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

Third Quarterly Report, April 1—June 30, 1978

By
R. K. Gould

August 1978

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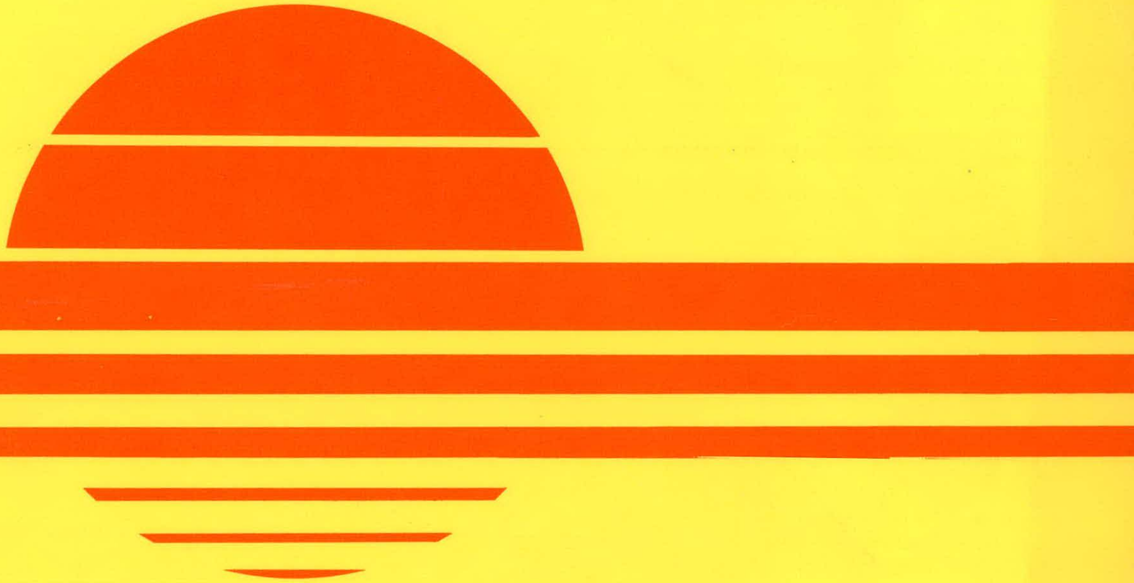
Princeton, New Jersey



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THIRD QUARTERLY REPORT

R. K. GOULD

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Approved by

Hartwell F. Calcote
Director of Research

AeroChem Research Laboratories, Inc.
Princeton, New Jersey

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FOREWORD AND ACKNOWLEDGMENTS

This report covers the period 1 April 1978 to 30 June 1978. During this period D.B. Olson contributed to the program and Prof. D.E. Rosner (Yale University) consulted on 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 work has centered on obtaining working versions of the particle "chemistry" (nucleation, coagulation, evaporation, and condensation) routines within the large code. The nucleation model in particular proved troublesome; efforts to debug it have led to the writing of a smaller independent nucleation code. This smaller code allows the model to be examined in more detail than is possible in the large code. This report discusses this model in detail. A considerable amount of time was also spent during this period on streamlining the LAPP code to allow accommodation of the large number of equations describing particle processes. This effort has been successful in reducing memory requirements by as much as 50%.

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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[1] (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.[2,3] 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. The extent of these modifications depends, to a large degree, on the thoroughness with which phenomena occurring in boundary layers must be studied. Appropriate means of treating boundary layer phenomena are currently being examined.

II. TECHNICAL DISCUSSION

The code, in its final form, must be able to model gas-phase reactions which yield refractory products with extremely low equilibrium vapor pressures. Very large supersaturation ratios ($> 10^3$) of these species (e.g., Si and NaCl) are encountered, and small gas-phase species such as Si atoms (g) formed by chemical reaction rapidly grow into bulk Si (ℓ). The growth process involves the passage through a size range of maximum free energy; above this critical size free energy rapidly drops to approach the bulk condensed-phase value.

The rate of passage through the critical size must be modeled. One approach is to utilize the idea of a surface energy (tension) which accounts for the free energy peak at a certain size. This liquid drop model can be used to predict rates of nucleation. However, for the cases of interest in the present program, calculations using the large supersaturations yield critical sizes which are sometimes < 1 atom, in which case the idea of a surface energy is clearly invalid.

