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SILICON HALIDE - ALKALI METAL FLAMES AS A SOURCE OF SOLAR GRADE SILICON

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FINAL REPORT

D.B. OLSON, W.J. MILLER, AND R.K. GOULD

JANUARY 1980

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DoE.

AeroChem Research Laboratories, Inc.
Princeton, New Jersey

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Approved by

Hartwell F. Calcote
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Princeton, New Jersey

FOREWORD AND ACKNOWLEDGMENTS

This is the final report on a program covering the period from 17 May 1977 to 15 August 1979. The following people contributed significantly to this program: H.F. Calcote, C.T. Dickson, L. Koenig, and G. Rolland.

ABSTRACT

The object of this program was to determine the feasibility of using continuous high-temperature reactions of alkali metals and silicon halides to produce silicon in large quantities and of suitable purity for use in the production of photovoltaic solar cells. Equilibrium calculations showed that a range of conditions were available where silicon was produced as a condensed phase but the byproduct alkali metal salt was a vapor. A process was proposed using the vapor phase reaction of Na with $SiCl_4$.

Low pressure experiments were performed demonstrating that free silicon was produced and providing experience with the construction of reactant vapor generators. Further experiments at higher reagent flow rates were performed in a low temperature flow tube configuration with co-axial injection of reagents. Relatively pure silicon was produced in these experiments. A high temperature graphite flow tube was built and continuous separation of Si from NaCl was demonstrated. A larger-scaled well-stirred reactor was built.

Experiments were performed to investigate the compatability of graphite-based reactor materials of construction with sodium. At 1100-1200 K none of these materials were found to be suitable. At 1700 K the graphites performed well with little damage except to coatings of pyrolytic graphite and silicon carbide which were damaged.

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I. INTRODUCTION

The object of this program was to determine the feasibility of using continuous high-temperature reactions of alkali metals and silicon halides to produce silicon in large quantities and of suitable purity for use in the production of photovoltaic solar cells. Reactions of gaseous Na or K with silicon halides (e.g., $SiCl_4$, $SiHCl_3$, or SiF_4) are highly exothermic and luminescent, producing high adiabatic flame temperatures. Using reliable thermochemical data, equilibrium calculations show that silicon is the only condensed phase in the product stream; the alkali metal salt is in the vapor phase. This difference in physical state of desired and undesired products is proposed as a basis for separating the silicon from the byproduct salt. This research program, begun on 17 May 1977, set out to experimentally demonstrate the practicality of a production/separation process based on these concepts. As part of Task I of the JPL Low-Cost Solar Array Project the overall objective is to produce solar-grade silicon at a cost of less than $10 per kg (in 1975 dollars). Present technology produces semiconductor-grade silicon at a cost between $50 and $150 per kg, so an order of magnitude reduction in cost is desired with only slightly less stringent purity requirements.

Initial experiments were performed at low pressures in an opposed-jet diffusion flame configuration. This work, discussed in Section III, provided information on reagent vaporizer construction, and established that free silicon was produced in the flames. The experiment was then scaled up and run in a flow-tube configuration with co-axial injection of reagents. Section IV of this report presents details of this work as the production rate of silicon and the reactor temperature were progressively increased.

As an outgrowth of experience gained in our experiments and at the request of JPL a limited series of material compatibility studies was performed to investigate the effects of sodium (vapor) on graphite materials. These results are presented in Section V.

Finally, the current status of the program is appraised, the conclusions reached are presented, and recommendations for further work are made. We believe that, although some technical difficulties remain to be mastered, the proposed process is a strong viable candidate for the production of low-cost high-purity silicon.

II. BACKGROUND

The reaction of silicon halides with an alkali metal was the process used in the first[1] preparation of metallic silicon in the early 1800's. The configuration of these early experiments, however, was such that the bulk of the reaction took place in the condensed phase and extensive product separation procedures had to be employed to isolate the silicon. A more elaborate version of this preparative method has more recently been employed[2] in which the reactions apparently occur mainly in the gas phase with a silicon product of variable and controllable purity being deposited on the heated walls of the reactor. In all of these studies, the preparation was carried out in batches. No continuous reactions were sustained although steady-state gas phase reaction surely must have taken place for some time in all cases.

Other studies,[3-6] conducted primarily for purposes of studying chemical kinetics and chemi-excitation phenomena, have demonstrated that the halides of silicon comprise but one member of an extensive series of compounds which react spontaneously when their vapors are brought into contact with gaseous alkali metals at low pressures. The reactions which ensue are self-igniting, exothermic, rapid and emit visible and ultraviolet light; they thus may be classified quite properly as flames. The fact that these reactions are spontaneous precludes premixing of the reactants and the rates of consumption are therefore controlled by mass transport of reactants to the flame zone rather than by chemical kinetics within the flame itself. Combustion systems of this kind are classified as "diffusion flames" although in most cases, convection, rather than diffusion, is the operative mass transport mechanism. They are typically characterized by an intense high temperature reaction zone located at the intersection of two reactant streams; products diffuse away from this reaction zone, or are convected away, depending on the pressure and geometry of the burner employed. Since the reactions involved in flames of this type are characteristically very fast, scale-up considerations are largely gas dynamic in nature and tend to be somewhat more straightforward than in reaction rate-limited systems.

The mechanism involved in all of these inorganic halide and halomethane/alkali metal flames appears[6-10] to comprise successive halogen abstraction reactions to produce, e.g., KX or NaX and parent metal atoms (M). Although the silicon halide reactions have not themselves been extensively investigated in terms of their reaction mechanisms, the evidence strongly indicates that they are representative members of this large class of reactions and therefore can be expected to react in a similar fashion. In fact, the thermochemical stability of Si atoms in these flames is considerably greater than many of the other parent metals and the probability of the silicon reacting with other flame species upon cooling can be expected to be considerably lower.

Evaluation of any potentially attractive combustion system is best begun with calculations of equilibrium compositions and adiabatic temperatures. These ideal compositions are quite closely approached in most flames with only certain relatively minor species concentrations exhibiting significant deviations due to the effects of diverse rates of chemical reactions, particularly slow radical recombination; the adiabatic flame temperature assumption forces all the heat released in exothermic reactions to appear as product temperature. It thus represents a theoretical maximum which, in real systems, is often closely approached; heat losses due to radiation typically lower the temperature only a few percent and conduction to the burner and other cooler surfaces can be made quite small by careful design. Regardless of the influence of possible heat loss and kinetics problems, equilibrium is an unambiguous description of the state of the system which nature is striving to reach and affords the experimenter an opportunity to anticipate optimum conditions for his specific purposes.

Our equilibrium calculations were performed using the Air Force Rocket Propulsion Laboratory "ISP" Computer Code. The thermochemical data used as input to the calculations come from the JANAF Tables.[11] In reviewing available thermodynamic information on Si/H/Cl compounds it appears that the only significant difference between the JANAF data used in these calculations and recent literature values is the $\Delta H^\circ_{f,298}$ for $SiHCl_3$; JANAF gives -112.0 kcal mol^{-1} whereas the recent work of Sirtl and Hunt[12] indicates -116.9 kcal mol^{-1}. The uncertainty in this value, as reflected in a variation in the free energy changes involving this species, comprises only a minor perturbation in the results obtained. As the data reported below indicate, only a small proportion of the Si contained in the mixtures of interest is present as gaseous species; nearly all of the Si appears as either liquid or solid phase and the uncertainties in the gas phase composition distributions are therefore irrelevant in terms of the desired experimental objective.

Calculations were first made for reagents in their standard states at 298 K. Adiabatic flame temperatures for the Na/$SiCl_4$ and K/$SiCl_4$ systems are given in Fig. 1 as a function of pressure. The results exhibit significant pressure dependence due mainly to the heat released in the dimerization of the alkali metal salt in the vapor phase.

To further illustrate these latter effects, the equilibrium compositions of the system K/$SiCl_4$ at the pressures cited above are given in Table I. The increase in temperature with increasing pressure is due almost entirely to the formation of K_2Cl_2 and the heat released is sufficient not only to raise the temperature but also, at pressures above about 0.5 atm, to melt the Si produced. The Na/$SiCl_4$ system is somewhat more complex; analogous dimerization of NaCl liberates heat in this system as well, but although the reaction is more exothermic and more extensive than in the case of KCl, liquid NaCl appears in the products at the two higher pressures due to the higher melting point and heat of vaporization of NaCl. At pressures up to 1 atm, all KCl remains in the gas phase in systems of this stoichiometry.

TABLE I

EQUILIBRIUM COMPOSITIONS OF K/$SiCl_4$ MIXTURES AS A FUNCTION OF PRESSURE

	Mole Fractions			
Pressure, atm	0.036	0.1	0.36	1.0
Product				
Si(liq.)	----[a]	----[a]	1.17(-1)[b]	2.28(-1)
Si(solid)	2.06(-1)	2.09(-1)	1.01(-1)	----[a]
SiCl	2.62(-6)	4.01(-6)	3.99(-6)	4.17(-6)
$SiCl_2$	1.10(-3)	1.24(-3)	1.10(-3)	1.01(-3)
$SiCl_3$	2.01(-5)	2.51(-5)	2.82(-5)	3.10(-5)
KCl	7.57(-1)	7.38(-1)	6.81(-1)	6.23(-1)
K_2Cl_2	3.38(-2)	4.92(-2)	9.75(-2)	1.45(-1)
K	2.26(-3)	2.54(-3)	2.28(-3)	2.11(-3)

[a] $< 1.06(-6)$

[b] $1.17(-1) = 1.17 \times 10^{-1}$

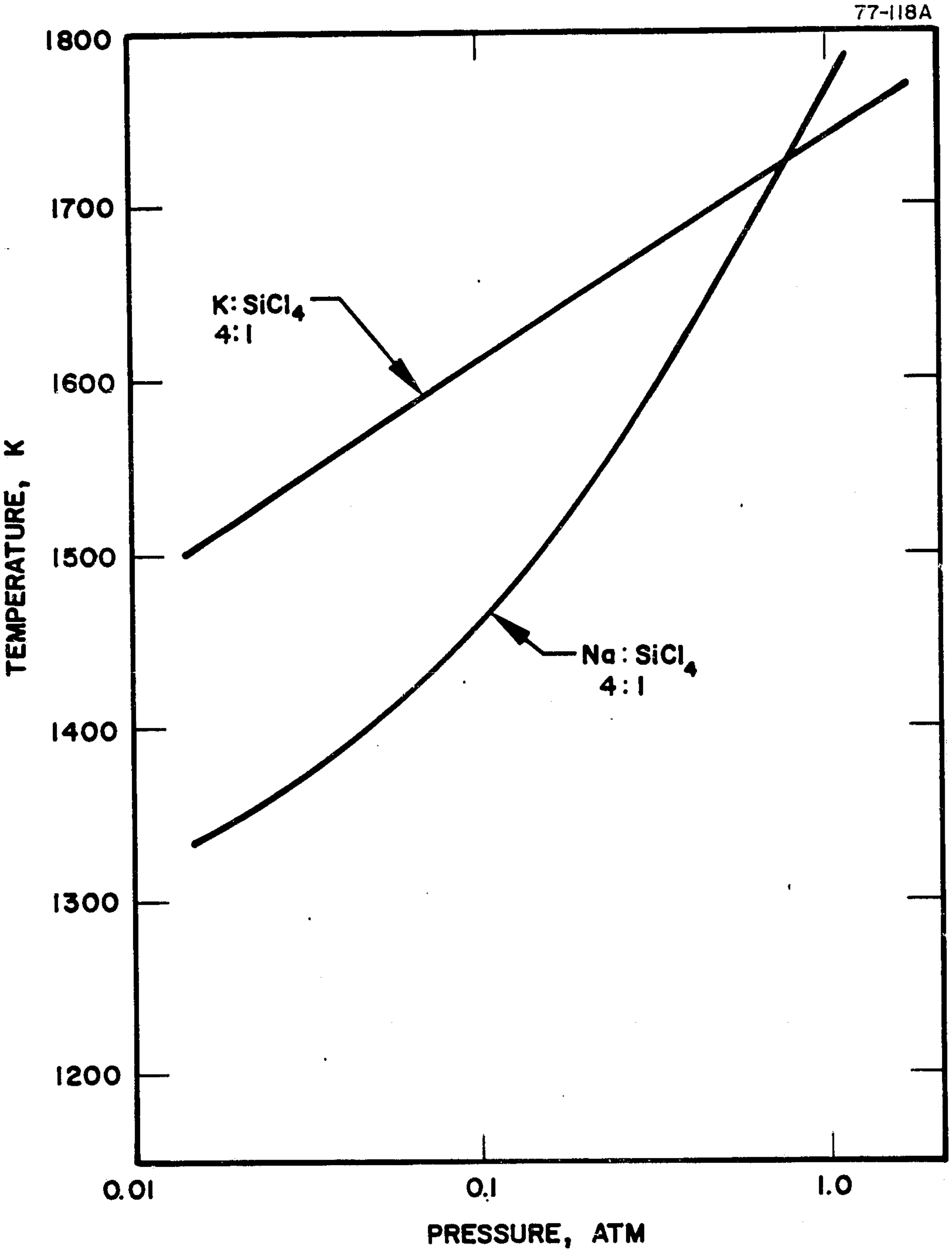

FIGURE 1 ADIABATIC FLAME TEMPERATURES FOR ALKALI METAL/$SiCl_4$ MIXTURES AS A FUNCTION OF PRESSURE

All reagents at 298 K.

The effect of addition of H_2 to these mixtures was also investigated, again with the reagents in their standard states at 298 K. This addition lowers the adiabatic temperatures somewhat and changes the composition of the gases above the condensed phase NaCl and/or Si but the proportion of silicon in the mixture which ends up as the metal is changed very little. These effects are demonstrated by the product distributions and temperatures given in Table II for mixtures containing (initially) 50 mol % H_2. Calculations in which the temperature is varied above and below the adiabatic values, as would be the case if the reactants were heated or a heat sink provided, reveal that concentrations of volatile products are enhanced somewhat by the addition of H_2 but the effects are minimal; the predominant Si-containing species at equilibrium remains liquid or solid Si up to a temperature of 2000 K.

TABLE II

EQUILIBRIUM COMPOSITION OF A K/$SiCl_4$ MIXTURE CONTAINING 50% H_2

P = 1 atm, T = 1560 K

Product	Mole Fraction	Product	Mole Fraction
Si (solid)	1.07(-1)	SiH_3Cl	3.58(-5)
KCl (liquid)	6.75(-2)	$SiCl_2$	1.04(-5)
KCl	2.17(-1)	HCl	1.30(-3)
K_2Cl_2	7.10(-2)	H	2.32(-5)
K	1.35(-3)	H_2	5.34(-1)

Since a major objective of this project was to continuously separate the silicon from the alkali metal salt, it was necessary to operate the reactor at a temperature above both the melting point of silicon and the boiling point of the salt. One way of increasing the flame temperature is to use gas phase reactants. This technique has the possible added advantage of purifying the reagents at the inlet stage if a distillation column is used as a vapor source. An additional series of equilibrium calculations was performed for injection of the alkali metal as a gas at its boiling point. The resulting flame temperatures are plotted in Fig. 2 for the K/$SiCl_4$ system. The added enthalpy results in higher flame temperature but, except for this rather obvious effect, no other significant changes are observed. The chemical composition remains qualitatively very similar to those of the lower temperature system.

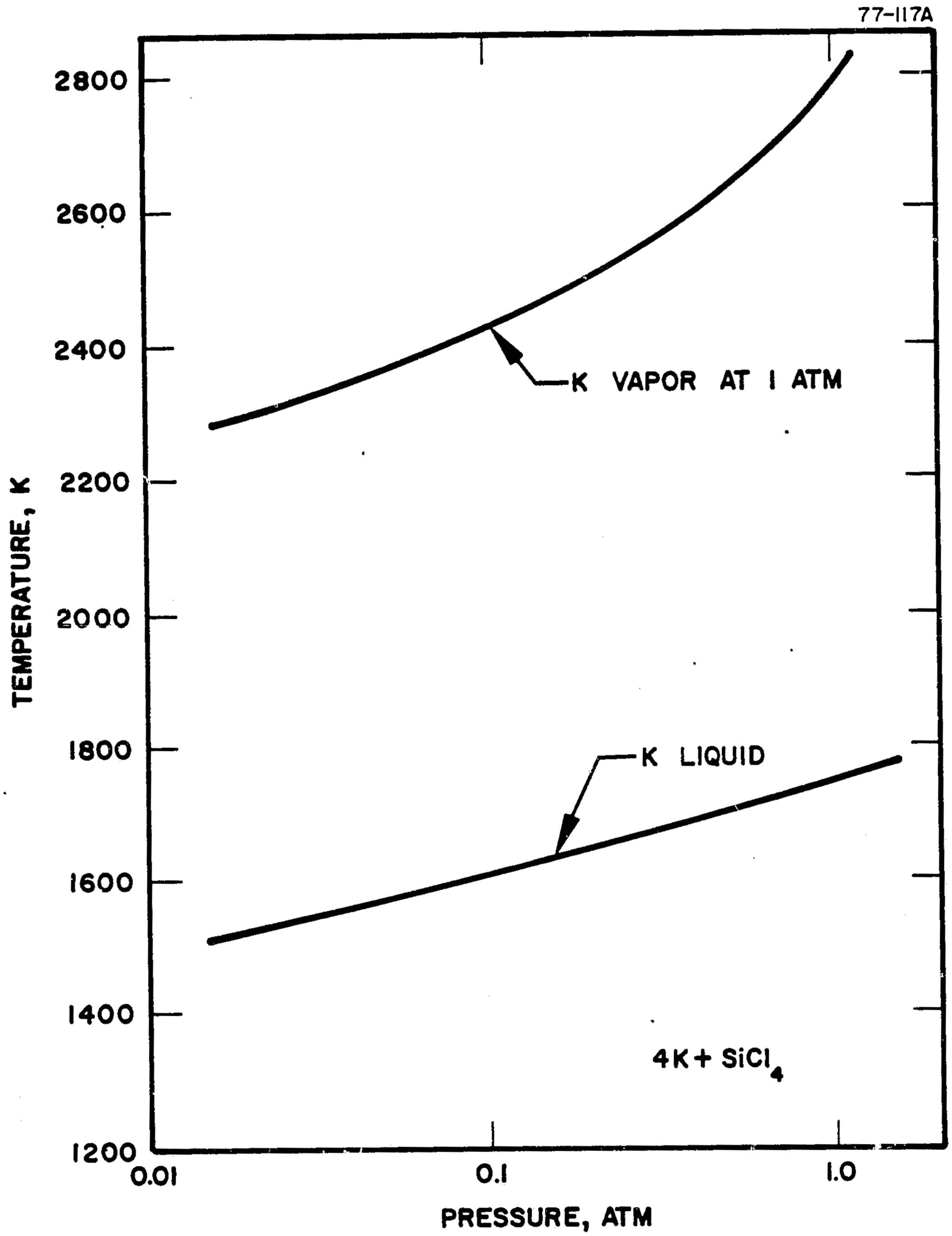

FIGURE 2 EFFECT OF VAPORIZING POTASSIUM ON ADIABATIC FLAME TEMPERATURE FOR STOICHIOMETRIC K/$SiCl_4$

Since all of the contemplated reactants undergo spontaneous reaction when brought into contact with alkali metal, the flames of this study must be diffusion flames and very steep concentration gradients will necessarily prevail across the reaction zone. At the halide inlet, there will be no alkali metal present, only the halide itself and perhaps some combustion products. In order to gain some insight into the nature of the equilibrium product/reactant distribution across a reaction zone, a series of composition calculations was performed over a range of metal/halide ratios. The results for various $K/SiCl_4$ mixtures are given in Fig. 3. To a first approximation, the different $K/SiCl_4$ ratios correspond to different distances across the reaction zone; thus, at low values of $K/SiCl_4$ the calculated composition reflects that to be found near the $SiCl_4$ inlet where the extent of reaction is small; conversely at high $K/SiCl_4$, the composition reflects that to be found near the point of K vapor introduction. Most important, liquid Si is found in abundance throughout indicating that, at least at equilibrium, the desired product should be extractable from a large portion of the reaction volume.

The adiabatic flame temperatures produced by K reduction of three readily available halide reactants are given in Fig. 4. The curve presented for each of these materials (solid lines) corresponds to a stoichiometric mixture in terms of alkali halide product, i.e., $SiCl_4$:K and SiF_4:K = 1:4 and $SiHCl_3$:K = 1:3. The much lower temperatures produced by the fluoride is due to its much lower heat of formation which, in turn, reduces the exothermicity of the reaction. Compare, for example, the ΔH values for the following:

$$SiCl_4 + 4K \rightarrow 4KCl + Si \qquad \Delta H_{298} = -344 \text{ kcal/mol}$$

$$SiHCl_3 + 3K \rightarrow 3KCl + Si + 1/2H_2 \qquad \Delta H_{298} = -258 \text{ kcal/mol}$$

$$SiF_4 + 4K \rightarrow 4KF + Si \qquad \Delta H_{298} = -144 \text{ kcal/mol}$$

Also shown in the figure is the potential operating region of a reactor producing silicon from the reduction of $SiCl_4$. This operating region is the temperature-pressure domain between the adiabatic flame temperature, as the highest possible temperature, and the melting point of silicon or the boiling point of KCl, whichever is higher. It is seen that for the $SiCl_4$ or $SiHCl_3$ system a wide operating region would be available. For K + SiF_4, however, the flame temperature is below the boiling point of KF and a continuous separation of products would not be possible under these conditions.

