole fraction</u>
0.0	1100	2.2(-7)	1.67(-6)	1100	1.28(-7)	1.03(-6)
0.2	1100	1.86(-6)	1.53(-5)	1100	1.04(-6)	1.00(-5)
0.4	1101	2.9(-5)	3.0(-4)	1101	1.61(-5)	2.1(-4)
0.6	1115	2.8(-4)	4.3(-3)	1115	1.56(-4)	3.2(-3)
0.8	1248	1.62(-3)	4.0(-2)	1250	9.9(-4)	3.1(-2)
1.0	1868	1.07(-2)	2.6(-1)	1999	1.34(-2)	2.6(-1)
1.2	2038	6.7(-6)	2.5(-1)	2140	7.0(-7)	2.2(-1)
1.4	2003	1.8(-8)	1.04(-1)	2015	1.02(-8)	8.2(-2)