The gas-phase chemical kinetics scheme in codes like LAPP involves solving the differential equations describing elementary gas-phase chemical reactions for which either a forward or reverse rate coefficient and the equilibrium constants are known or estimated. An alternative to the liquid drop nucleation scheme which fits easily into the gas-phase kinetic model would treat nucleation as a series of elementary reactions involving the step-by-step combination of gas-phase molecules. The rate coefficients and equilibrium constants for the series of reactions leading to particle formation must be calculated since in no case are they experimentally available, and the critical size must be small (< 100 monomers) if the number of reactions involved is to be manageably small. Such gas kinetic models avoid any use of bulk surface energy; even if poor estimates of rate coefficients are used, rates of particle formation are apt to be more reliably predicted since the strong exponential dependence of the liquid drop theory on surface energy is avoided. Such a gas kinetic theory has recently appeared in the literature.[4] In the following section it is examined in the context of $Si(\ell)$ nucleation.

A. NUCLEATION MODEL

The model used to treat particle nucleation is one which treats the series of Si n-mer reactions

$$Si_k + Si_n + M \xrightleftharpoons{k_{n+k}} Si_{n+k} + M \qquad (1)$$

The model allows the forward and reverse rate coefficients for Reaction (1) to be estimated for all n. Using these rate coefficients it is possible to obtain a gas-kinetically determined critical size (as opposed to one based on classical liquid drop concepts) and a nucleation rate.

Examination of processes like Reaction (1) leads one to write a realistic detailed mechanism for them as

$$Si_k + Si_n \underset{\kappa_{n+k\to n}}{\overset{\kappa_{n\to n+k}}{\rightleftarrows}} Si^*_{k+n} \tag{2a}$$

$$Si^*_{k+n} + M \xrightarrow{\kappa_{s,k+n}} Si_{k+n} + M \tag{2b}$$

where Reaction (2a) leads to an excited cluster which may either decompose into its original constituents or may be stabilized by collision with another molecule via Reaction (2b). The overall forward rate coefficient for the overall Reaction (1) is then given by the following equation for k_{n+k} in terms of the rate coefficients for Reaction (2).

$$k_{n+k} = \frac{\kappa_{s,n+k}\ \kappa_{n\to n+k}}{\kappa_{n+k\to n}} \bullet \frac{1}{1 + \frac{\kappa_s}{\kappa_{n+k\to n}}[M]} \tag{3}$$

The forward rate for Reaction (1) is then

$$\frac{d}{dt}[Si_{n+k}] = k_{n+k}\,[Si_n]\,[Si_k]\,[M] \tag{4}$$

Following the model development of Bauer and Frurip,[4] we estimate the values of $\kappa_{s,\ n+k}$, $\kappa_{n\to n+k}$ and $\kappa_{n+k\to n}$ as follows: $\kappa_{n\to n+k}$ is assumed to be gas kinetic (each collision yields Si^*_{n+k}) so that

$$\kappa_{n\to n+k} = \pi(r_{n+k})^2\, v_{rel,n,k} \tag{5}$$

where r_{n+k} is the radius of a spherical molecule containing (n + k) atoms. (The bulk liquid density is used to obtain this radius.) The ratio $\kappa_{n\to n+k}/\kappa_{n+k\to n}$ is the equilibrium constant for Reaction (2a); its value is given by

$$\kappa_{n\to n+k}/\kappa_{n+k\to n} = 4\pi\int_{r_{n+k}}^{\infty} dr\ r^2\ \exp\left(-\frac{U_{n,k}}{k_BT}\right) \tag{6}$$

where $U_{n,k}$ is an interaction potential between the n-mer and the k-mer and k_B is Boltzmann's constant. The stabilization rate coefficient, κ_s, is also assumed gas kinetic and is given by

$$\kappa_s = \pi(r_{n+k} + r_M)^2 \, v_{rel,n+k,M} \tag{7}$$

where r_M is the radius of the bulk gas molecules and $v_{rel,n+k,M}$ is the average relative velocity of cluster and bulk gas molecules. Using Eqs. (5), (6), and (7) the overall forward rate coefficient $k_{n\rightarrow n+k}$ is obtained once the interaction potential $U_{n,k}$ is found. $U_{n,k}$ is estimated by Frurip and Bauer by a Lennard-Jones potential