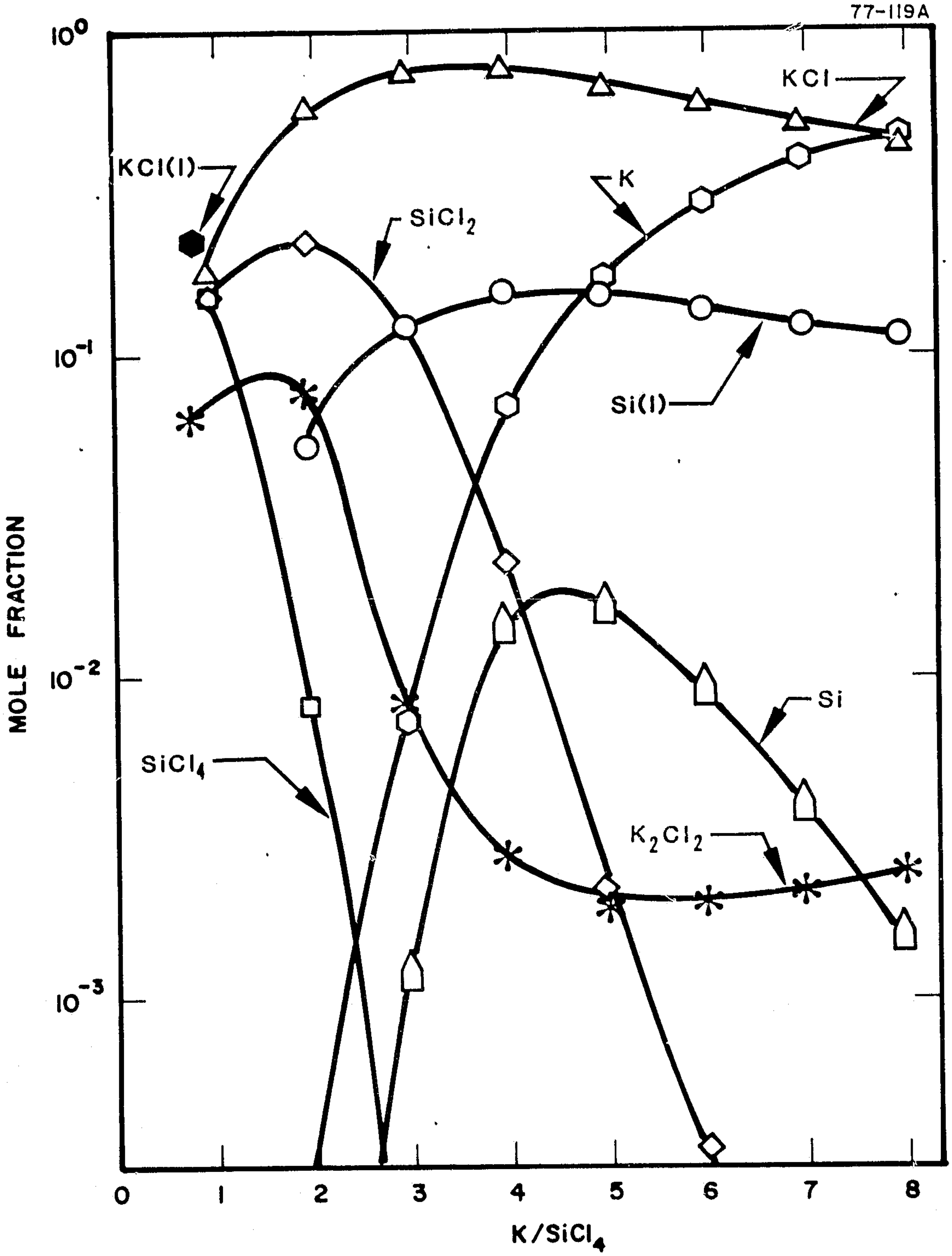

FIGURE 3 EQUILIBRIUM PRODUCT CONCENTRATIONS FOR VARIOUS $K/SiCl_4$ MIXTURES

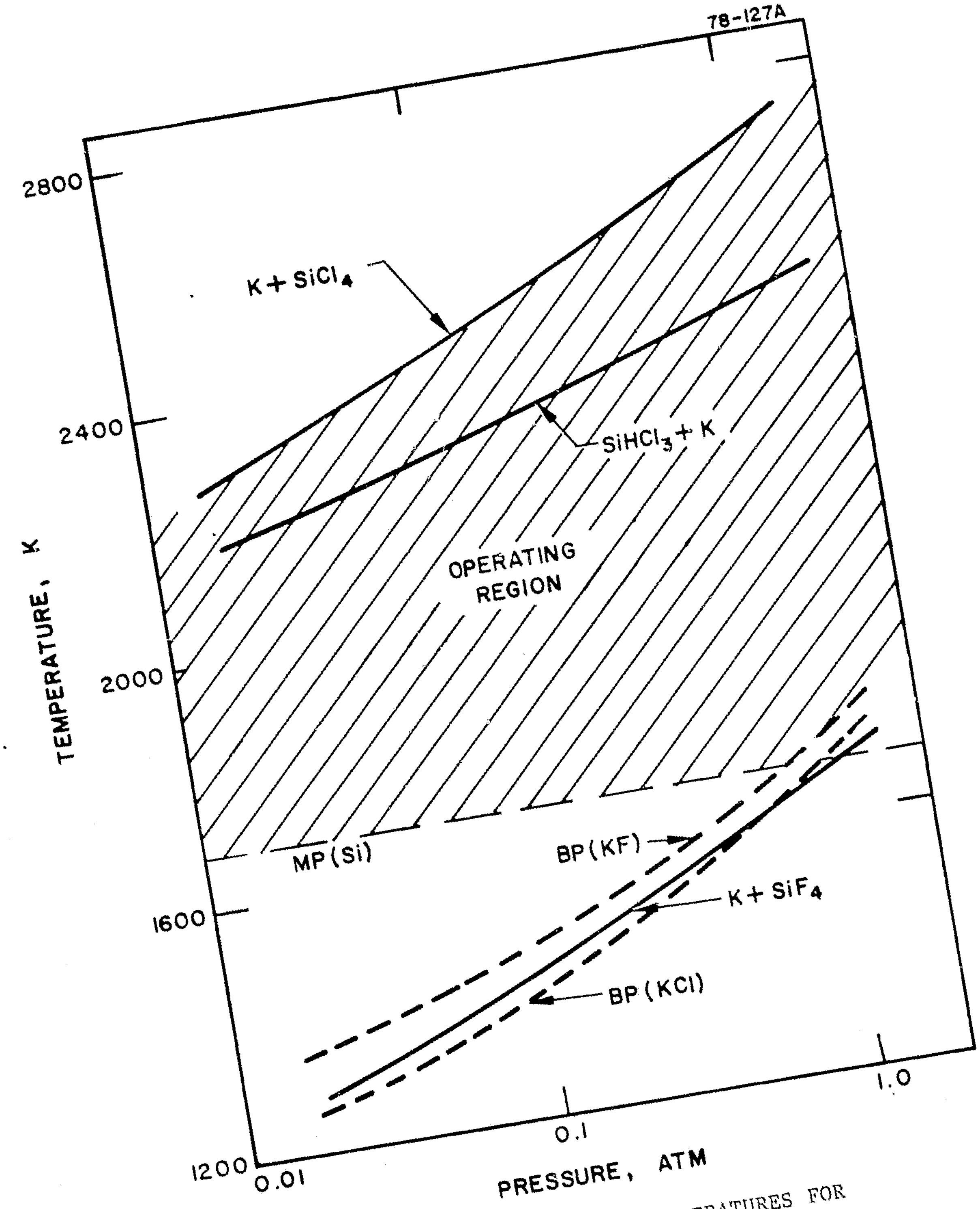

FIGURE 4 ADIABATIC FLAME TEMPERATURES FOR K(GAS AT 1030 K) + $SiCl_4$, $SiHCl_3$, AND SiF_4

The dashed lines indicate the boiling point of KCl and KF and the melting point of silicon.

Similar results calculated for Na/$SiCl_4$ are shown in Fig. 5. The use of vaporized Na is seen to give a wide operating region, whereas additional heat input would be necessary in order to use liquid Na. The Na/$SiHCl_3$ system is analogous to K/$SiHCl_3$ but Na/SiF_4 is even less attractive than K/SiF_4 due to the higher boiling point of NaF over KF. Vapor pressure data for these species are shown in Fig. 6 where one can see the advantage of either using potassium as a reducing agent or using a chloride of silicon. Sodium has important economic advantages over potassium and, in addition, reduces the mass flow of alkali metal salt produced as a byproduct in the proposed technique.

Further details of the stoichiometric Na/$SiCl_4$ system using vapor phase reagents are given in Fig. 7. The computed mole fractions of the reaction products are shown as a function of pressure. Liquid silicon is the only condensed product and accounts for $\approx$ 90% of the total silicon with $SiCl_2$ being the only other silicon-containing species of importance. Operation with slight excess alkali metal reduces the concentration of this radical significantly (cf. Fig. 3).

No detailed attempt was made at this point in the program to assess the potential of these self-sustaining flames for the elimination of impurities from the condensed phase Si product. Preliminary estimates indicate that at least one of these contaminants, boron, can be largely eliminated from the product silicon quite simply by virtue of the high volatility of its equilibrium products in halogenated systems. This can, for example, be envisioned as follows: At 1500 K, using Na as reactant, the most likely final Cl-stripping process for any BCl_x impurities in $SiCl_4$ involves the thermodynamically favored BCl radical:

$$BCl + Na \rightleftarrows NaCl + B \qquad (1)$$

This reaction has an equilibrium constant, $K_1 = 4 \times 10^{-4}$ while for the corresponding Si-producing reaction

$$SiCl + Na \rightleftarrows NaCl + Si \qquad (2)$$

$K_2 = 30$. Thus, prior to condensation, the bulk of the boron will be in the form BCl while the silicon is largely present as metal atoms. If a kinetic means can be found to take advantage of the metal atom composition in the gas phase, the potentially attainable degree of enrichment will be given by the ratio of the equilibrium constants K_1/K_2, i.e., the equilibrium constant for the reaction

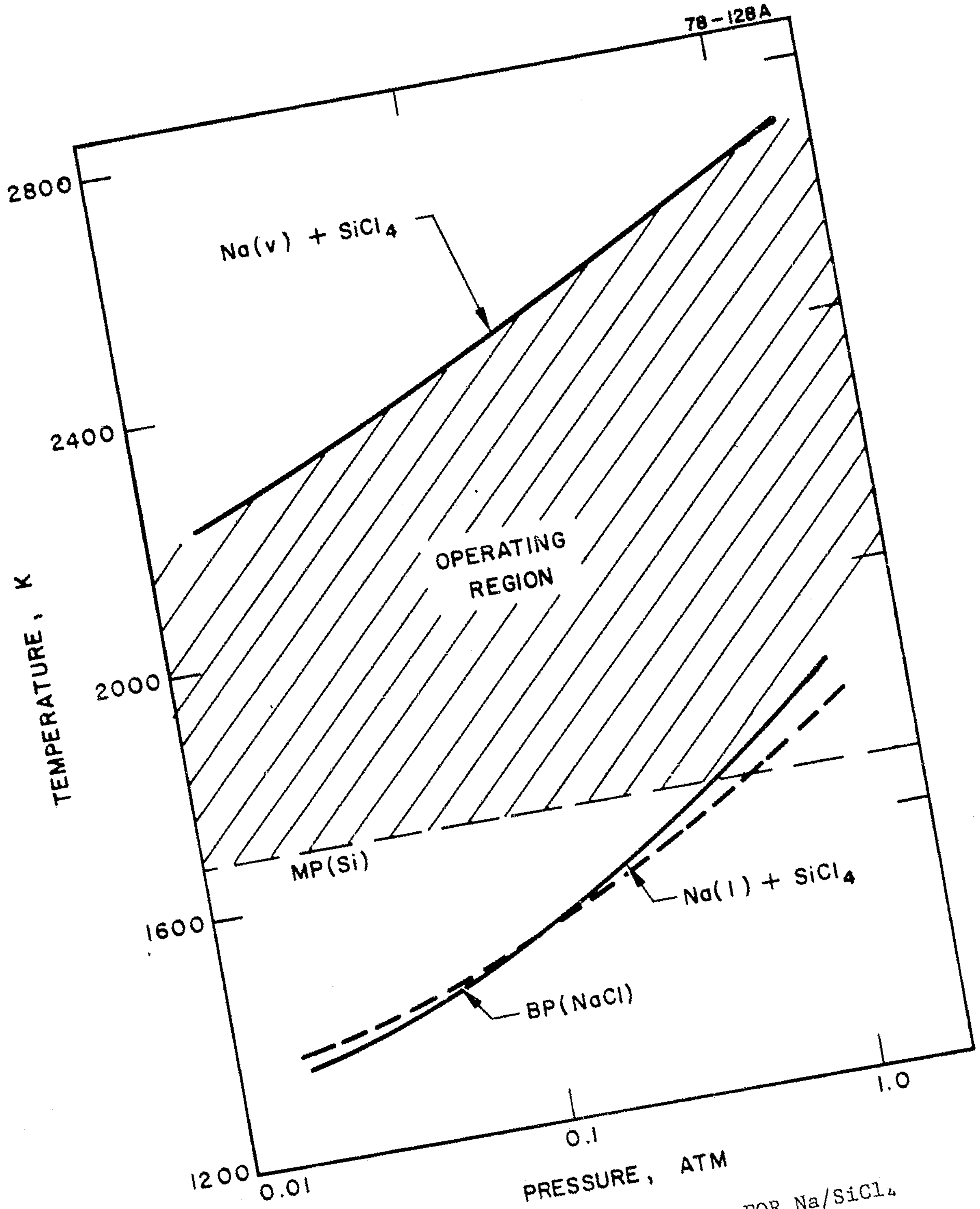

FIGURE 5 ADIABATIC FLAME TEMPERATURES FOR Na/SiCl$_4$

The upper solid curve is for Na vapor at its boiling point while the lower solid curve is for Na liquid. The dashed lines indicate the boiling point of NaCl and the melting point of Si.

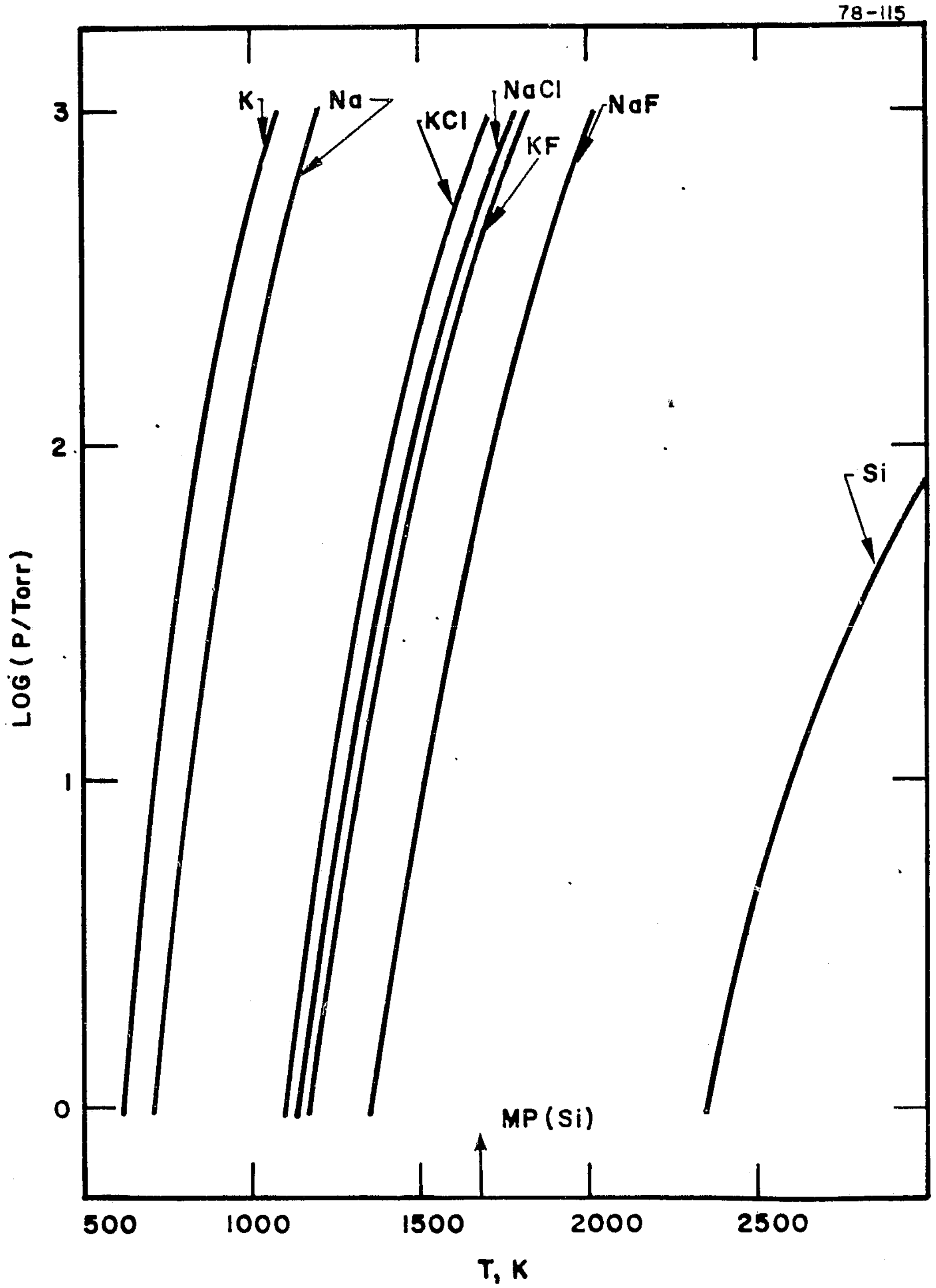

FIGURE 6 VAPOR PRESSURE DATA FOR SEVERAL SPECIES IMPORTANT IN ALKALI METAL-SILICON HALIDE FLAMES

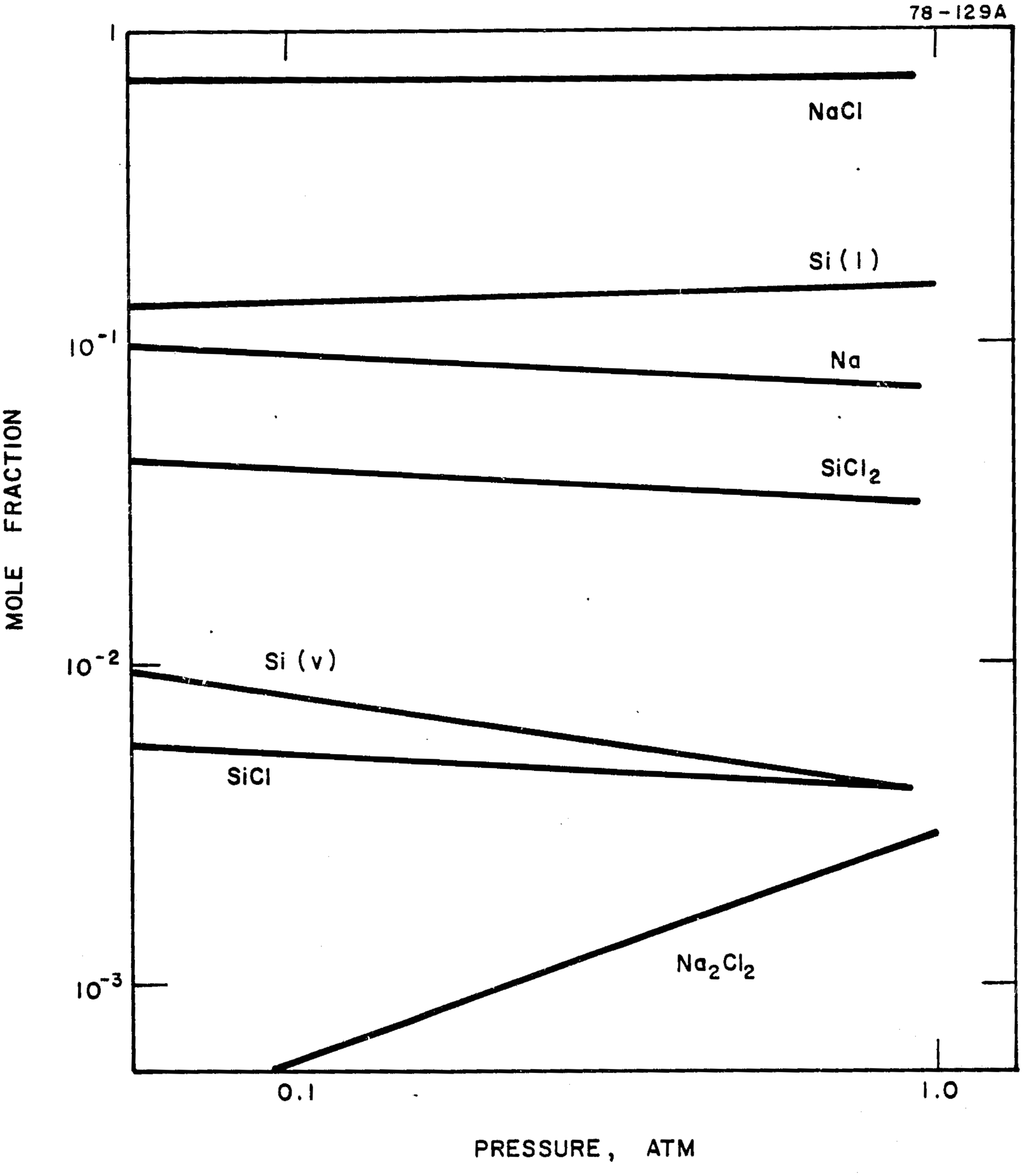

FIGURE 7 PRODUCT CONCENTRATIONS FOR STOICHIOMETRIC $Na/SiCl_4$ USING VAPOR PHASE REAGENTS

$$BCl + Si \rightleftarrows SiCl + B \qquad (3)$$

obtained by subtracting Reaction (1) from Reaction (2). Thus

$$\frac{[Si]}{[B]} = \frac{K_2[SiCl]}{K_1[BCl]} = 7 \times 10^4 \frac{[SiCl]}{[BCl]}$$

which implies, assuming BCl and SiCl are present in direct proportion to their their concentrations ~~in the~~ reactants, an enrichment factor of $1/1.3 \times 10^{-5} = 7 \times 10^4$.

In the reactions analogous to (1) and (2) involving condensed phase Si and B rather than gaseous metal atoms, boron is again less favored than silicon, the equilibrium constants for the respective reactions being in the ratio $30 \times 10^8 : 1.5 \times 10^8$. This implies that an enhancement of at least 20 in Si/B ratio in the condensed phase products over that prevailing in the halide reagents is attainable.

These results show the likelihood that a practical process for the production of silicon can be achieved using vapor phase reagents in the $Na/SiCl_4$ (or one of several other) reaction system. These reactions are known to produce stable, self-sustaining "diffusion flames" even in dilute gas mixtures at low pressures, indicating that they should be readily amenable to scale-up to higher pressures and higher reactant flow rates. The flame reactions are spontaneous and thus require no ignition source; they are luminous and therefore easily monitored and they are strongly exothermic with respect to standard state reactants at 298 K thereby minimizing the need for external energy input. Consequently, they appear ideally suited to utilization as a practical preparative method. It is emphasized, however, that these are equilibrium compositions and it would be surprising if reaction kinetics and condensation rates would all be sufficiently fast that they could be safely ignored in predictions of actual composition distributions.

III. OPPOSED-JET EXPERIMENTS

A. REAGENT GENERATORS

The initial experiments in this program were low pressure diffusion flames using vapor phase reactants. The objective was to determine the stability of the flames, demonstrate that the reaction rates were very rapid, and develop the techniques for producing and handling the vaporized reagents. A brief survey of the spectroscopic characteristics of several flames was also made to possibly identify intermediate reaction species and to determine the reaction temperature.

As discussed in the previous section, the use of vaporized reagents results in high adiabatic flame temperatures, above the boiling point of the product alkali metal salt. This technique also has the advantage that one may put a distillation stage at the input to the reactor, reducing the impurity concentration in the reagents. Gas-phase alkali metals are not, however, used extensively in the chemical industry and so some work was necessary to develop the needed expertise.

Vapor generators of a common basic design were used to produce both alkali metal and silicon halide reagent streams (with the exception of SiF_4 which is a gas at room temperature). A schematic diagram of the first alkali metal source is shown in Fig. 8. It is an electrically heated boiler equipped with a reflux column which can be pressurized from the top with an inert gas. It may also be thought of as a distillation column functioning as a "heat pipe" with the vapor pressure of the metal being equal to the pressure imposed by the inert gas. Construction of this source was from welded 304 stainless steel. The heating coils were 1/8 in. diam stainless steel rod, powered by a 250 A adjustable welding supply. This power supply operated in the constant current mode and therefore was insensitive to minor variations in the heater circuit resistance. The tube through which the alkali metal vapor was delivered was incorporated into the heating current path to prevent condensation of Na or K in the tube and blockage of reagent delivery. The vapor to be reacted with silicon halide ($SiCl_4$ initially) was drawn off between the boiler and the condensation point in the column through a 0.25 mm diam sapphire orifice mounted in the delivery tube. If a higher flow rate was desired, the inert gas (Ar) pressure was increased, more heat was withdrawn from the boiler, and the vapor pressure of the metal increased to match the Ar pressure being

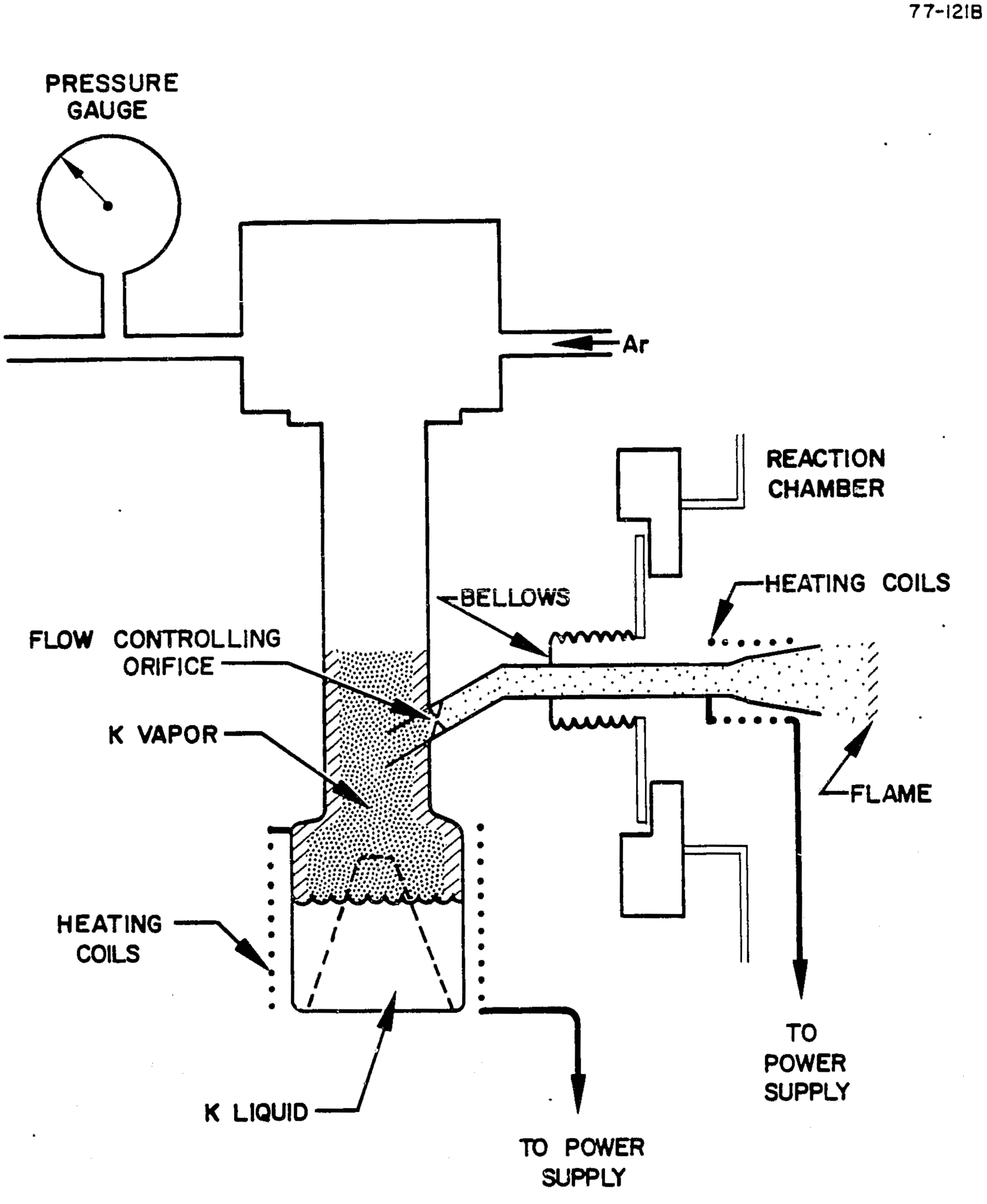

FIGURE 8 ALKALI METAL VAPORIZER

superimposed. At all times, the pressure downstream of the sapphire orifice was maintained at half the generator pressure or less to insure that critical (sonic) flow was maintained. Under these conditions, the flux of reactant vapor was directly proportional to the upstream pressure only.

Attempts to find an acceptable material from which to fabricate the orifice required considerable effort. The sapphire used in our first model was found to crack and erode after three to four hours of operation; it was replaced with 304 stainless steel. The steel, too, eroded rapidly. A 0.33 mm diam orifice opened to about 1 mm diam in the course of three runs of less than one hour duration each. The flow control aspect of the problem could be solved by replacing the fixed size orifice with a valve that could be adjusted to compensate for the increasing aperture size as the orifice eroded; however, the contamination introduced by erosion still predicated the use of an alternative material.

The sodium vaporizer was later modified to give better flow control and to allow complete shutoff of Na delivery with the boiler hot. This was accomplished by adding a needle valve to the delivery tube capable of operating at $T \approx 1200$ K. The tapered needle and seat were located in the vaporizer at the upstream end of the delivery tube (see Fig. 9) while the valve body (threads and Teflon sealing material) was located at the end of a stainless steel extension rod some 20 cm away from the extremely hot region. This arrangement gave good control of the metal vapor delivery rate and cool operation of the valve body. The needle and seat were first constructed of 304 stainless steel and later nickel, but both materials were significantly eroded in less than two hours of operation. A needle and seat of Inconel were then made and found to be much more corrosion resistant. However, at this time we also modified our procedures to remove small amounts of oxygen and/or oxides which might be present in the alkali metal vaporizer and which existing information indicated was a prime source of corrosion problems. A scavenger material which would react with any available oxygen to form a stable oxide was placed in the vaporizer along with the alkali metal. In order to prevent contamination of the sodium reactant, silicon was used as the scavenger. With these modifications the vaporizer performance was quite satisfactory.

The first silicon halide vaporizer was similar in design but, due to the lower temperatures required, heating was achieved by circulating hot water through a jacket surrounding the boiler. The whole assembly was constructed

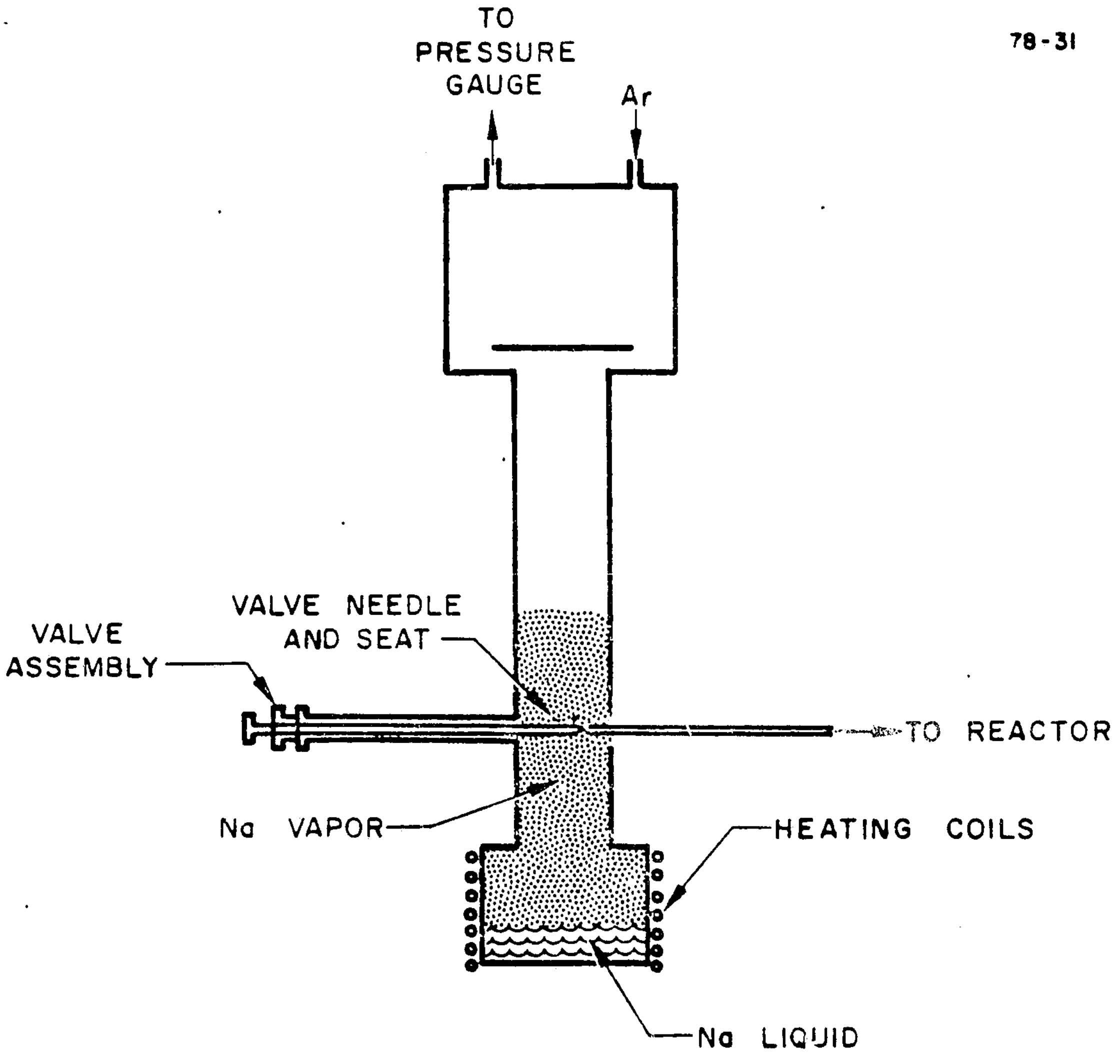

FIGURE 9 MODIFIED ALKALI METAL VAPORIZER

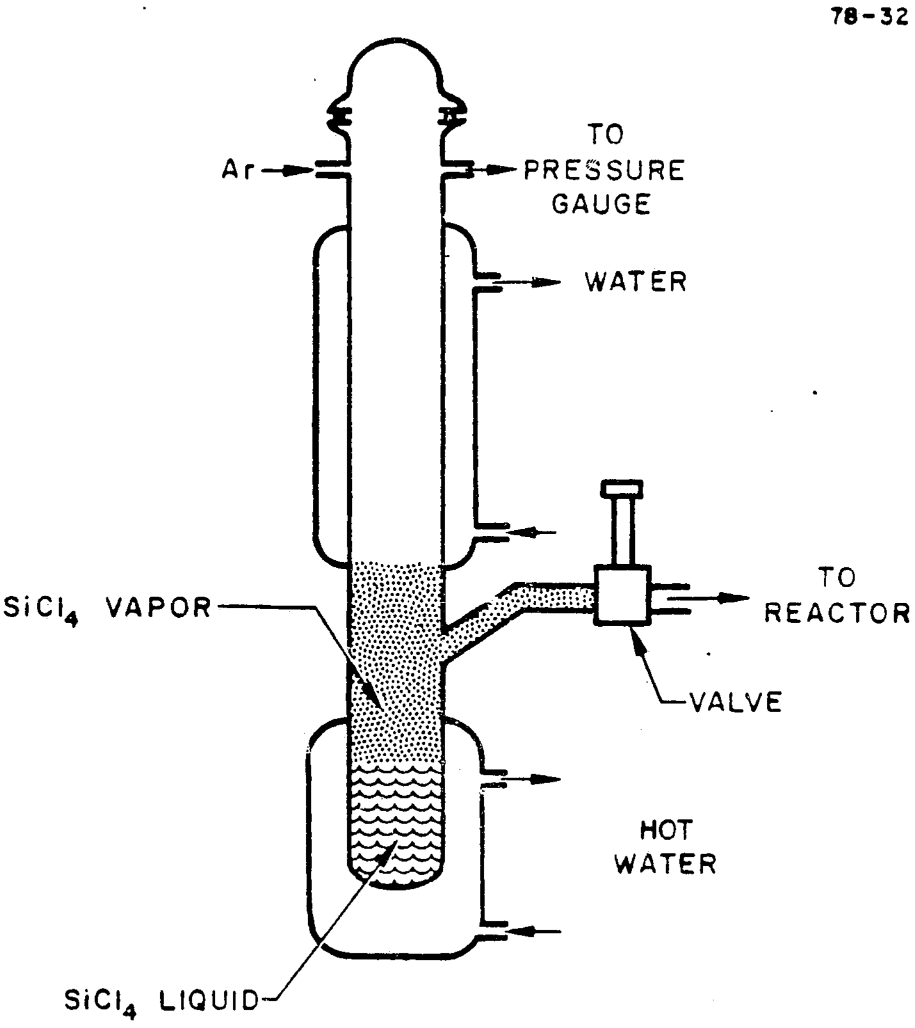

FIGURE 10 SILICON HALIDE VAPORIZER

of glass and the vapor flow was controlled by a stainless steel valve. $SiCl_4$ and $SiHCl_3$ were supplied from this apparatus, shown in Fig. 10, while SiF_4 was delivered directly from a high pressure cylinder using a corrosion resistant regulator and stainless steel needle valve.

B. REACTOR

Initial low pressure experiments were performed in a steel reaction chamber of 35 cm diam with five ports, two sets of opposed ports with one port perpendicular to the plane of the other four. Two opposed ports were used for reagent inlets as indicated in Fig. 11. The other two are used for viewing and spectroscopic measurements. We chose to initiate the program with low pressure flames of K and $SiCl_4$ with the reagents being introduced as opposed jets. The burner housing was therefore equipped with pumping capability comprising a 8500 ℓ min^{-1} mechanical pump. Since this reaction produces only condensable products there is, in principle, no need for the pump after the reactor has been exhausted initially. However, in practice, it was found desirable to sweep the windows and the reactor volume with small flows of Ar to maintain visibility.

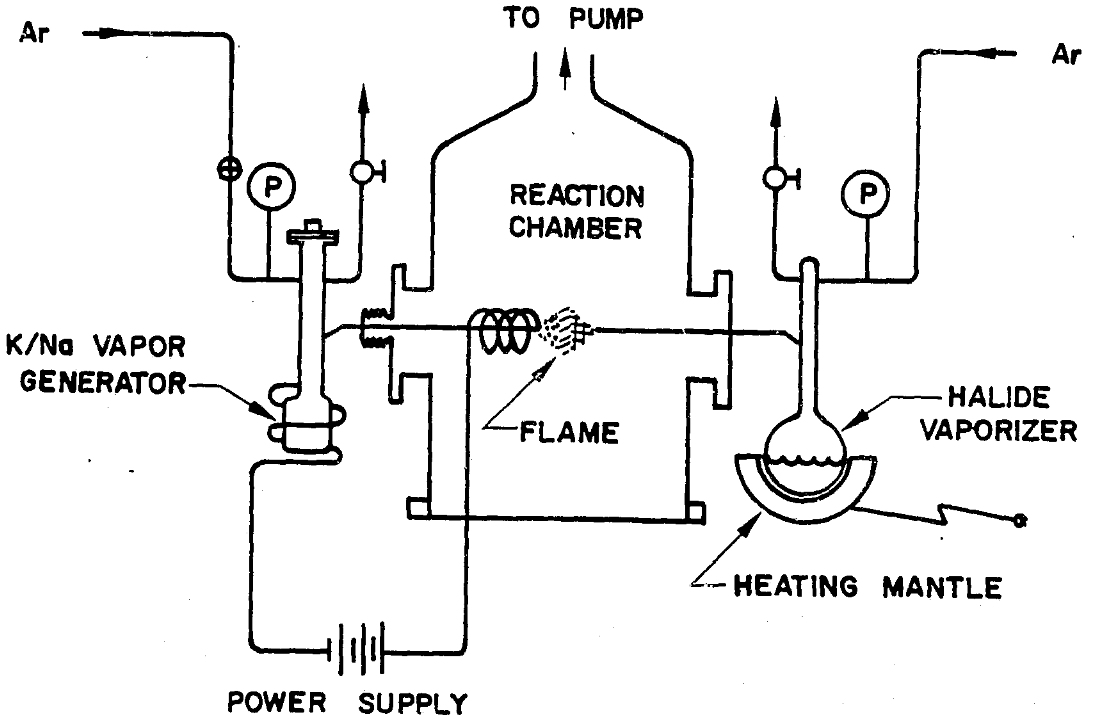

FIGURE 11 SCHEMATIC DIAGRAM OF LOW PRESSURE OPPOSED JET EXPERIMENTS

C. EXPERIMENTAL OBSERVATIONS

Both reagent generators performed well. Some irregularities in the boiling of Na or K were encountered, particularly when a fresh charge of metal was heated for the first time. Also heat losses in the alkali metal delivery tube caused condensation and clogging in some experiments. Additional heating of this stainless steel tube prevented this behavior.

Initially flames of $SiCl_4$ were established with K and later with Na. Low pressure, 1 to 10 Torr flames were blue-green in color and diffuse in character. The flow of each reactant was varied over the range of about 0.1 to 1.5 g min^{-1} by adjusting the appropriate vaporizer pressure (Ar). These flow rates were based on critical flow through orifices of known diameter. At stoichiometry the mass flow ratio of $Na/SiCl_4$ is 4(23)/170 = 0.54 and of $K/SiCl_4$ is 4(39)/170 = 0.92. When the flows were close to stoichiometric ratio the flame positioned itself nearly midway between the two opposed reagent jets. Flames stabilized in 100-200 Torr Ar were yellow in appearance and spacially very compact. No visual difference was observed in using K or Na as reducing agent.

To better characterize reaction zone temperatures and to gain information about the transient species present and the energy-transfer processes occurring in alkali metal-silicon halide flames, we have recorded the emission spectra of these flames and, in the same experiments, collected solid product samples. The low pressure diffusion flames of K + $SiCl_4$ and Na + $SiCl_4$ exhibit similar spectra[5] characterized by strong K or Na atomic emission lines along with several chemiluminescent bands in the blue and green. Our initial instrumental examination of this flame was made using an f/4 Spex "Mini-mate" 0.25 m monochromator with a 1P28 photomultiplier detector. The monochromator was oriented at a right angle to the axes of the opposed reagent inlet tube; light from the flame between the inlets was focused on the entrance slit with a 6.5 cm diam lens. Although this instrument had low resolving power, its large aperture made it appropriate for the rapid survey work desired in preliminary experiments. The spectra of the $K/SiCl_4$ flames contain strong emissions from both K, at 405 nm, and Na at 589 nm. A continuum underlies the visible portion of the spectrum with an intensity maximum near 450 nm.

A typical spectrum from a $Na/SiCl_4$ flame which exhibits identical features to those from K flames with the exception of the K atomic lines, is given in Fig.12. The intensities are not corrected for the wavelength response of the grating or the detector. The strong lines at 569, 498, 467, and 450 nm (in addition to the resonance doublet at 589), are attributable to Na emission from exceptionally high energy levels. The 569 nm line, for example, arises from the 4D level of Na, nearly 100 kcal above the ground state. Excitation of this magnitude is usually the result of energy transfer processes. In the Na/Cl_2 system the production of excited Na has been attributed[3] to the reactions

$$Na_2 + Cl \rightarrow NaCl^{\ddagger} + Na$$

and

$$Na + NaCl^{\ddagger} \rightarrow NaCl + Na^*$$

i.e., transfer of vibrational energy deposited in the diatomic product of a highly exothermic reaction to the free atom.

The only other identifiable features of this spectrum were lines which appear to be due to excited Si atoms. These emissions were detectable only from the brightest regions of the flames and are quite weak. This was due to the fact that the Si lines in the visible portion of the spectrum originate from very high energy levels; a search into the ultraviolet was indicated.

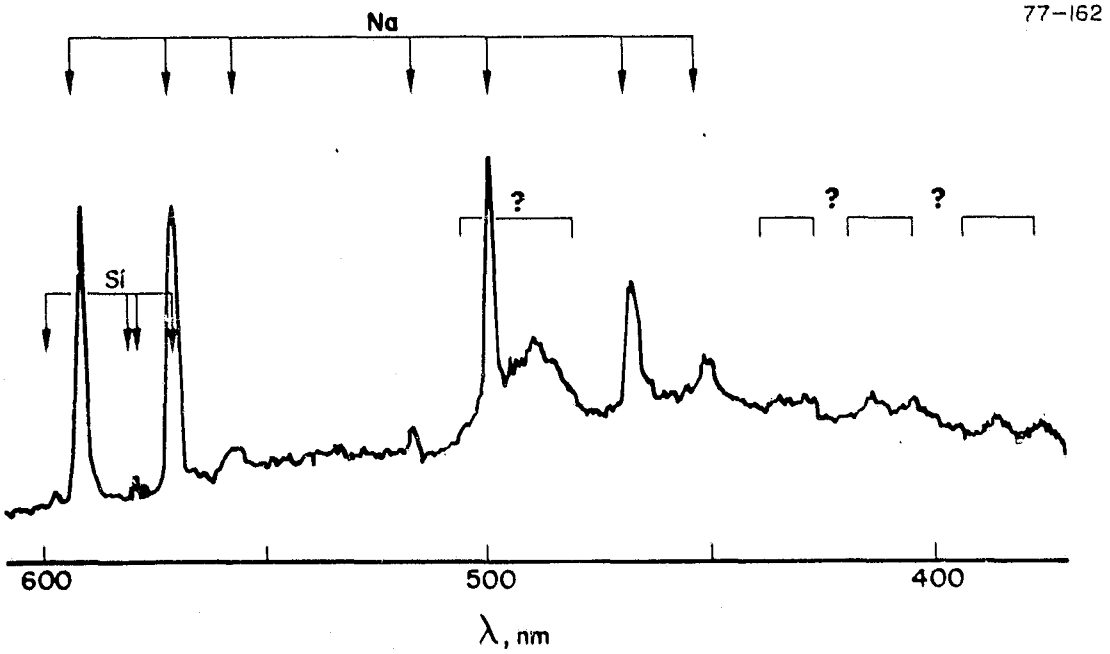

FIGURE 12 SPECTRUM FROM LOW PRESSURE $Na/SiCl_4$ FLAME

The bands in the 400-500 nm region were not identified. It is worth noting, however, that bands of a very similar nature were observed in the reaction zones of the $SiCl_4/H$ non-equilibrium plasma jet.[13] The most likely candidate emitters, then, would appear to be Si_2, SiCl or $SiCl_2$ although if either of the former two are responsible, they must be in extremely high energy states, as well.