$$U_{n,k}(r) = 4\,\varepsilon_{n,k}\left[\left(\frac{r_{n+k}}{r}\right)^{12} - \left(\frac{r_{n+k}}{r}\right)^{6}\right] \tag{8}$$

where $\varepsilon_{n,k}$ is a function of the heats of formation of the n-mers

$$\varepsilon_{n,k} = \left\{|\Delta H^\circ_{n+k}| - |\Delta H^\circ_n| - |\Delta H^\circ_k|\right\}/2 \tag{9}$$

and

$$\Delta H^\circ_n = -\,n\left\{L(1 - n^{-1/4}) + \Delta H^\circ_1\right\} \tag{10}$$

where L is the latent heat of vaporization.

The overall reverse rate, $k_{n+k\rightarrow n}$, for Reaction (1) may be determined from the forward rate once the Gibbs free energies of formation, ΔG°, of the n-mers are specified. The enthalpies of formation necessary to derive ΔG° are estimated using Eq. (10). The entropies associated with the formation of n-mers from Si atoms are also obtained from Ref. 4 and are given by

$$\Delta S^\circ_n = R\left\{-\frac{14n^3}{3n^2} + (n-1)\ln 2 + \frac{2}{3}\sum_{j=1}^{n-1} \ln j\right\} \tag{11}$$

for $n \geqq 10$. For $n \leqq 10$, the configuration terms, on the RHS of Eq. (11) (the second two terms) are replaced by values obtained from the graph (Fig. 7) of Ref. 4. Using these estimates, the free energies are given by

$$\Delta G_n^\circ = \Delta H_n^\circ - T\Delta S_n^\circ + \Delta G_1^\circ \tag{12}$$

The reverse rate coefficients are given by

$$k_{n+k\to n} = k_{n\to n+k}\, RT \exp\left[\frac{\Delta G_n^\circ + \Delta G_k^\circ - \Delta G_{n+k}^\circ}{RT}\right] \tag{13}$$

The rate coefficients of Table I were calculated using this model. It can be seen that the forward rate coefficients rise fairly rapidly with increasing n while the reverse coefficients decrease rapidly, reflecting the greater stability of the excited clusters with increasing n.

For $n \leq 10$, the reverse rate coefficients range up to $\approx 10^{-7}$ ml molecule^{-1} sec^{-1}. For a simple two-body reaction between neutral, small molecules such rate coefficients are unreasonably large (by > 2 orders of magnitude). Their large size here reflects the fact that, at the high temperatures involved, the excited clusters of Reaction (2a) usually undergo decomposition as they are formed, before collision with another molecule can stabilize them. Larger (n > 10) clusters live longer due to their ability to channel excitation energy into the many available bonds and thus for these, realistic two-body reverse rate coefficients are formed for the overall Reaction (1).

In order to use this model to obtain rates of particle formation it is necessary to define a critical size cluster analogous to the critical size nucleus obtained from liquid drop nucleation theory. In the kinetic nucleation model used here this critical size is determined by establishing where the "bottleneck" in the series of reactions represented by Reaction (1) occurs. This is done by finding that n-mer for which the rates of reactions creating it are most nearly equal to the rates destroying it. The critical size determined in this fashion is compared to that obtained from liquid drop theory in Table II. To determine the number of Si atoms in the liquid drop critical nucleus, the Kelvin equation is used for computing the critical radius, r^*,

$$r^* = \frac{2\gamma M_{Si}}{RT\rho \ln S} \tag{14}$$

TABLE I

COMPUTED RATE COEFFICIENTS FOR Si POLYMERIZATION

$$\mathrm{Si} + \mathrm{Si}_n + \mathrm{M} \rightleftharpoons \mathrm{Si}_{n+1} + \mathrm{M} \qquad (\mathrm{M} = \mathrm{Ar})$$