Additional experiments were performed to record the ultraviolet spectra of $Na/SiCl_4$ flames from 200 to 400 nm using the same equipment as in our earlier experiments but viewing through a quartz window. An ultraviolet bandpass filter (Corning 7-54, $240 < \lambda/\text{nm} < 400$) was also used in some experiments. Figure 13 shows a typical spectrum obtained without the bandpass filter. Strong emissions attributable to Na were observed at 330, 309, 285, and 268 nm and to Si at 288 and 252 nm. Several weaker emission bands from 225 to 249 nm were first attributed to SiCl, but later higher resolution spectra allowed a determination that the emitting species was SiO produced from reaction with either oxygen in the reagents or with residual O_2 in the reaction chambers. The band at 259 nm remains unidentified.

A calculation of the effective temperature of the Si, assuming equilibrium excitation, was made from the relative intensities of the Si atomic emission observed at 288 and 252 nm and the corresponding published transition probabilities.[14] Emission at the latter wavelength was assumed to be due to a combination of the Si lines at 251.4, 251.6, 251.9, 252.4 and 252.8 nm. This procedure yielded a temperature of 4900 K--some 2500 K above the adiabatic maximum. Non-equilibrium excitation of this nature indicates either that the emitting silicon atoms are produced in highly exothermic chemical reactions leading directly to excited states, or possibly that Si atoms are long-lived enough to undergo energy-pooling collisions from high-energy electronic/vibration states of diatomic molecules. These Si atoms, then, are not in thermal equilibrium with the remainder of the gas, so an accurate flame temperature was not attainable from this species.

We also obtained emission spectra from flames of $Na + SiHCl_3$, $Na + SiF_4$, and $K + SiF_4$. The spectrum from a $Na + SiHCl_3$ flame is shown in Fig. 14. The spectrum is dominated by Na lines with an overlapping broad continuum peaking at a wavelength of about 500 nm. The emission due to SiH[15] observed at 414 nm in this flame had not been observed in the $Na + SiCl_4$ flames.

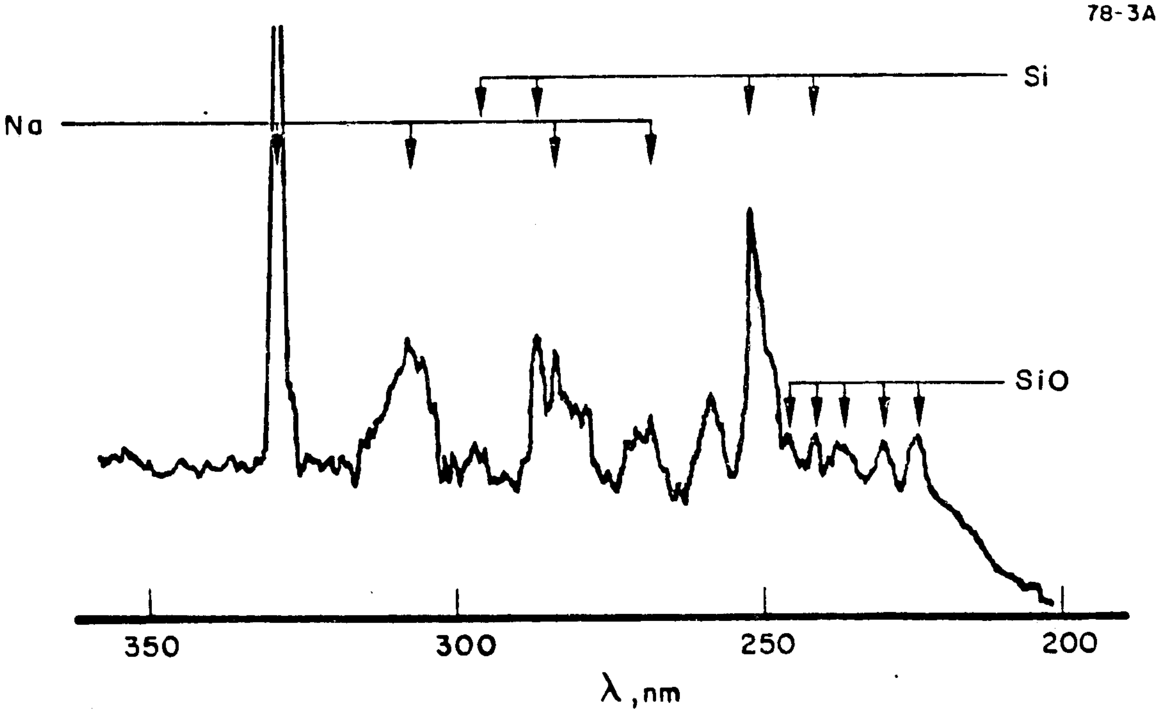

FIGURE 13 Na + $SiCl_4$ FLAME ULTRAVIOLET SPECTRUM

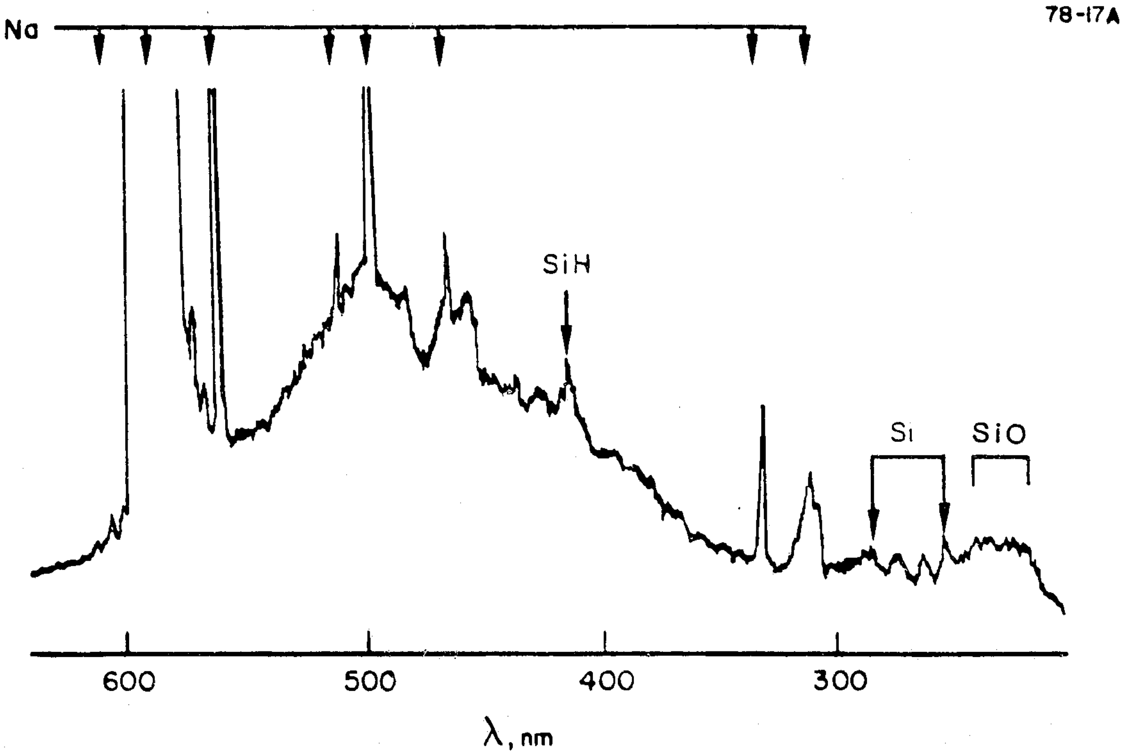

FIGURE 14 Na + $SiHCl_3$ FLAME SPECTRUM

The ultraviolet portion of this spectrum consists of Na lines at 330 and 309 nm plus a number of weaker bands at wavelengths less than 300 nm. The SiO bands from approximately 215 to 245 nm and the Si atomic emission at 251 and 288 nm were again observed as in the Na + $SiCl_4$ flame but at much lower intensities.

Flames of SiF_4 with either Na or K were not found to exhibit the strong emissions that characterize the $SiCl_4$ and $SiHCl_3$ flames. Both SiF_4 flames were just barely visible, the spectrum showing only Na lines at 589 and 569 nm. No ultraviolet emission was observed. From the difference in the adiabatic flame temperature between SiF_4 and $SiCl_4$ systems (see Section II) the sodium emission intensity would be expected to be smaller by more than two orders of magnitude, roughly in accord with our observations.

Solid product material was observed to deposit on the reactor walls and reagent inlet tubes during these opposed-jet experiments. Several samples were taken off the walls after runs with $SiCl_4$ and either K or Na. The reaction product appeared to be a mixture of brown and white powders. The configuration of the reactor precluded determination of the time required for particle formation since there was no bulk gas flow. The deposits accumulated on all the walls of the apparatus; they adhered very loosely to the walls and did not form dense agglomerates. At some positions in the reactor the powder was nearly all white, at others, a dark brown.

There were no apparent visual differences in the products of the two alkali metals. After the powders were collected, they were placed in a filter funnel and washed with distilled water and dilute HCl. After drying, the product was in the form of a dark brown cake which crumbled readily into a freely flowing powder. Examination under a metallurgical microscope revealed agglomerates of irregular shapes and sizes that appeared to be composed of sub-micron roughly spherical particles.

In order to determine whether impurities in the reagents become more or less concentrated as they are converted to product, we performed a series of qualitative analyses for heavy elements using X-ray fluorescence. Samples of the technical grade $SiCl_4$ reagent were hydrolyzed in distilled H_2O and the resultant SiO_2 used as the basis of comparison for product purity. The reagents exhibited fluorescence from the contaminants Fe, Hg, Cu, Ni, Zn, and Br. The washed, brown amorphous silicon product contained no detectable Hg or

Br and reduced quantities ($<$ 10 ppm) of Cu, Ni, and Zn. The Fe content of both reagents and products was highly variable; rust from the inside of the reactor and contamination by stainless steel laboratory utensils used in the washing processes were probably responsible. Quantitative measurements were deferred until experiments could be run under more carefully controlled conditions.

For both of the SiF_4 flames the solid product collected from the reactor walls was found, after washing with water, to be a tan powder unlike the dark brown product of the $SiCl_4$ and $SiHCl_3$ flames. Since the abstraction reactions of Na with SiF_x, x = 1-4, are endothermic and, by analogy with similar reactions, are expected to occur slowly, the production of silicon and nucleation of the solid would be expected to be slower than for the reactions of other silicon halides.

IV. FLOW REACTOR EXPERIMENTS

A. APPARATUS

In the opposed-jet experiments the reaction products had little net flow velocity and a majority of the product either settled to the bottom of the chamber or condensed on its walls. Reagent flow rates were quite low and the configuration did not allow variations of parameters such as wall temperature or bulk gas (Ar) flow velocity. A tubular flow reactor was therefore designed to study the overall reaction rate, product condensation and deposition rates, and separation and collection efficiency. Higher mass flow rates and wall temperatures were also to be investigated.

Basically, the tubular flow reactor consisted of a 200 cm long, 15 cm diam, heavy-walled Pyrex pipe with reagent and inert gas delivery system at one end and connection to a vacuum system at the other end. Figure 15 shows the overall configuration of the apparatus. An inner tube of smaller diameter was used to increase the linear flow velocity of the gas and to allow insulation and/or heating of the inner reactor tube walls. The figure shows the apparatus as run with uninsulated walls using a 120 cm long, 6.4 cm diam Pyrex reaction tube insert. Various tube materials and dimensions were used during the course of the program. A glass wool particle filter was used to prevent fine dust from reaching the vacuum pump (a Stokes 300 $ft^3\ min^{-1}$ pump). The apparatus was capable of operating at pressures from 2 atm down to a few Torr and was segmented to provide access for product sample removal.

The inlet flange is shown in Fig. 16. The alkali metal and silicon halide vaporizers have been described in Section III and were simply moved from the opposed-jet reactor to this apparatus. In the initial configuration, the $SiCl_4$ was added using a 4 cm diam injector ring of 0.3 cm stainless steel tubing. In these experiments reagent mixing was poor and the silicon production in the tube was relatively inefficient. A modified inlet region was constructed, as shown in Fig. 17, to increase the mixing rate and flame intensity. A third annular nozzle was also incorporated to allow the addition of an inert gas or a H_2/Ar mixture. The configuration shown in Fig. 17 has the inert gas exiting the nozzle between the reagents; the $SiCl_4$ and Ar inlet were exchangeable for experiments with an outer sheath of gas. The nozzles were constructed of stainless steel; the main flange was gold-plated aluminum and water-cooled to transfer away the heat of reaction.

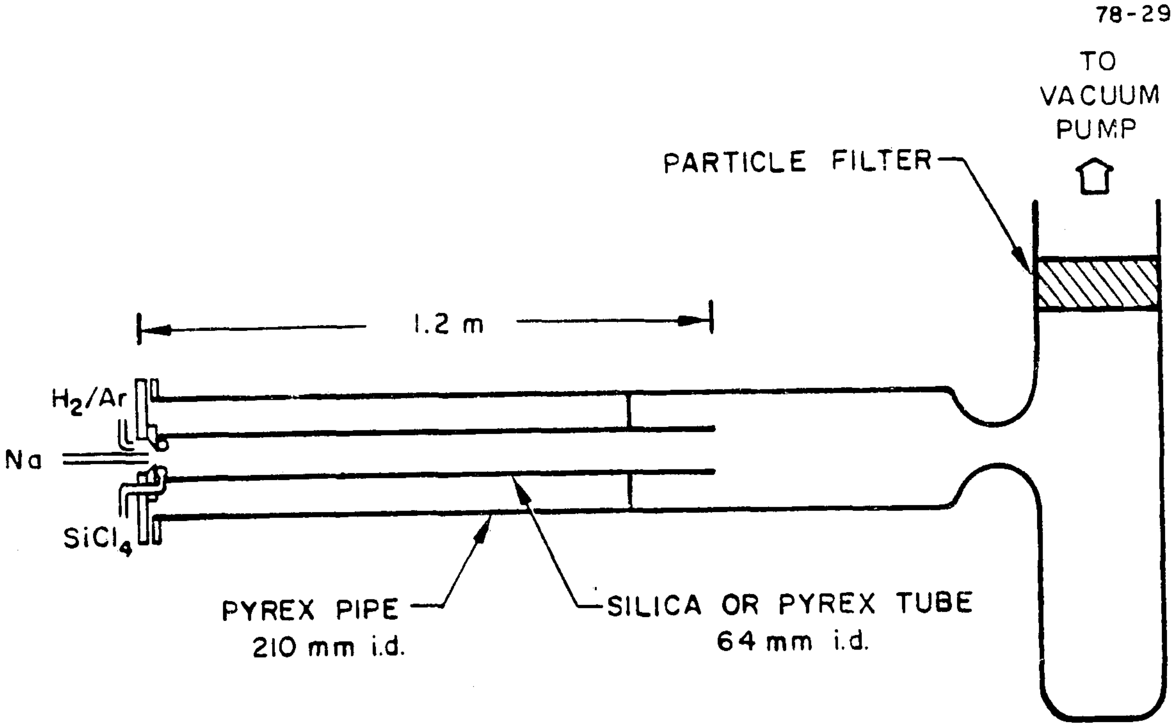

FIGURE 15 TUBULAR FLOW REACTOR

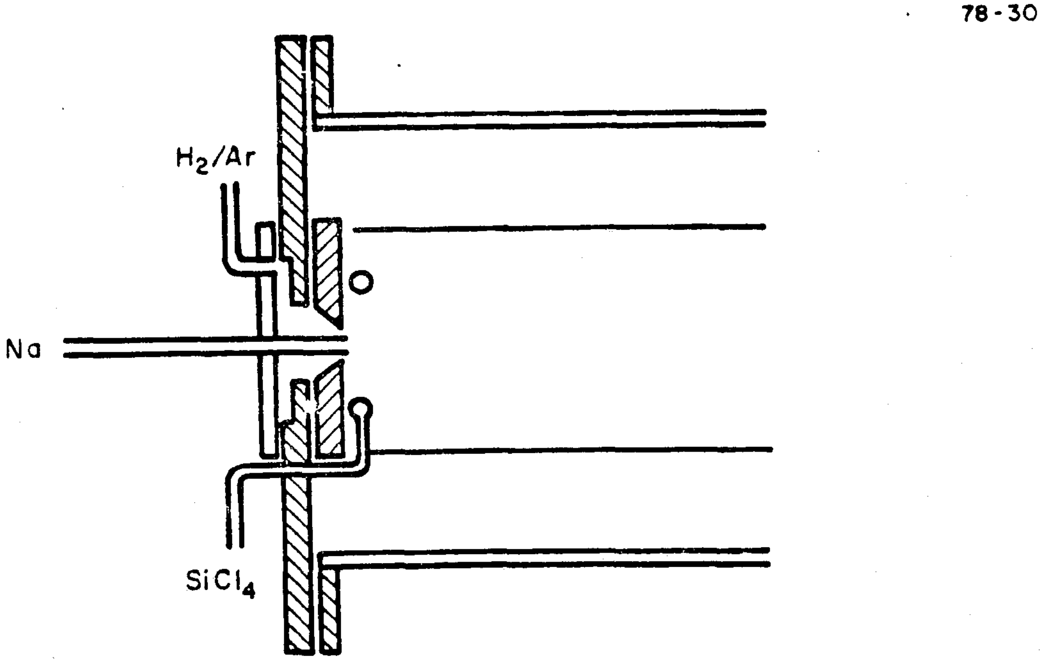

FIGURE 16 INITIAL FLOW REACTOR INLET FLANGE

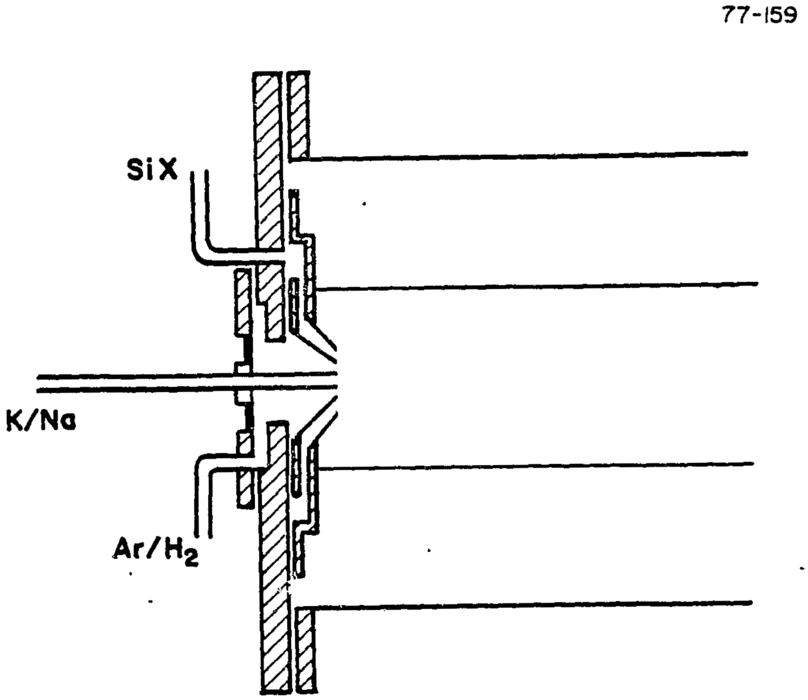

FIGURE 17 ANNULAR NOZZLE FLOW REACTOR INLET SECTION

One of the objectives of experiments with this apparatus was to simulate conditions of the proposed Westinghouse arc-jet process[16] for silicon production in which silicon halide is reduced by reaction with sodium. In this design the reagents are sprayed in as liquids and additional heat input is supplied by a jet of H_2/Ar arc-heated to $T \approx 3500$ K. It was recognized at the outset that it would be impossible, and indeed unnecessary, to construct an exact small scale analog of the Westinghouse apparatus. Instead reactions were to be run under thermodynamically identical conditions with the input enthalpy distributed among all the reactants rather than being concentrated mainly in the H_2/Ar arc-jet stream as in their apparatus. Table III summarizes the input conditions of each of the two reactors. The enthalpy of the H_2/Ar (mol ratio 4:1) stream issuing from the arc jet was taken as 57.6 kcal mol^{-1} (6 kcal g^{-1}), a value lying in the center of the 90 to 135 kg h^{-1} operating envelope for silicon production. The enthalpies for liquid Na at 500 K and $SiCl_4$ in its standard state at 298 K for the arc-jet input were taken from the JANAF Thermochemical Tables.[11] After multiplying by the appropriate mole fractions specified in Ref. 16 and summing, a value of -1.9 kcal mol^{-1} is obtained.

TABLE III

COMPARATIVE THERMOCHEMICAL PARAMETERS FOR ARC-JET PROCESS SIMULATION

		AeroChem Simulation Reactor			Westinghouse Arc-Jet Reactor		
Reactant	Mole Fraction	State	T (K)	H (kcal)	State	T (K)	H (kcal)
$4H_2/Ar$	0.33	gas	1300	2.2	gas	$\sim 3600^a$	19.2
Na	0.53	gas	1200	16.1	liquid	500	1.1
$SiCl_4$.	0.14	gas	600	-20.2	liquid	298	-22.2
			Total	-1.9			-1.9

[a] Estimated from Fig. 5.2 Ref. 16 for heating value of 6 kcal g^{-1}.

To match this enthalpy in the apparatus of Fig. 15 in which the Na and $SiCl_4$ are both introduced as vapor at the temperatures indicated in Table III, the H_2/Ar fraction must have a heat content of 2.2 kcal or 6.7 kcal mol^{-1}. This enthalpy is achieved in a H_2/Ar = 4:1 mixture at a temperature slightly in excess of 1300 K. These conditions are easily attainable with conventional resistively heated laboratory furnaces such as the one indicated in Fig. 18. The oven consists of a standard 1.2 kW resistance heater in a well insulated container. Tests showed that this apparatus could achieve temperatures greater than the required 1300 K. A small heater for the $SiCl_4$ (or other silicon halide) vapor was also added. This was simply a heated quartz tube in the flow line between the halide vaporizer and the reactor, with a thermocouple at its exit. A stainless steel tube was first used but the metal was rapidly attacked by the hot $SiCl_4$. The quartz showed no signs of reaction with the $SiCl_4$ and no decomposition products were found in the exit tube. This heater allows some flexibility in the temperature to which the H_2/Ar stream had to be heated in experiments designed to simulate the Westinghouse process. The polyatomic $SiCl_4$ (and other silicon halides as well) has a considerably higher heat capacity than a H_2/Ar mixture, so higher input enthalpies could be achieved by rather modest preheating of this reagent stream. For example, the ratio $Cp(SiCl_4)/Cp(4H_2/Ar)$ at 500 K is 3.5, thus requiring heating of the $SiCl_4$ only 100 K to provide additional reaction zone enthalpy equivalent to heating the H_2/Ar 350 K.

The adiabatic flame temperatures in both reactors are, of course, identical since the total input enthalpies and compositions have been matched. This temperature is 2370 K. The product composition at this temperature, calculated again with the Air Force ISP thermochemical equilibrium code, is given in

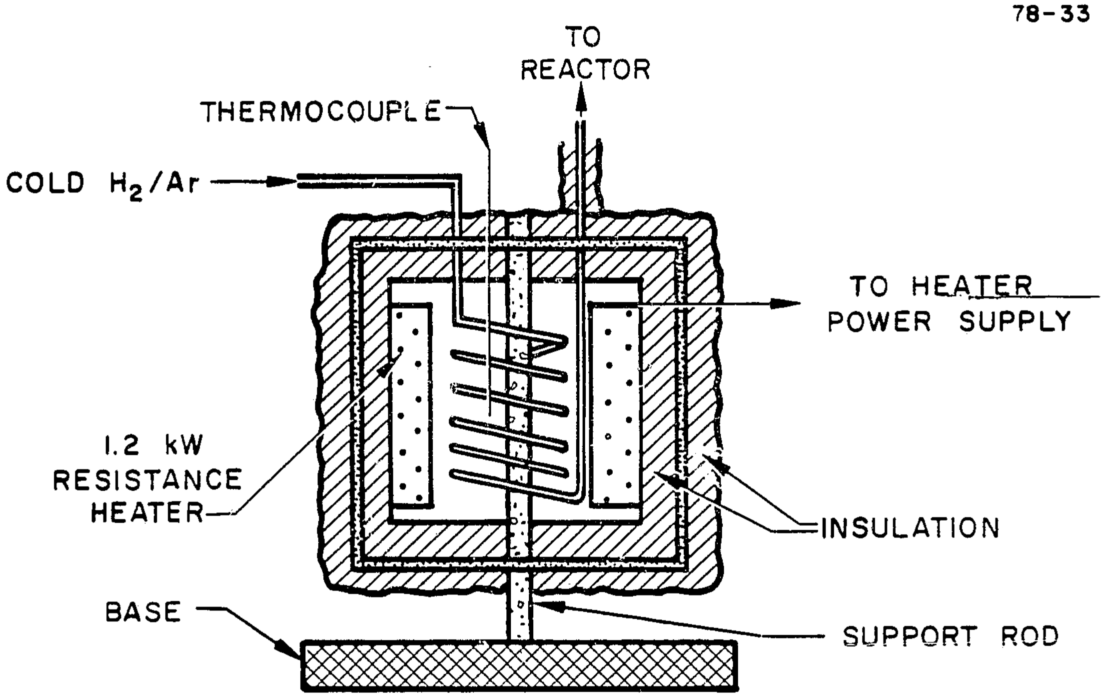

FIGURE 18 H_2/AR OVEN

Table IV. Silane, the chlorosilanes, Si_2, and Si_3 were calculated to be present in quantities less than 10^{-4} mole fraction and are not listed in the table. The only significant gas-phase silicon-containing species is seen to be $SiCl_2$, accounting for 7% of the total silicon present. Hydrogen is only slightly reactive, producing small amounts of HCl in the product distribution.

B. FLOW REACTOR EXPERIMENTS

Over fifty Na + $SiCl_4$ experiments were run in the flow tube reactor under a variety of conditions. The first group of experiments was run under conditions similar to those of the Westinghouse process. Heated H_2/Ar diluent was used to increase the flame temperature to about 2400 K. Reactor pressures and linear flow velocities were relatively low at ≈ 0.1 to 0.25 atm and 50 to 200 cm s^{-1}, respectively. Nominal reagent deliver rates were 0.03 and 0.12 mol min^{-1} for $SiCl_4$ and Na. An unheated 6.0 cm i.d. quartz tube was used. These conditions resulted in rapid cooling of the reaction products walls. Samples of this product were found (as in prior experiments) to be composed of very fine particles ($<$ 1 μm diam). If the two condensed products deposit

TABLE IV

CALCULATED EQUILIBRIUM PRODUCT COMPOSITION OF Na + $SiCl_4$ REACTION DILUTED WITH H_2/Ar[a]

Species	Mole %	Weight %
Ar	6.57	7.01
Cl	0.07	~~0.07~~
H	0.62	0.02
HCl	3.65	3.55
H_2	23.92	1.27
Na	5.41	3.15
NaH	0.03	0.02
NaCl	46.40	72.37
Na_2Cl_2	0.21	0.66
Si(g)	0.14	0.10
Si(l)	11.91	8.90
SiCl	0.11	0.18
$SiCl_2$	0.94	2.48
$SiCl_3$	0.01	0.03
$SiCl_4$	(7.6×10^{-7})	(0.001)
SiH	0.03	0.02

[a] Conditions as in Table III for an adiabatic reaction temperature of 2370 K.

in their stoichiometric 4NaCl + Si ratio, the samples would be 89.3% salt and 10.7% silicon by weight. Since the salt is easily removed by washing with slightly acidic (HCl) water, an investigation was made to see if samples taken from different parts of the reaction vessel contained higher silicon fractions. Samples taken from the flame region of the reactor (the first 20 cm of the tube) were found to be 50% richer in silicon than stoichiometric, with insoluble fractions of 16-22%. Samples taken from the downstream portion of the reactor were found to be 10-12% insoluble. Thus we see that in these experiments, which appear to be characterized by rapid nucleation of both products, silicon is apparently depositing onto the walls faster than the salt. Samples of the washed product from these experiments were subjected to impurity analysis (see Section III.C).

The second series of experiments was performed in this same 6.0 cm quartz tube heated to approximately 900 K prior to starting the reaction. The flame exothermicity further heats the tube walls in the reaction zone. Two experiments were performed with H_2/Ar diluent at approximately 1000 K and two with 300 K pure Ar diluent, both sets at volume flow rates of 50(STP)cm^3 s^{-1} (linear flow velocities ≈ 70 cm s^{-1}). Another run was made with hot H_2/Ar at half the diluent flow rate. In these experiments most of the product collected in the first half of the 100 cm long quartz tube. Specifically, in several runs an average of 76% of the solid was in the upstream half of the tube, 6% in the downstream half, and 18% collected on the particle filter in the line to the vacuum pump. The particle size of the material from the filter was smallest and was found to be slightly rich in salt content. Little difference was noted in solid product deposition or character between the experiments using the hot H_2/Ar and cold Ar diluent. The flame, however, was less luminescent when H_2 was present in the diluent. The reason for this difference is not understood. Samples of the washed product from these experiments were also analyzed for impurities.

To increase the linear flow velocity and reactor wall temperature we also used a quartz tube with 2.1 cm diam. Flow velocities were increased by a factor of eight and much higher wall temperatures were achieved. The NaCl/Si mixture was fused to the reactor walls, demonstrating that temperatures in excess of the melting point of salt (1074 K) were achieved. Following these experiments the small quartz tube was brittle, cracked easily, and it was impossible to separate the fused product from the reactor walls without destroying the tube. Other tube materials or better temperature control along the pipe were needed for these high temperature experiments so several experiments were performed using a high purity alumina tube of 2.5 cm i.d. Alumina is not, however, expected to be an acceptable material for the reactor walls, since the sodium does react with this material and Al contamination of the silicon would be expected. Very high wall temperatures were achieved in these experiments, estimated to be 1300-1500 K. Almost all of the solid product was found in the 10 cm downstream from the flame zone. This material was dark brown, crystalline, and covered most of the cross sectional area of the tube. Large fused salt crystals were found at the downstream end of the deposit.

A Na + SiF_4 experiment was run in the 6.0 cm i.d. unheated tubular flow reactor using Ar diluent at $T \approx 1000$ K. As was observed in our earlier experiments in the opposed-jet reactor, this flame was not as intensely chemiluminescent as the $SiCl_4$ flames. Large quantities of solid product, similar in appearance to the product of $SiCl_4$ reactions, were deposited onto the reactor walls. The washed product was dark brown, in contrast to the tan color of the product from our earlier SiF_4 experiments. Weight-loss measurements showed a large insoluble fraction near the flame zone, with 18.2% insoluble compared to 6.5% remaining after washing of the downstream product. The stoichiometric product of this reaction would be 14.3% silicon. However, a possible interference to the production of silicon exists[17,18] due to the reaction $SiF_4 + 2NaF \rightleftarrows Na_2SiF_6$, this product also being insoluble in water. To test whether our insoluble product was Si or a mixture of Si and Na_2SiF_6, we heated a sample to 1300 K under vacuum. At this temperature the equilibrium vapor pressure of SiF_4 would be greater than one atmosphere[18] and the Na_2SiF_6 would be completely decomposed. The residue was found to be 26% insoluble, the remainder presumably being NaF. The amount of silicon in the original product was therefore quite small, less than 18.2% x 26% or 4.7%. This Na + SiF_4 experiment was run with an unheated, uninsulated quartz tube, giving very rapid quenching of products. Higher reaction temperature and wall temperature should shift the equilibrium of the SiF_4 + NaF reaction away from the direction of Na_2SiF_6 production.

Further experiments were performed using a heated quartz flow tube. No Na_2SiF_6 was found in the product deposited in the hot zone of the reactor where the wall temperature was approximately 1000 K. The solid deposited downstream of the heated tube did, however, contain some Na_2SiF_6; heating a washed sample of this cold-zone product to 1250 K, produced measurable weight loss (due to SiF_4 evolution) and a corresponding amount of water soluble NaF(s). We concluded from these experiments that Na_2SiF_6 formation would not be a problem in an actual process reactor where the wall temperature could be maintained at or above 1000 K. There appeared to be little difference with respect to color, particle size, or purity between silicon produced at high temperatures using either SiF_4 or $SiCl_4$. The Na + SiF_4 adiabatic flame temperatures are, however, significantly lower than those of Na + $SiCl_4$ and, in addition, the boiling point of NaF is almost 300 K higher than the boiling point of NaCl; both of these factors make the separation of products in the Na + SiF_4 case more difficult. The boiling point of KF, however, is almost equal to that of NaCl and so product separation would be more favored in the K + SiF_4 system than in the Na + SiF_4 case.

C. PRODUCT ANALYSES

Scanning electron microscope (SEM) photographs of unwashed and washed samples of Na + $SiCl_4$ product from flow tube experiments were obtained and are shown in Figs. 19 and 20, respectively. The unwashed samples contain a larger portion of submicron "dust" along with larger (2-50 μm) particles. The larger entities appear to be rather loosely adhering agglomerates of small particles, with a highly textured surface. Similar SEM photographs of the washed product show particles in the 2- 40 μm range, with none of the loose "dust" visible. The washed particles appear to be more crystalline in character with smoother surfaces and more sharply defined edges. Apparently in the unwashed sample these Si particles are covered by a coating of small particles which are soluble in water. The small particles and "dust" are therefore tentatively identified as NaCl while the silicon appears to be present in the larger sizes.

Impurity analysis of silicon samples by X-ray fluorescence has proved to be unreliable and alternate methods were required. Eight samples from Na + $SiCl_4$ experiments and one from the Na + SiF_4 experiment were sent to a commercial laboratory for analysis by emission spectroscopy. Although this technique is not extremely sensitive, it offers a relatively simple and inexpensive analysis for a wide variety of possible impurities. Silicon samples with precisely known amounts of impurities were obtained commercially to standardize the measurements and calibrate the results. Samples were tested for thirty-one elements, and only nine elements were detected. Several other impurities of special interest in silicon for solar cell applications (boron, titanium, and zirconium, for example) were not detected at threshold levels of 10 ppm. Table V shows the results of these analyses. The product was confirmed to be silicon with an average of 0.016% Na (as NaCl). No special efforts were made in the washing process to be thorough in removing the salt. Sample #9 however contains Na as a principal component, lending additional support to the suggestion that large amounts of Na_2SiF_6 were present in this particular Na + SiF_4 reaction product. Samples #1 and #2, from an early experiment in an unheated quartz tube, contain considerable amounts of impurities from stainless steel (Fe, Cr, and Ni). The other samples show a much reduced level (2 ± 1 ppm) of Fe, with

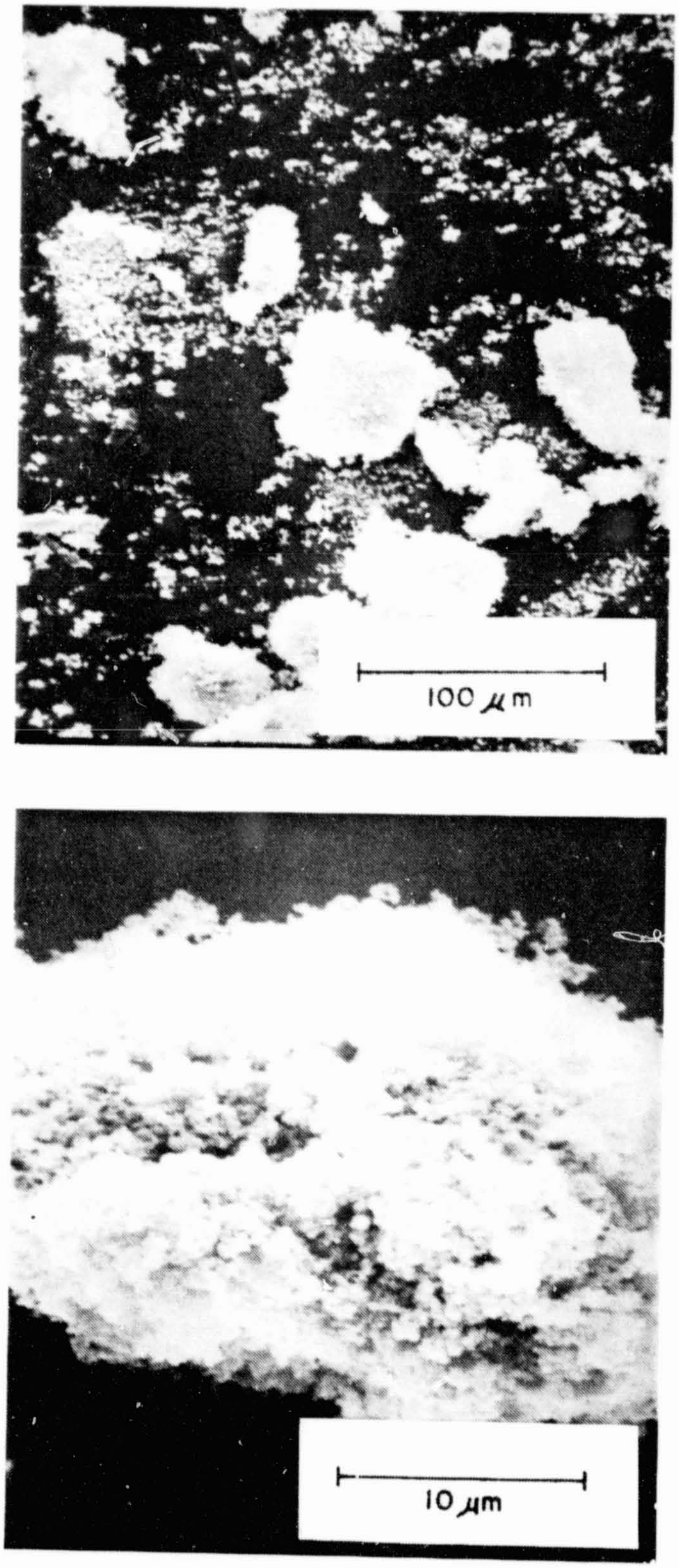

FIGURE 19 ELECTRON MICROSCOPE PHOTOGRAPHS OF UNWASHED PRODUCT ($4NaCl + Si$)

(Viewed at 45 degrees)

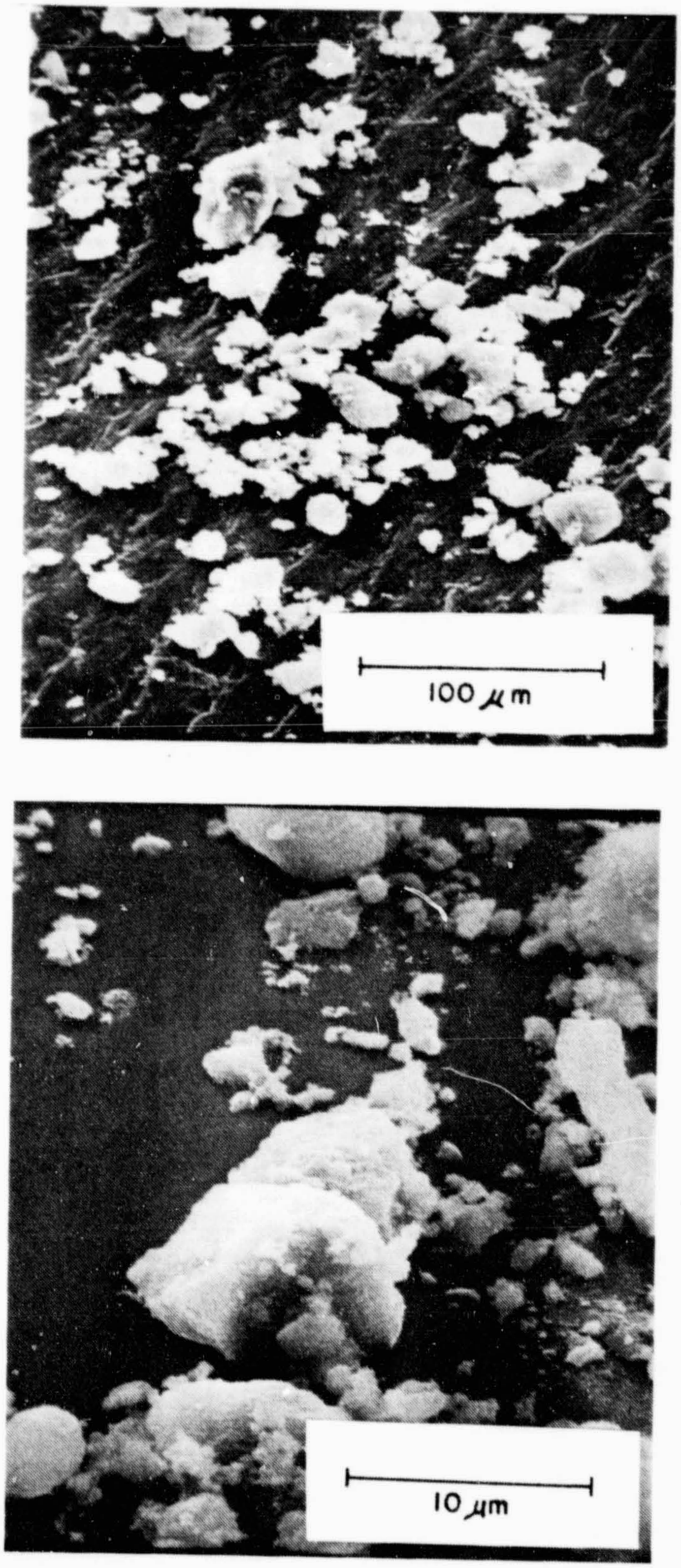

FIGURE 20 ELECTRON MICROSCOPE PHOTOGRAPHS OF WASHED PRODUCT

(Viewed at 45 degrees)

TABLE V

SPECTROCHEMICAL ANALYSIS OF SILICON PRODUCED IN SODIUM/SILICON HALIDE FLAMES

Element	Concentration, ppm								
Sample:	1	2	3	4	5	6	7	8	9
Si	P[a]	P	P	P	P	P	P	P	P
Na	100	200	350	200	150	100	90	90	P
Fe	150	5	3	3	2	2	–[b]	2	1
Cr	50	–	–	–	–	–	–	–	–
Ni	20	5	–	–	–	–	–	–	–
Al	< 1	< 1	–	–	–	–	–	5	–
Cu	10	10	1	4	2	2	2	5	1
Mg	< 1	< 1	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Ag	–	–	< 1	< 1	–	–	–	< 1	–

[a] P = principal component
[b] – = below threshold and not detected

Sample	System	Reactor	Diluent	Volumetric Flow Rate (STP cm^3 s^{-1})	Remarks
1	Na + $SiCl_4$	6 cm unheated quartz tube	hot H_2/Ar	150	sample from flame zone
2	Na + $SiCl_4$	6 cm unheated quartz tube	hot H_2/Ar	150	sample from downstream tube walls
3	Na + $SiCl_4$	6 cm heated quartz tube, T ≈ 950 K	hot H_2/Ar	50	
4	Na + $SiCl_4$	6 cm heated quartz tube, T ≈ 950 K	hot H_2/Ar	50	
5	Na + $SiCl_4$	6 cm heated quartz tube, T ≈ 950 K	300 K Ar	50	
6	Na + $SiCl_4$	6 cm heated quartz tube, T ≈ 950 K	300 K Ar	50	
7	Na + $SiCl_4$	6 cm heated quartz tube, T ≈ 950 K	hot H_2/Ar	25	
8	Na + $SiCl_4$	2.5 cm heated alumina tube, T ≈ 1400 K	hot H_2/Ar	50	
9	Na + SiF_4	6 cm unheated quartz tube	hot Ar	75	probably contains Na_2SiF_6

Cr and Ni not detected. Possibly Sample #1 was contaminated in the laboratory during handling. Sample #9 from the experiment in the alumina tube shows 5 ppm of Al, demonstrating the unsuitability of this tube material for high purity work. Considerable traces of Cu and Mg are present from unknown sources (the Mg was detected but the actual concentration not determined).