T = 2400 K, P = 1 atm

n	Forward Rate Coefficient (ml^2 molecule^{-2} sec^{-1})	Reverse Rate Coefficient (ml molecule^{-1} sec^{-1})
1	4.45 (-30)[a]	4.59 (-7)
2	1.01 (-29)	4.46 (-8)
3	1.53 (-29)	4.33 (-8)
4	1.97 (-29)	1.57 (-8)
5	2.35 (-29)	1.68 (-8)
6	2.68 (-29)	3.90 (-9)
7	2.97 (-29)	9.57 (-10)
8	3.24 (-29)	7.32 (-10)
9	3.48 (-29)	6.90 (-10)
10	3.71 (-29)	2.46 (-10)
15	4.68 (-29)	1.78 (-10)
20	5.32 (-29)	9.18 (-11)
25	6.16 (-29)	5.72 (-11)
30	6.78 (-29)	3.97 (-11)
35	7.36 (-29)	2.96 (-11)
40	7.80 (-29)	2.31 (-11)
45	8.42 (-29)	1.87 (-11)
50	8.90 (-29)	1.55 (-11)

[a] The notation A(-B) implies A × 10^{-B}.

TABLE II

COMPARISON OF CRITICAL CLUSTER SIZES FOR GAS KINETIC AND LIQUID DROP NUCLEATION MODELS

			r^* (nm)	
T (K)	P(Si) (atm)	Supersaturation Ratio	Liquid Drop Model	Gas Kinetics Model
1800	0.001	325	0.44	1.19
1800	0.01	3247	0.32	0.93
1800	0.05	16230	0.26	0.79
2400	0.1	45.7	0.16	1.11

where γ is the surface tension, M_{Si} the molecular weight of silicon, ρ the droplet density, and S the supersaturation ratio. The number of Si atoms, n^*, is obtained using M_{Si}, ρ, r^*, and Avagadro's number N_A, from

$$n^* = 4/3\ \pi(r^*)^3 \rho N_A / M_{Si} \qquad (15)$$

The surface tension of liquid Si is obtained from Ref. 5.

$$\gamma = 720 \left[1.67 - 0.67\ (T/1685) \right]^{1.2} \ (\text{dyne cm}^{-1}) \qquad (16)$$

The density of liquid Si used is given in Ref. 6.

$$\rho = 3.0247 - 0.355 \times 10^{-3}(T - 273.15) \qquad (17)$$

The supersaturation, S, is computed using JANAF thermochemical data[7] for silicon equilibrium vapor pressures for Si(g), Si_2(g), and Si_3(g) above Si(ℓ).

From Table II it can be seen that the kinetic model used selects a critical size larger than the liquid drop model predicts. For these large supersaturations the liquid drop model predicts nuclei radii which are on the order of one Si atom radius (0.17 nm) if one uses the surface tension of bulk Si(ℓ) in Eq. (14)

(e.g., $\gamma = 681$ dynes cm^{-1} at 1800 K). The use of such a value for γ is clearly meaningless here since the surface energy of an Si(g) atom is simply zero. Thus the selection of larger critical sizes by the present model is physically more realistic for cases where very large supersaturations are encountered.

B. CODE MODIFICATIONS

The addition of equations for the chemical reactions describing n-mer growth

$$Si_n + Si_i \rightleftharpoons (Si)_{n+i}$$

and the equations describing particle coagulation resulted in the LAPP code becoming unacceptably large. A particular problem was the use, in the code,[1] of a large three-dimensional array (CM) with dimensions (number of reactions × number of reactions × number of streamtubes) for up to 100 reactions (including coagulation) and 26 streamtubes. The size of this array alone made the code very large, expensive, and impractical to run for systems with very large numbers of chemical reactions. The code has therefore been rearranged to remove this large array (as well as to clean it up in a number of other, less significant ways). The result has been to reduce the memory requirements of the code by ≈ 50% without a noticeable increase in run time. As the number of reactions is further increased, the potential economy will be much greater.

III. PLANS

During the next quarter work will center on performing test runs with the enlarged LAPP code to check on its ability to obtain reasonable rates of particle formation and growth in systems in which the $SiCl_4/Na$ reaction is occurring. Modifications to allow it to calculate interior flows (contained in a flow reactor vessel) will be initiated.

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