X-ray diffraction studies were performed on several samples of washed product to determine whether the silicon produced in these flames has a crystal structure. Products from (i) two Na + $SiCl_4$ flow tube experiments, (ii) three opposed jet K + $SiCl_4$ experiments, and (iii) a Na + SiF_4 flow tube experiment were analyzed. The diffraction results from (i) showed three peaks at angles of 28.4, 47.3, and 56.1 degrees corresponding well with standard angles for crystalline silicon of 28.44, 47.34, and 56.08 degrees. The relative peak intensities of 1.00/0.57/0.32 also compared closely with the standard 1.00/0.60/0.35 intensity ratios. No other significant peaks were observed; in particular the diffractions due to NaCl at 27.35, 31.69, and 45.45 degrees were not visible. Results from the opposed jet samples showed much less crystalline nature material; the diffractions were considerably weaker and broader. Microscopic examination of these samples showed them to be much less uniform in particle size and color. Many white crystals, presumed to be salt, were also observed. The last sample, that from the Na + SiF_4 reaction, showed a very different result. Ten relatively large peaks (and six smaller peaks) were observed, including the three due to silicon, but at reduced intensities about half that of sample type (i). The other peaks were due neither to NaCl or NaF and were determined to correspond to those from Na_2SiF_6.

D. PRODUCT SEPARATION EXPERIMENTS

Independent experiments were performed to treat the problem of separating the silicon from the byproduct alkali salt without the added complexity of running the Na + $SiCl_4$ flame. A high temperature crucible/heater made of graphite and heated by passing high currents (up to 150 A) through the graphite was constructed. This 10 cm long, 2.0 cm diam crucible was made of ultra-high purity graphite, MacKay grade UF4S, with 0.13 cm wall thickness, and was used to heat samples of NaCl, Si, or Si/NaCl. Samples of NaCl in direct contact with the graphite crucible could be melted and vaporized with the rate of the process easily controlled by varying the heater current. Granular samples of crystalline silicon were also melted, but the liquid Si appears to either wet the graphite and simply flow through the thin walls, or react with the walls forming silicon carbide. In either case a portion of the liquid silicon escaped to the outside of the crucible where it solidified as it cooled. In another experiment a high purity quartz liner was used to hold a sample of silicon inside the graphite crucible/heater while the Si was melted. This experiment was not successful because, although the silicon melted, the quartz was softened enough to flow. There is only a small temperature range above the melting point of silicon within which quartz retains its integrity, and apparently in our experiments the temperature control or homogeneity was inadequate to stay within this range. A few preliminary experiments were also performed in which Si/NaCl powder samples obtained from Na + $SiCl_4$ flame experiments were heated in a quartz crucible to a temperature above the boiling point of NaCl but considerably below the melting point of silicon. It may be possible to separate the product species by boiling the salt away in this manner, but experimental problems (e.g., leaks, etc.) plagued the tests and they were discontinued.

E. HIGH TEMPERATURE FLOW TUBE EXPERIMENTS

Wall temperatures in our first series of flow tube experiments were limited to less than about 1300 K. Under these conditions the post-flame gases cooled sufficiently rapidly that the alkali metal salt and the silicon appeared to condense simultaneously and deposit on the reactor walls in an approximately stoichiometric (4NaCl + Si) ratio. In order to separate these products on a continuous basis, higher temperatures were needed. To this end, a modified apparatus was constructed using resistively heated thin-walled graphite reaction tubes, similar in design to the graphite crucible described in the previous section. Two types of experiments were performed in this apparatus. In the first, the effluent gas/particle stream from a 15 cm long 2.5 cm diam unheated quartz flow reactor was directed into a 10 cm long, 2.2 cm diam graphite crucible heated to a temperature above the melting point of silicon. Optical pyrometry was used to measure the crucible temperature which could easily be maintained above 1700 K.

At the conclusion of a 65 min run, using a stoichiometric low pressure ($\approx$ 50 Torr) Na + $SiCl_4$ flame with 25(STP)cm^3 s^{-1} Ar flow in the nominal 1 g min^{-1}

Na vapor stream, no solid product of any form was found in the heated graphite crucible itself. However, in the 1 to 3 cm region of the quartz exit tube just downstream from the crucible, a very hard silver-colored silicon deposit was found. A considerable amount of solid product with the brown appearance of a Si/NaCl mixture was also deposited upstream of the crucible inside the cooler quartz delivery tube. Downstream of the heated crucible a powder ranging in color from light brown to almost pure white deposited on the walls. We conclude from these observations that, although the solid product delivery from the flame zone to the graphite crucible was not highly efficient, a considerable quantity of NaCl/Si did reach the high temperature region of the crucible. Under these conditions of pressure, temperature, and residence time, proper conditions for depositing Si on the walls while maintaining the NaCl as a vapor were apparently achieved just downstream of the crucible. No Si was retained in the crucible because the Ar flow rate was probably too large, resulting in too short a residence time in the hot region.

Subsequent experiments were performed without Ar in the reactant flow and with hot walls surrounding the flame zone. This experimental arrangement is shown in Fig. 21. Slightly thicker walls (0.20 cm instead of the earlier value of 0.13 cm) in the graphite reaction tube were also used. The wall temperature prior to beginning the experiment was somewhat lower than the melting point of Si, the wall temperature estimated optically to be between 1500 and 1600 K. However, the heat release from the flame would be expected to significantly raise this temperature. A Na + $SiCl_4$ flame without diluent was sustained for 50 min consuming about 135 g of $SiCl_4$ and 75 g of Na. The initial (static) reactor pressure was constant at 175 Torr throughout the experiment since the reaction products are all condensables. Since no argon was added during the experiment, no pumping was needed.

Upon disassembly of the reactor, the graphite tube was found to have a hard coating of silicon, some as crystals and some as sintered powder. NaCl was observed only around the exit opening. The solubility of samples taken from various areas of the apparatus was determined in order to estimate the amount of NaCl remaining. The silicon from the upstream area of the reaction tube, where the majority of the product deposited, was found to be essentially all insoluble ($>$ 95%). A sample from the downstream area of the reaction tube near the exit was $\approx$ 70% insoluble, whereas just past the tube exit on the outer walls, where the temperature was significantly lower, the sample was completely

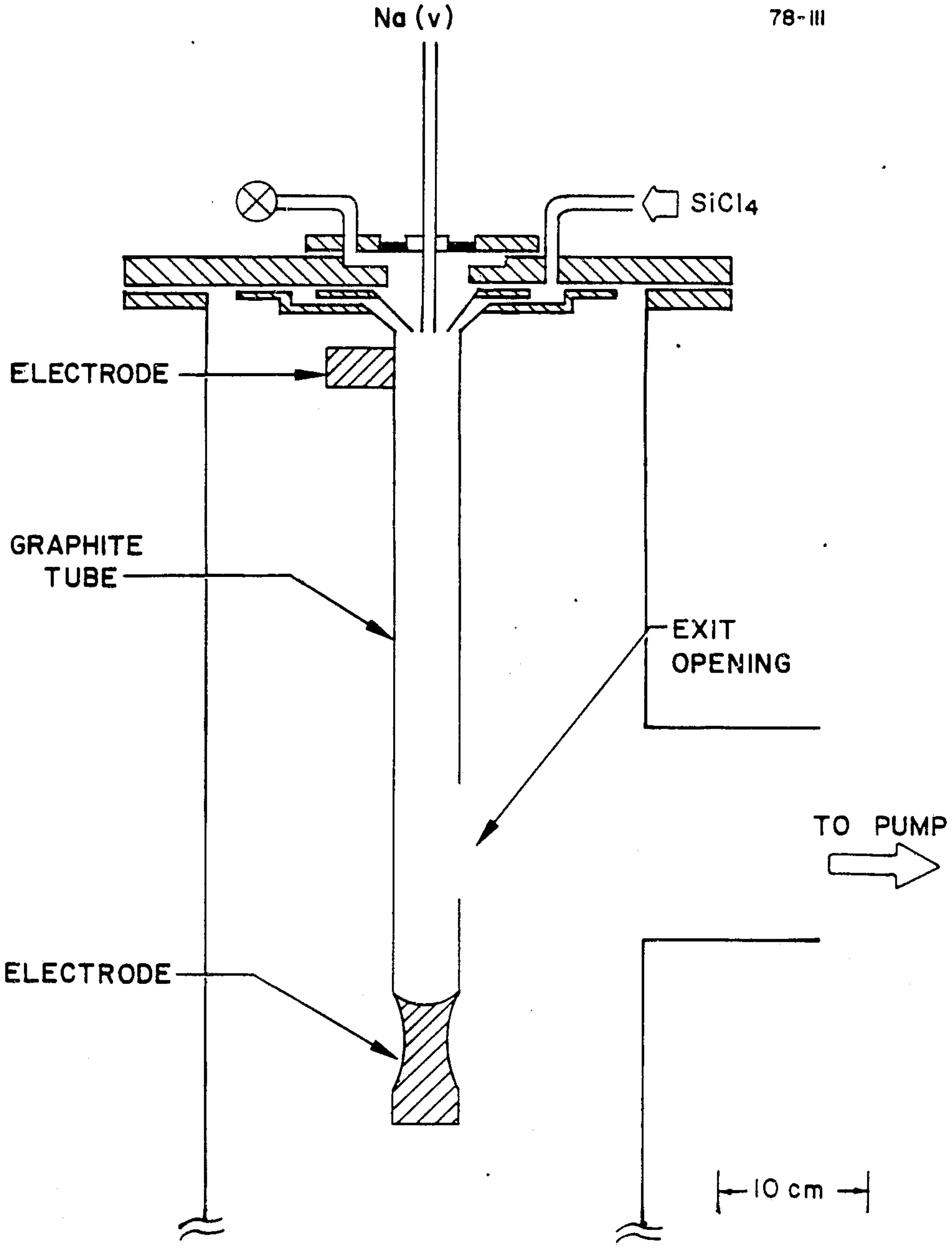

FIGURE 21 HIGH-TEMPERATURE GRAPHITE FLOW-TUBE APPARATUS

soluble. Further away from the graphite tube in the room temperature area where a small amount of very fine particles settled, the solubility of a sample was found to correspond to stoichiometric product (13.2% insoluble).

From these observations we concluded that a fully successful high temperature separation of the Si from the NaCl was demonstrated in this experiment. The key factors in this success appear to be the ability to sustain wall temperature approximately equal to the melting point of silicon and not using argon in either reagent stream. The diluent, if present in the reagent flows, raises the reactor pressure and reduces the product residence time during which silicon collection on the walls must take place. The silicon/salt mixture found downstream from the reactor represents only a small fraction of the total amount of silicon produced, but demonstrates that the separation-collection product was not 100% efficient.

F. HEAT RELEASE AND PRODUCT CONDENSATION MEASUREMENTS

Having shown that relatively pure silicon could be produced in low temperature reactors where the silicon and alkali salt particles codeposited onto the walls, an experimental program was designed to test the proposed separation/collection techniques. We also scaled up the experiment to alleviate problems due to heat losses and to produce larger amounts of silicon. As an initial guideline we chose a scale factor such that the reaction exothermicity (without salt condensation) would be about equal to the electrical power previously used to heat the graphite flow reactors, about 1.2 kW, i.e., a scale-up by about a factor of 25 to a production rate of silicon of ≈ 0.5 kg h^{-1}. To produce silicon at this rate, 3.1 kg h^{-1} of $SiCl_4$ is consumed requiring $\approx$ 150 W for its vaporizer. This energy flux could not be maintained across the glass vaporizer walls so a platinum wire immersion heater was built. A $SiCl_4$ recharging system was also added since the 150 cm^3 capacity of our vaporizer was inadequate at the much higher flow rate. With this system the reaction is not limited by $SiCl_4$ flow rate or capacity. Flow meters were installed in the halide delivery line to allow close adjustment of the Na/$SiCl_4$ equivalence ratio.

The required 1.7 kg h^{-1} of Na corresponds to a flow rate of 220 ℓ min^{-1} of vapor at 1200 K and 0.5 atm. It was decided that an experimental confirmation of the Na flow rate would be required. The heat input needed to vaporize this quantity of Na is 2.0 kW and was found to be easily within the existing vaporizer capability. Experiments were performed in which the gaseous Na delivered during a ten minute period was condensed and weighed to determine the flow rate. An orifice with 3.0 mm diam was found to produce the desired flow rate with one atmosphere Na vapor pressure in the vaporizer. (Higher pressures are not used for reasons of safety.) The 0.8 ℓ capacity of the liquid reservoir in this vaporizer allows runs of about 30 min duration without recharging.

In the first test of these scaled-up systems the reactor was a 1.5 cm i.d., 0.3 cm wall thickness graphite tube loosely held inside a stainless steel tube. This combination was heated to 1200 K by a "clam shell" resistance heater prior to beginning the experiment. The Na + $SiCl_4$ flame was run for six minutes before solid product deposits clogged the reaction tube. Approximately 4.7 moles Na and 1.4 mole $SiCl_4$ were delivered, corresponding very closely to the desired silicon production rate of 0.5 kg h^{-1}. The graphite tube was found to be fractured into pieces and saturated with silicon. Both reagent systems performed without problems.

Subsequent experiments were carried out in larger (4.3 cm i.d.) alumina reaction tubes. With the tube preheated to 1400 K, introduction of the reagents quickly raised the wall temperature to 1900 K where it stabilized for the remainder of the experiment. From this initial wall heating rate, the reaction heat release was estimated to be 1.2 kW, corresponding closely to that computed assuming no NaCl condensation. Samples of deposits from the middle of the reaction zone were found to be ≈ 90% silicon and ≈ 10% NaCl. Near the cool reagent inlet flange and at the downstream end of the flow tube the product was ≈ 75% silicon. Thus good separation of the silicon from the alkali salt was occurring in the high temperature region of the reactor.

An experiment was also run without preheating the reactor tube. Figure 22 shows the measured wall temperature profile. Initially a rapid wall heating rate (800 K min^{-1}) was observed during the period in which both salt and silicon condensation occurred ("I" in Fig. 22). The reaction exothermicity under these conditions and flow rates is about 5.7 kW. The temperature then stabilized briefly at the boiling point of NaCl (II), and from there rose above 2000 K where the Pt/Pt-10% Rh thermocouple failed. Thus the ultimate reactor temperature was not measured. The experiment was terminated due

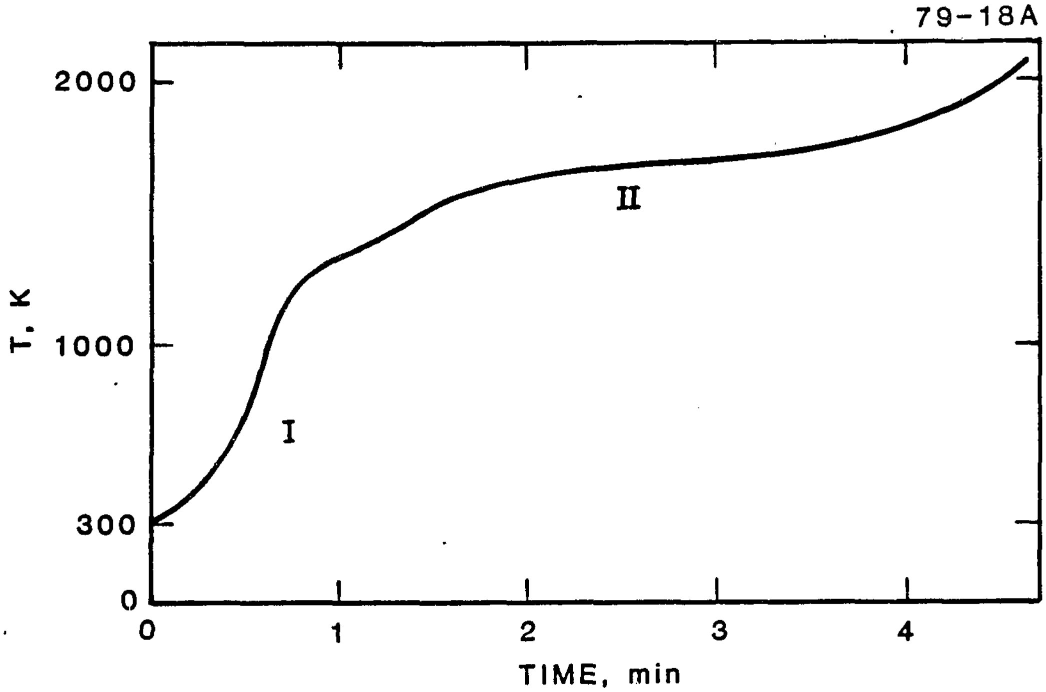

FIGURE 22 WALL TEMPERATURE PROFILE DURING A Na + $SiCl_4$ RUN WITH NO REACTOR PREHEATING

to excess heating of the outer glass vacuum system wall. Although the reaction tube deposits contain a high portion (≈ 75%) of NaCl, the amount of silicon recovered as elemental Si in this experiment was about 90% of the total which could have been produced. Figure 23 shows that the solid products (NaCl and Si) were collected predominantly in the section of the reactor near the inlet, while Fig. 24 indicates where the silicon fraction deposited.

Thus input of additional energy to preheat the reactor did not appear to be necessary. However, longer run times were needed to reach steady-state in the reactor to achieve good separation of the silicon from the byproduct salt. Nucleation and condensation rates appear to be large enough for efficient silicon collection under experimental conditions of about 160 ms residence time and 0.5 atm in the flow tube.

Heat release parameters needed to optimize the reactor size or further scale up to produce larger amounts of silicon have also been measured. To do this a 6 cm i.d. stainless steel tube with four separate cooling coils was installed into the reactor, cf. Fig. 25 and wall cooling air temperature profiles for each section were measured during reactor operation, from a cold

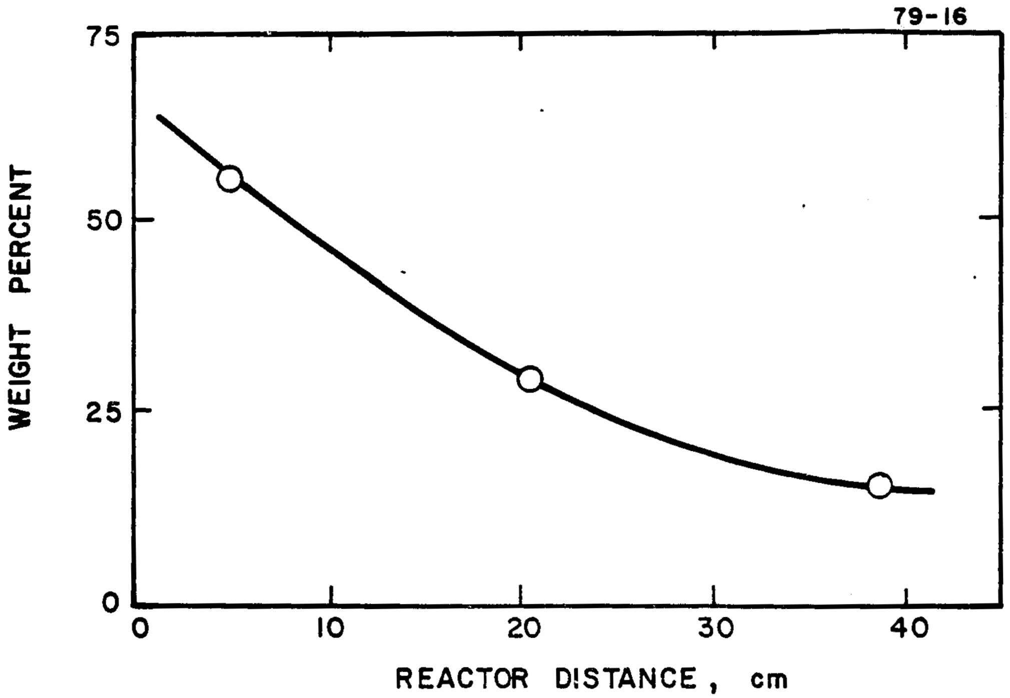

FIGURE 23 SOLID PRODUCT (Si + NaCl) DISTRIBUTION DURING A Na + $SiCl_4$ RUN WITHOUT REACTOR PREHEATING

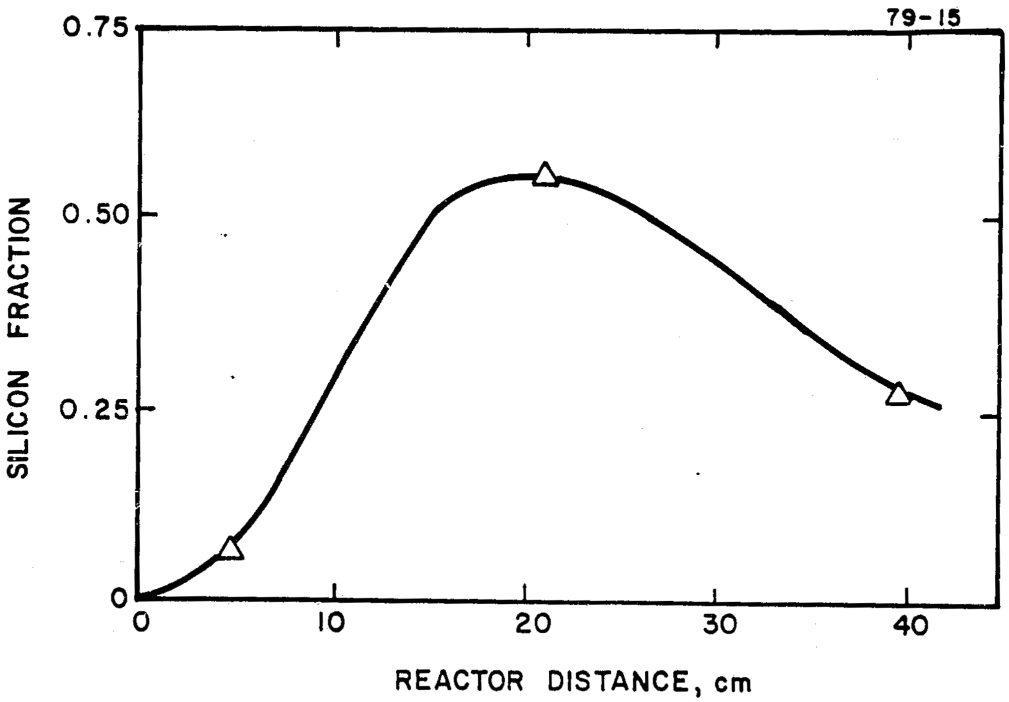

FIGURE 24 DISTRIBUTION OF SILICON DEPOSITION

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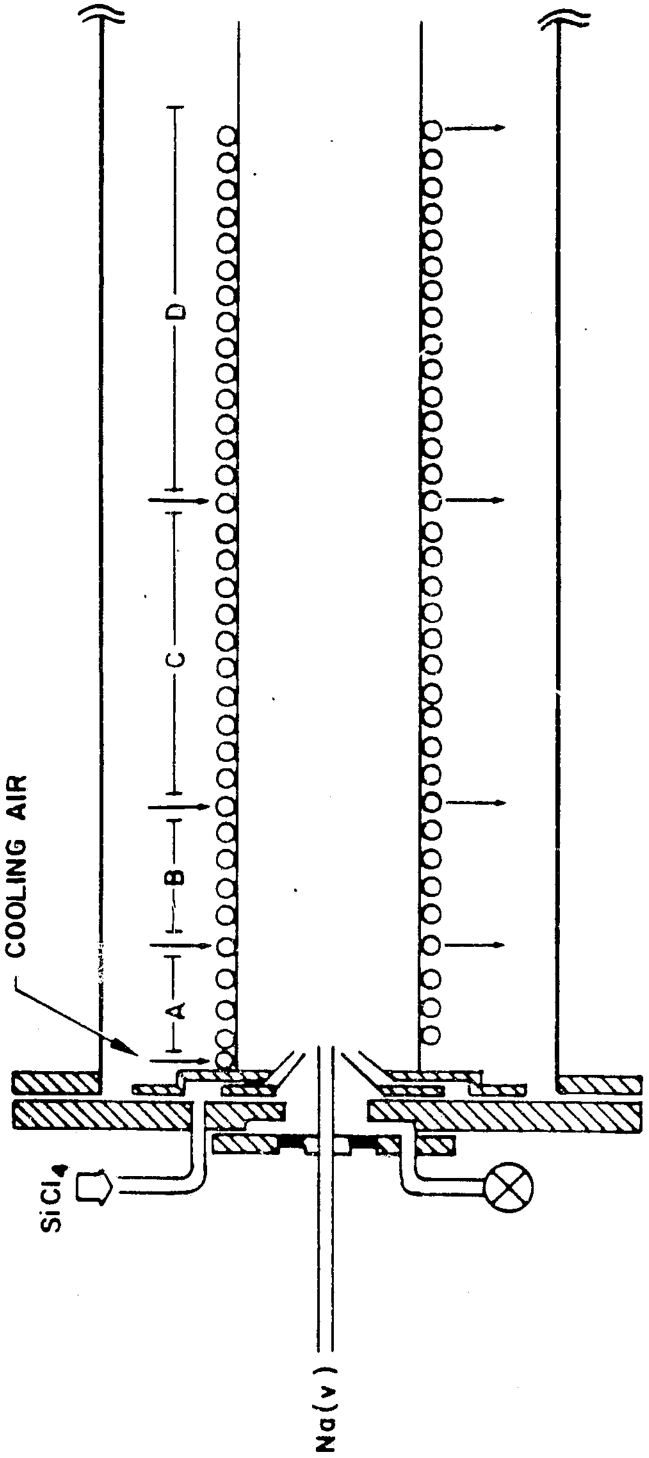

FIGURE 25 REACTOR CONFIGURATION FOR MEASURING HEAT RELEASE RATES

start. These profiles are shown in Fig. 26. The total heat production was computed from the temperature profiles and the heat capacity of the cooling air and reactor, and is shown in Fig. 27 for each reactor section and the total (Σ). Most of the heat was produced in zones A and B which were 10 and 16 cm long, respectively. From the reactant flow rates we calculated an exothermicity of 4.2 kW, in good agreement with the experimental results.

Measured heat flux through the reactor walls is presented in Fig. 28. In the first 25 cm of the reactor an average value of 5 W cm^{-2} was obtained. Volumetric heat release data are given in Fig. 29. An average value of 3 W cm^{-3} was measured for the portion of the reactor near the inlet while in the downstream regions the value dropped to less than 0.5 W cm^{-3}. These data clearly show that the reaction takes place in sections A and B of this reactor, confirming that the kinetics of the reaction are rapid, probably mixing limited. Thus smaller reactor volumes could be used, simplifying reactor design and construction.

G. NEW REACTOR AND TEST FACILITY

In some of the previous experiments we experienced severe heating of the outer Pyrex reaction chamber walls causing a safety hazard should the Pyrex break. In addition we needed a larger volume chamber, configured to allow quick changes to be made in the reactor without reconstructing the whole apparatus between successive runs. To meet these needs, a large (65 cm diam, 80 cm high) stainless steel vacuum chamber with 2 cm thick aluminum end flanges was purchased for the new experimental facility. All connections, vacuum, electrical, etc., were rigidly mounted on the fixed top flange. The water-cooled chamber could thus be quickly and easily lowered to gain access to the reactor. With this arrangement we expected to be able to test different reactor configurations, reactor construction materials, and operating modes with much shorter turnaround times than were previously required. The outer water-cooled walls provided surfaces for NaCl collection.

Using the data obtained in our earlier heat release experiments, we concluded that the $Na/SiCl_4$ reaction goes rapidly to completion, and a much smaller reactor volume than had been used in previous designs would be adequate. A new reactor was designed with smaller (8 cm diam, 16 cm long) reactor dimensions following these conclusions and is shown in Fig. 30.

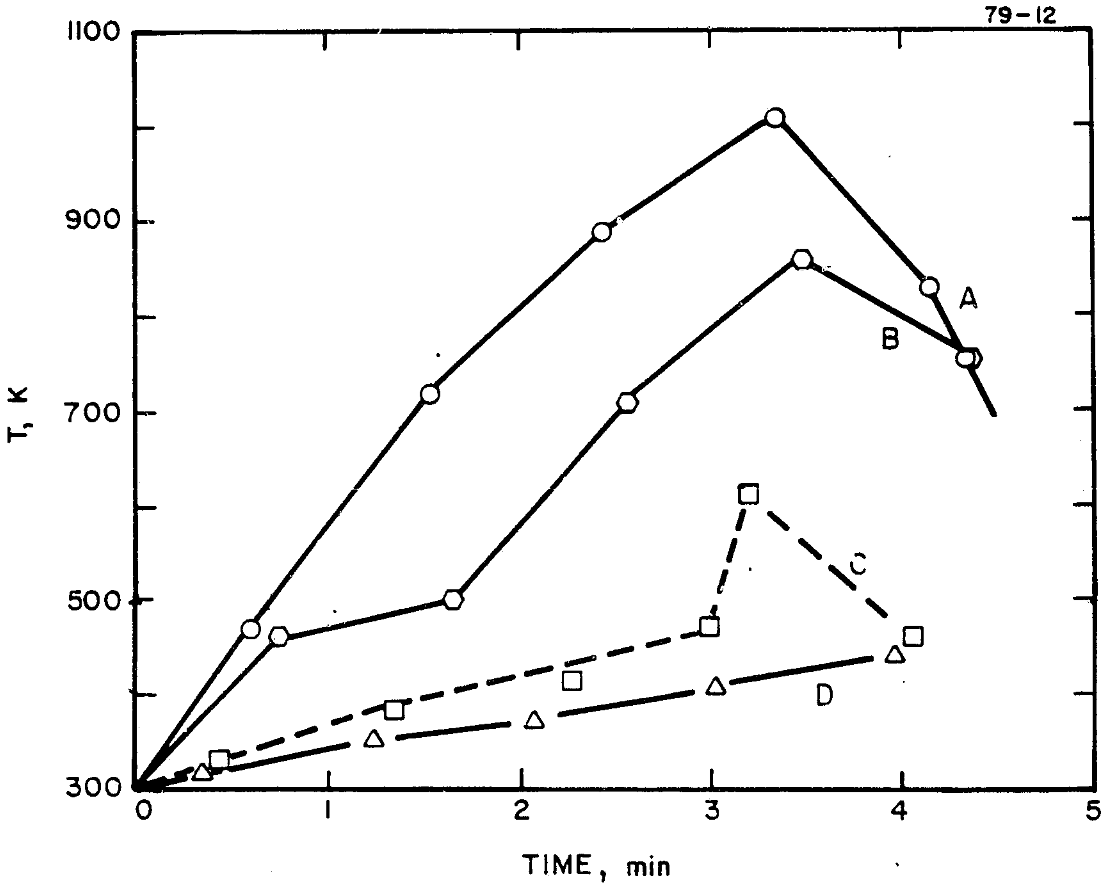

FIGURE 26 TEMPERATURE PROFILES OF THE WALL COOLING AIR FOR THE REACTOR AS SHOWN IN FIG. 25

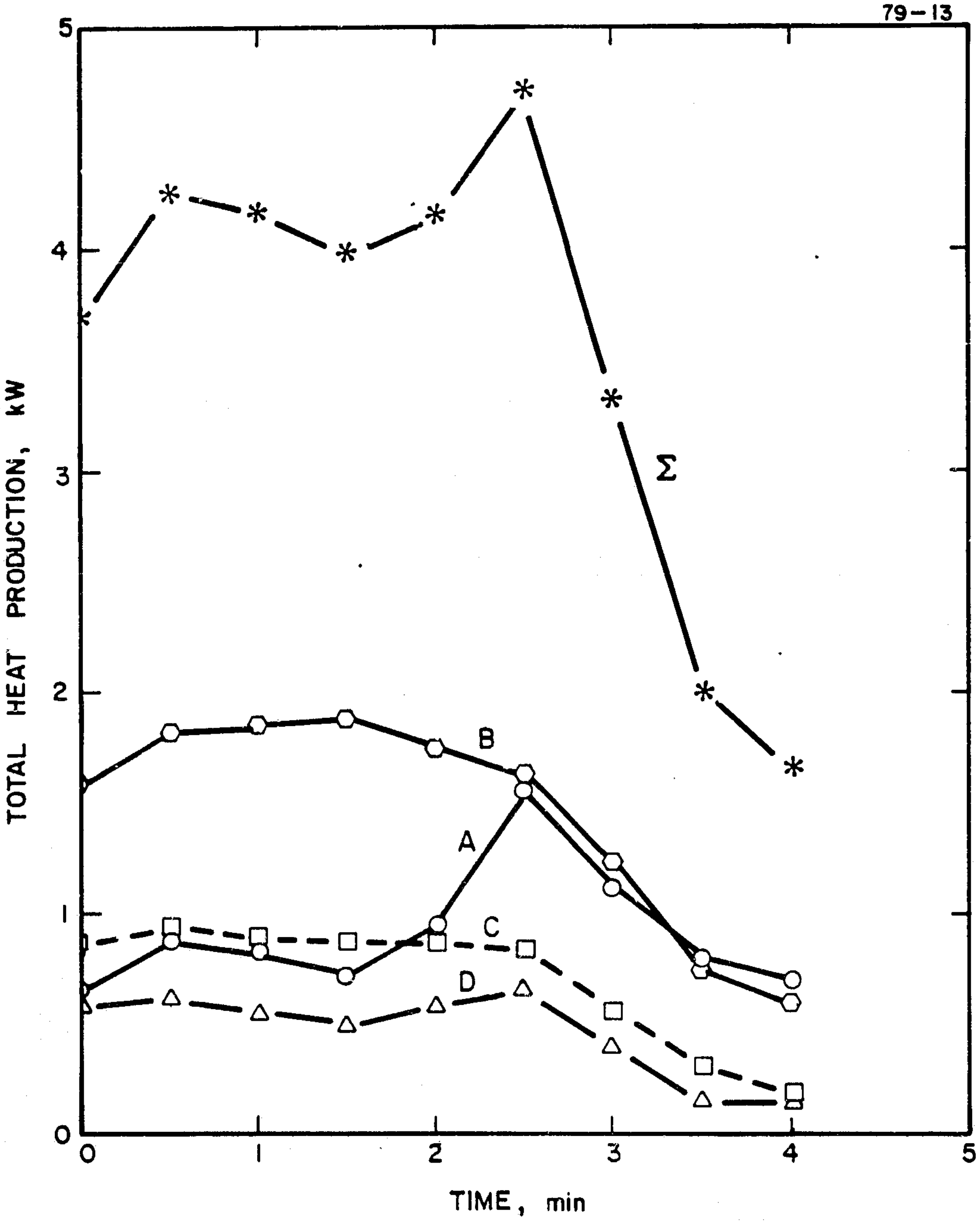

FIGURE 27 HEAT PRODUCTION PROFILES FOR THE REACTOR SHOWN IN FIG. 25

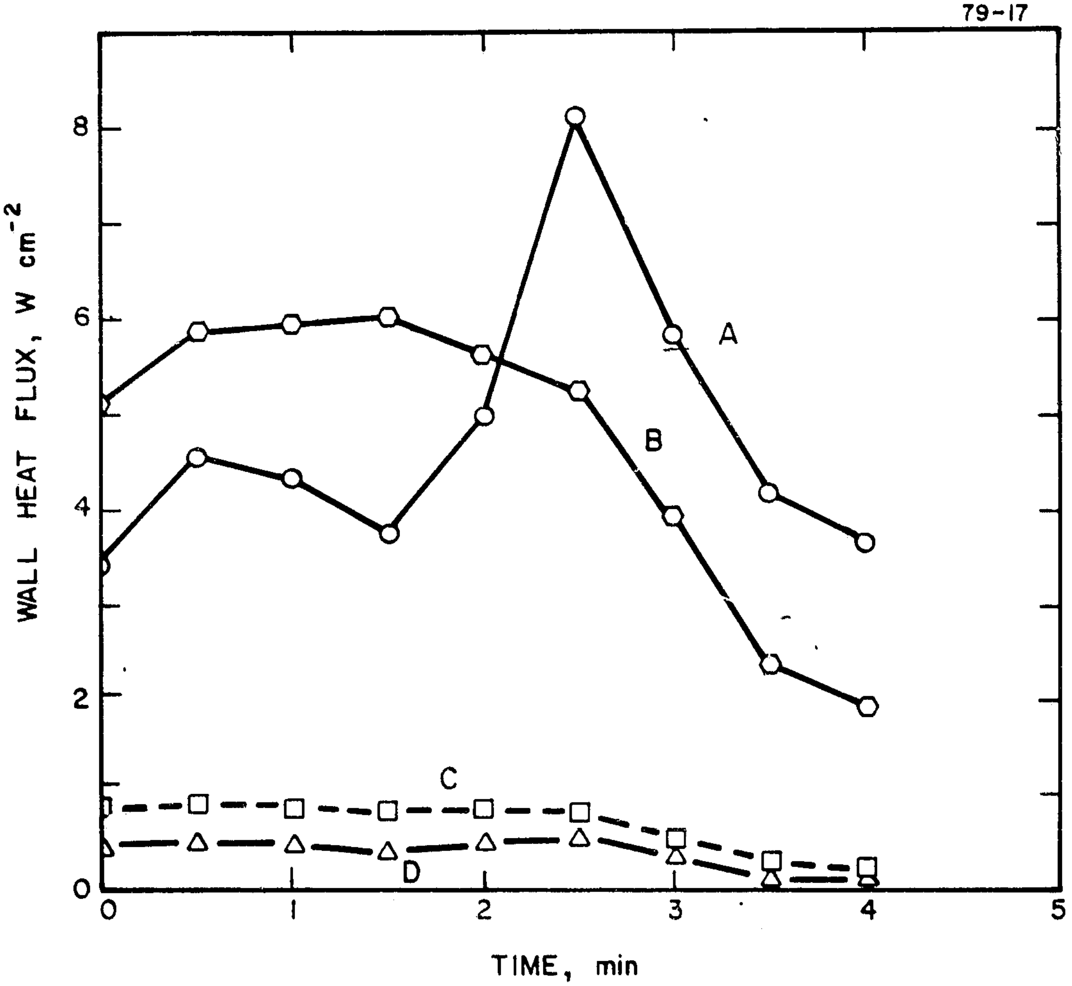

FIGURE 28 WALL HEAT FLUX PROFILES

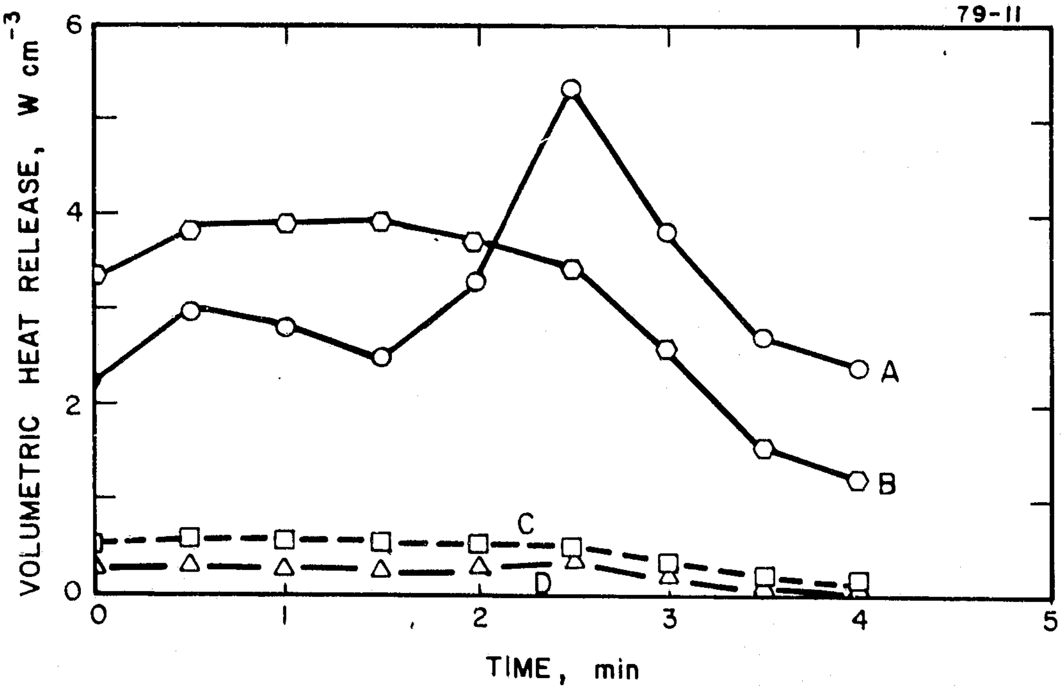

FIGURE 29 VOLUMETRIC HEAT RELEASE PROFILES

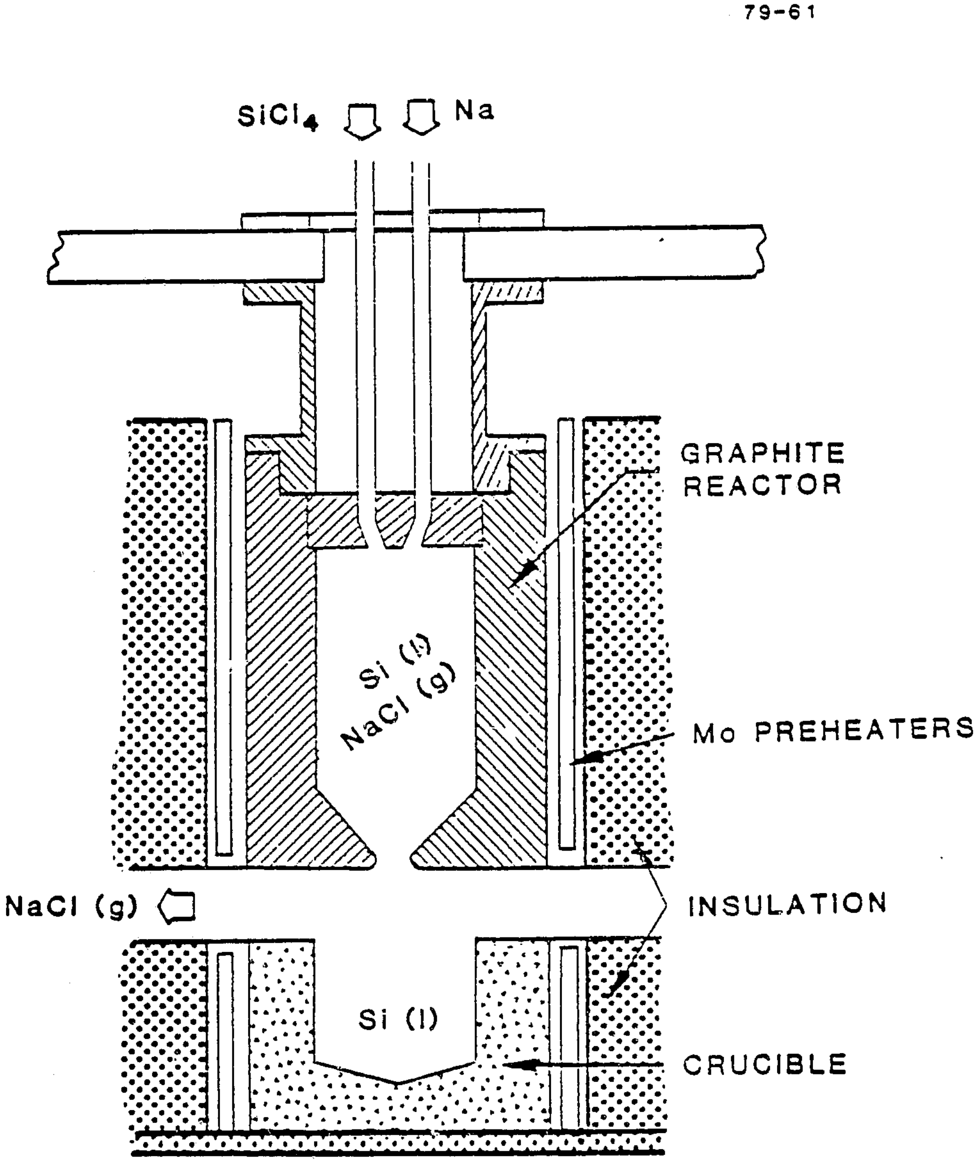

FIGURE 30 THICK-WALLED GRAPHITE REACTOR

Our aim was to collect high purity liquid silicon at the reactor outlet, with the NaCl (and, we hoped, most other impurities) being collected on cooled surfaces far from the Si collector. We would thus show that product collection and separation were easily achieved in the absence of carrier gases such as H_2 or Ar. A major innovation in the new design concerns silicon particle separation from the NaCl(g). The exit from the reaction volume was configured as a small converging nozzle. In the initial tests the reactor was planned to operate near 0.5 atm with the reactor walls near or above 1700 K. The reaction products, NaCl(g) and Si(ℓ), would leave the reactor through the nozzle, exhausting into a large volume held at a low ($<$ 10 Torr) pressure. The jet from the reactor would impinge on a hot ($\approx$ 1700 K) graphite crucible where the Si(ℓ) droplets would be collected. The NaCl would condense on the cold walls of the vacuum chamber. Using a low pressure is not unreasonable for a process where essentially all of the reaction products are condensible, since only a very small pumping capacity would be required to maintain the low pressure. The essential characteristics of this silicon collection technique are that the Si particles are given a large forward momentum in the nozzle, causing them to collect by impaction on the crucible. The lower pressure assists this process by increasing the stopping distance of the particles. Calculations indicated that even 0.1 μm diam silicon droplets would penetrate $\approx$ 5 mm into the shock layer above the Si liquid in the crucible. Impaction, diffusion, and thermophoretic collection would then remove many of even these very small droplets from the gas in this layer. Parameters to be varied were reaction zone volume, nozzle diameter or shape, crucible temperature, crucible to nozzle distance, and reagent flow rates. It was of additional interest to test whether the thick graphite walls would withstand exposure to the reactants and products without structural damage.

As shown in Fig. 30 preheaters were installed to heat both the reactor and crucible before beginning an experiment. Molybdenum resistance heaters were used for the early work with changeover to a noncontaminating heater planned after initial tests. The reactor and crucible were surrounded by heat shields and high temperature insulation material. The inlet region was made thin-walled to minimize heat transfer to the Al flange from which the whole reactor is suspended. Stainless steel tubes carried the reactants to the reactor area where they were mixed in a highly turbulent manner.

The first heaters were built using two 0.10 cm (0.04 in.) diam Mo wires inside dual bore alumina tubes. Inadequate heat transfer and temperature control caused failure of these heaters and, in some cases, melting of the alumina tubes. We then redesigned the heaters such that the wires were exposed except for small areas necessary for support. Radiative heat transfer from bare wires at $T \approx 2400$ K was expected to be very efficient. Initial tests of these heaters were not successful in raising the reactor and crucible to the desired operating temperatures (> 1700 K). Small air leaks causing excessive corrosion of the Mo wire were a major problem. Another problem was that the high temperature resistivity of the Mo proved to be greater than the published values assumed in the heater design. The voltages required to drive the heaters were thus greater than what the available power supplies could provide. The actual resistivity of the wire was subsequently measured and the heaters rebuilt. It was realized that Mo heaters were not an ideal environment for producing high purity Si. Transfer of Mo to the Si produced in the apparatus was probably unavoidable and the sensitivity of the electronic properties of silicon to traces of this element was recognized. Therefore, once the power levels required to operate the reactor and crucible using the redesigned Mo heaters were established, we planned to switch to more suitable (and more expensive) heater materials.

Further experimental difficulties were encountered with the reactor and crucible heaters but the tests did provide the power requirement data needed to redesign the heaters. Commercial silicon carbide heaters were considered but were not applicable because the required temperatures are too high, and the silicon carbide is not chemically stable in a reducing atmosphere. Drawing from experience gained earlier in this program we chose graphite resistance heaters for the new design. This material is stable when exposed to the required temperatures and environment. Easily obtained and inexpensive 0.62 cm (0.25 in.) diam spectroscopic rods were found to match closely the available high current (250 A) power supplies. Approximately 3 kW and 4.5 kW were required to heat the crucible and reactor to temperatures of 1450 and 1550 K, respectively.

The glass $SiCl_4$ reflux condenser used in previous experiments was inadequate in liquid capacity, vapor delivery rate, and in safety margin for the planned runs. Therefore a larger stainless steel model was constructed to allow longer runs without periodic fluctuations in the $SiCl_4$ flow. A refluxing rather than flash heating design was chosen because higher purity $SiCl_4$ vapor could be furnished, leaving many impurities behind in the boiler. The design also allowed a much larger safety factor when operating the boiler at elevated pressures.

During the first run, both stainless steel reagent delivery tubes failed due to $SiCl_4$ attack on the hot metal and the Na and $SiCl_4$ mixed in the inlet region. Since the reaction took place in the reactor holder rather than in the reactor itself, there was no separation of the Si from NaCl or collection of products in either the reaction chamber or the crucible. The sodium inlet tube was modified to provide temperature control of the inlet port by flowing N_2 gas through a double-walled assembly, and the reactor ran successfully for 20 min in the second run. Upon opening the system after this run, a considerable amount of product was found on the vacuum chamber walls. Very little silicon was found in the crucible, probably due to insufficient heating. During the third run, the reactor and crucible reached operating temperatures of 1650 K. Unfortunately, the sodium heat pipe clogged and the system was prematurely shut down.

The reactor holder was redesigned so that each reagent entered the reactor through a separate chamber. Argon initially flowed into the Na side to prevent the $SiCl_4$ from reaching the Na inlet tube. During one run the reagents mixed in the $SiCl_4$ chamber and in another they mixed in the Na chamber. The reactor holder was therefore again redesigned to prevent both the $SiCl_4$ and the Na from mixing until they reached the reactor. This new reactor holder contained a dual chamber assembly with the $SiCl_4$ entering the reactor through an alumina tube and the Na entering through a double-walled stainless steel inlet. At this point, by passing air or N_2 between the walls, it was discovered that the premature mixing in the reactor holder was due to the failure of the Na vaporizer valve. In an earlier run it had melted and it remained open during subsequent runs. As the vaporizer was brought to temperature before starting a run, both liquid and vaporized Na entered the reactor holder. A new type of valve to control the Na flow was made to prevent this type of failure.

To observe visually the high velocity reaction jet as it exits from the reaction chamber, one run was made without the crucible in place. A bright, yellow jet-like flame approximately 10 cm long was observed for a few seconds before the salt byproduct coated the observation window. During this run, a conical mound (≈ 10 cm high and ≈ 15 cm base diam) of reaction product collected on an aluminum plate placed one foot away from the reactor exit nozzle. This reaction product was 20% Si and 80% salt by weight. Microscopic examination showed that the particle aggregates ranged in size from 1 to 10 μ.

The reactor was also run with the silicon collection crucible in place. Three grams of the silicon product (containing ≈ 10% salt by weight) collected in the crucible. Since this product appeared amorphous, the inability to collect the silicon product may be due to an insufficient crucible temperature (≈ 1500 K during this run).

V. SODIUM GRAPHITE MATERIAL TESTS

In the course of performing the experiments discussed in the previous section several observations were made which brought into question the suitability of graphite as a material of construction in contact with silicon or sodium. Figure 31, for example, shows the destruction to a 2.5 cm graphite reaction tube caused by a Na/$SiCl_4$ flame. It was not possible to determine whether this was the result of reaction with sodium, silicon halide, or silicon, or simply due to expansion of silicon as it solidified. Since graphite is important in our work, and for other proposed processes, further investigation of the problem was made.

The first tests were performed as follows: Samples of graphite, nominally 3 × 5 cm, 1-2 cm thick, were suspended by a wire in the sodium vapor generator at a level such that they would be immersed in the refluxing sodium vapor (see Fig. 32). The samples were exposed to refluxing sodium at 0.5 atm and 1150 K for five minutes, cooled, and removed from the apparatus. Since these experiments were performed at the dew point of sodium, the samples were exposed to both liquid and vapor sodium. Table VI lists the manufacturer, grade, and physical characteristics of the tested samples. According to the manufacturers' literature, these are high quality graphites. Airco-Speer grade 580 is listed as "the densest and strongest extruded material commercially available." The Stackpole grade 2020 is a molded, high density material with small pore size. From Ultra Carbon we tested several coated graphites, including a pyrolytic graphite coated sample.

The results of the tests were essentially the same for every sample. Both the coated and uncoated graphites emerged expanded, sustained multiple cracks, and, in some cases, were even broken. The silicon carbide coating could no longer be seen, while the pyrolytic graphite coating was cracked, broken, and peeling from its substrate. The samples were quenched in water to remove excess sodium. After the initial reaction of sodium on the sample surface, evolution of bubbles was observed for hours, indicating that considerable sodium had permeated the samples.

We concluded from these simple tests that neither graphite, silicon carbide, or pyrolytic graphite coated graphite is structurally stable in contact with sodium, at least near the sodium dew point. It is likely that the observed effects are due to actual chemical reaction of the graphite with the alkali metal. Compounds resulting from such reactions have been observed,[19,20] although little

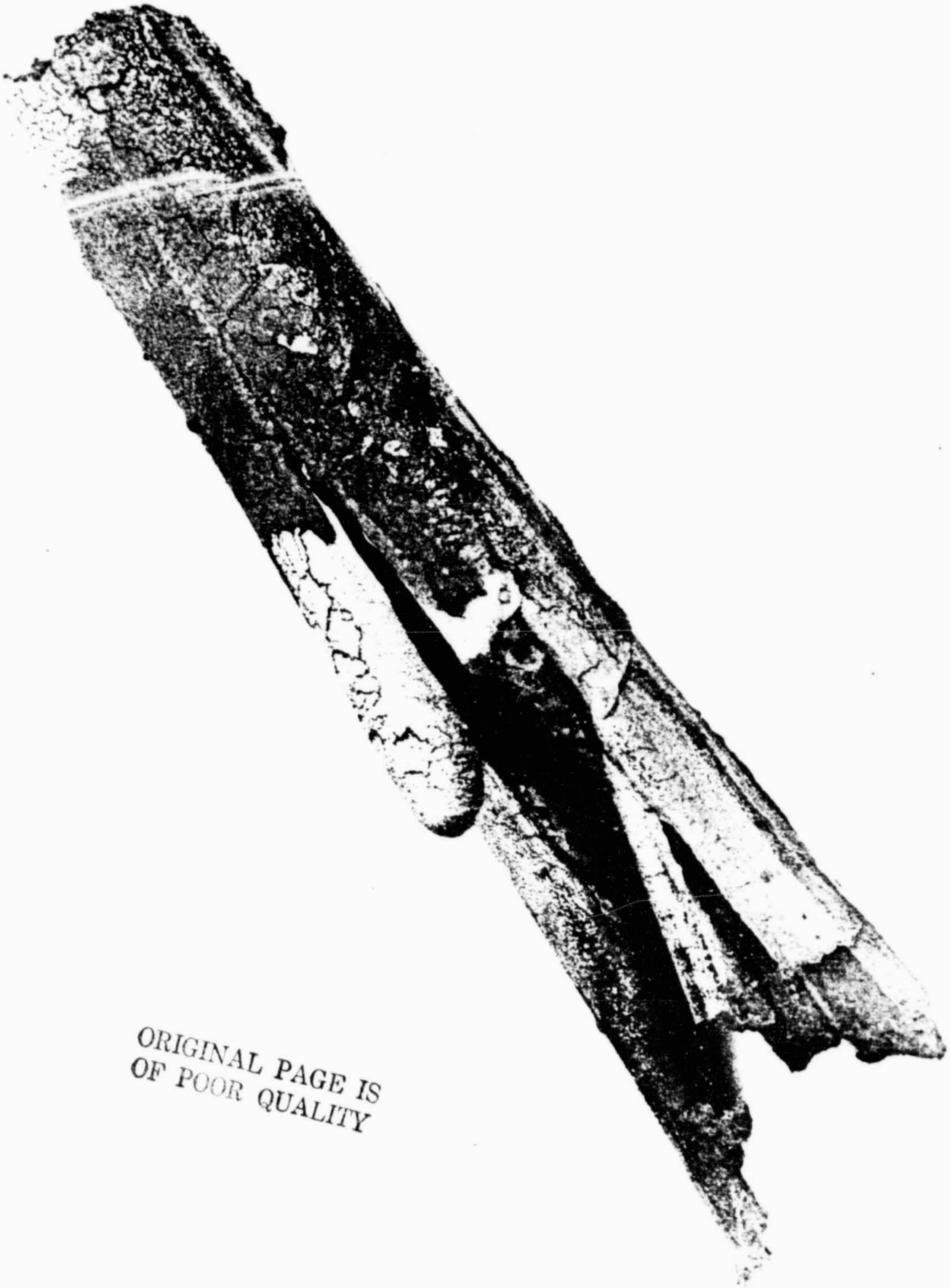

FIGURE 31 PHOTOGRAPH SHOWING DESTRUCTION OF A 2.5 cm DIAM REACTION TUBE BY A Na/$SiCl_4$ FLAME

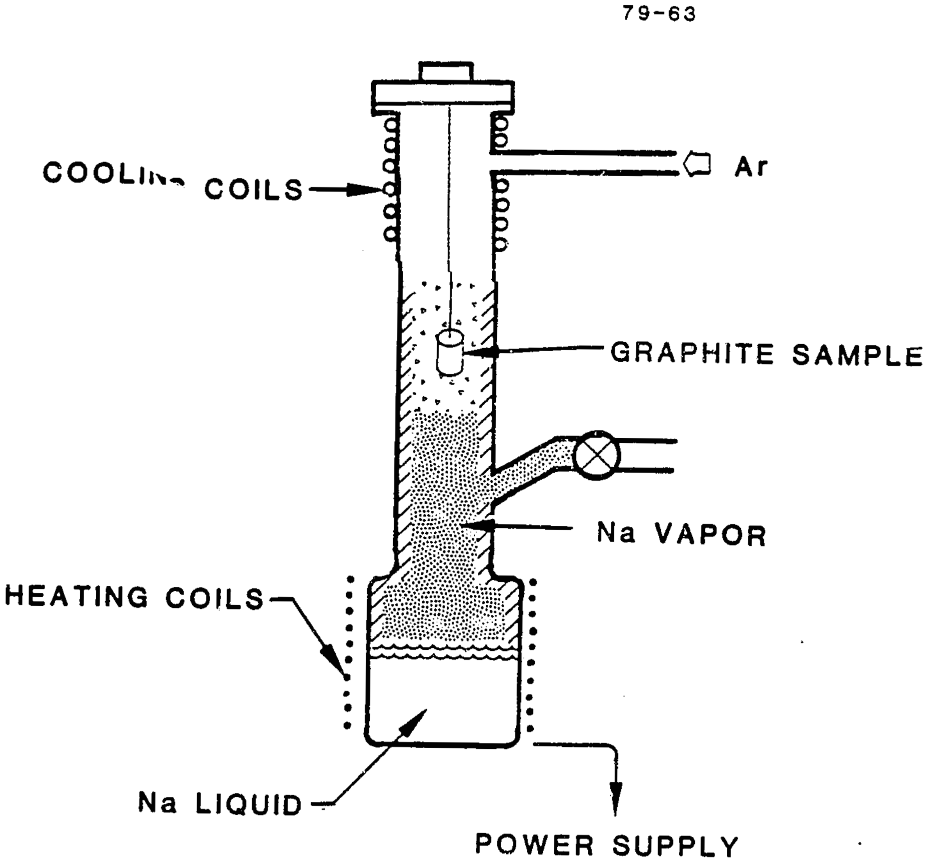

FIGURE 32 APPARATUS FOR Na/GRAPHITE TESTS AT 1150 K

TABLE VI

LIST OF MATERIALS TESTED IN CONTACT WITH SODIUM AT 1150 K

Supplier/Grade	Physical Characteristics
Airco-Speer/580	Graphite, extruded; 1.76 g cm^{-3} density, 22% porosity, 0.020 cm maximum grain size.
A.D. Mackay/UF4S	Graphite, similar to Airco-Speer 580 grade but purified to 5 ppm ash content.
Stackpole/2020	Graphite; density > 1.77 g cm^{-3}, 17% porosity, 0.004 cm maximum grain size, 1.5 μm average pore size.
Ultra Carbon/PT-101	Pyrolytic graphite coated graphite; coating thickness estimated to be ≈ 0.005 cm, substrate graphite grade unknown.
Ultra Carbon/PB-1300	Silicon carbide coated graphite; substrate graphite grade UT-22, 1.70 g cm^{-3} density, 21% porosity, 0.015 cm maximum grain size. Coating thickness unknown.
Ultra Carbon/PT-444	Silicon carbide coated graphite; manufacturer's code A-9648-6, substrate graphite properties unknown.

work has been done for sodium reactions. Potassium readily forms a C_8K intercalation compound, shown in Fig. 33, in which the plane-to-plane spacing of the graphite increases from 0.34 to 0.54 nm resulting in a 60% expansion of the material in this direction. A $C_{64}Na$ compound has been observed[21] where a sodium atom inserts itself into every sixth layer expanding the plane-to-plane spacing to 0.56 nm. Other compounds probably exist. The conclusion from these observations is that alkali metals are indeed reactive with graphite and the formation of interstitial compound is manifested in large macroscopic changes in the materials.

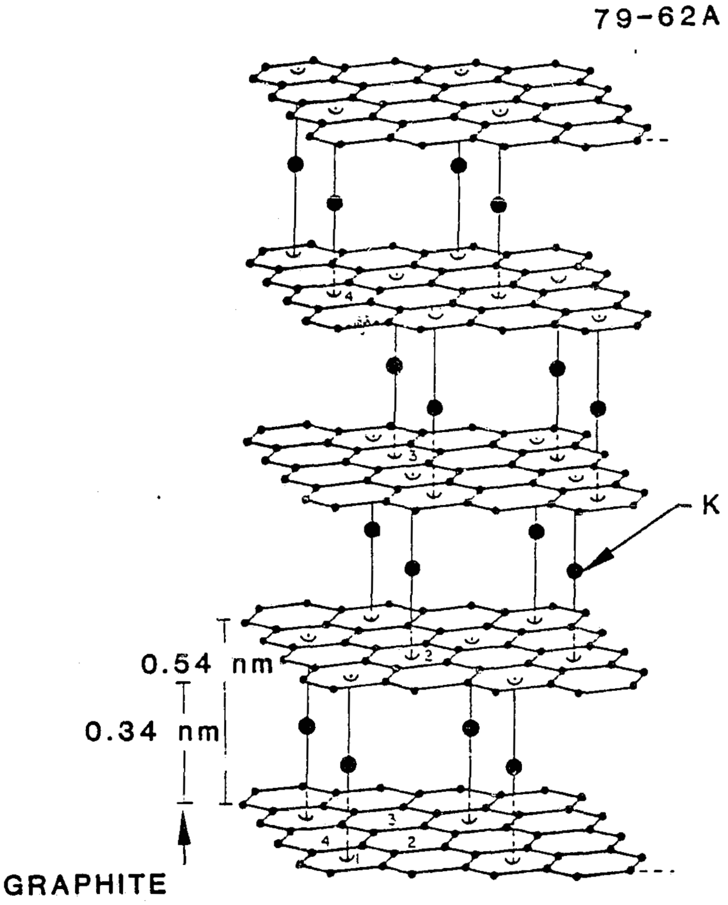

FIGURE 33 STRUCTURE OF C_8K
(after Ref. 19).

In order to make further tests under more closely controlled conditions and at higher temperatures, a heated flow reactor was constructed. Although not expected to survive more than a few experiments, a 46 cm long, 5 cm diam alumina tube was used for the flow tube (see Fig. 34). The first 30 cm of the tube were wrapped with 0.127 cm (0.050 in.) diam Mo wire in three separate heater windings connected in parallel to an ac arc welder power supply capable of supplying about 250 A. A dry run was performed with no reagents present in order to test this new flow tube design and also to check the functioning of the reactor facility.

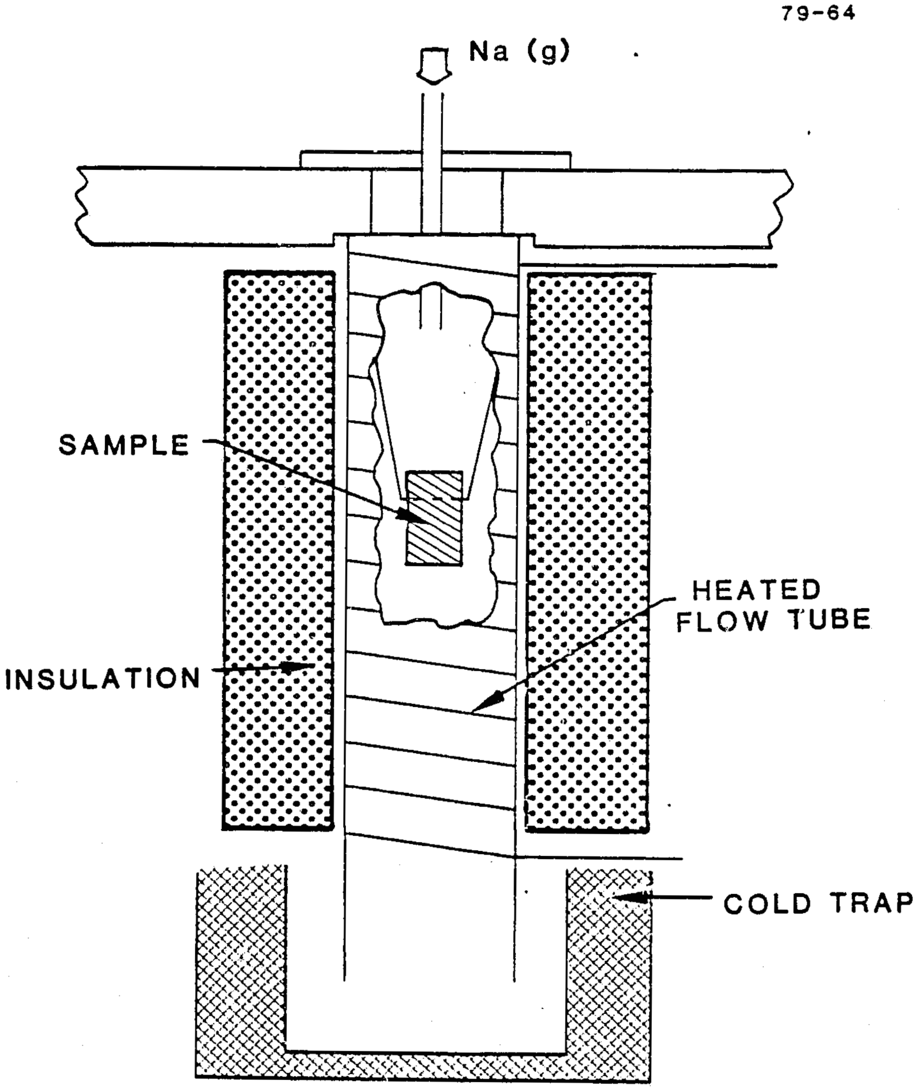

FIGURE 34 FLOW TUBE APPARATUS FOR Na/GRAPHITE TESTS AT 1200 K AND 1700 K

The first test produced temperatures in excess of 2200 K. Although the tube fractured at the end of the heated zone upon cooling, the failure was attributed only to our having heated the tube too rapidly and to too high a temperature. Consequently, another tube of similar design was constructed to replace it.

In order to perform tests directly applicable to the Westinghouse arc-jet reactor, we obtained from the same supplier samples of the specific grade of pyrolytic-coated graphite used in their design (Great Lakes Carbon Corp. grade HLM graphite coated with 0.013 to 0.025 cm (0.005 to 0.010 in.) of pyrolytic graphite and supplied by Pfizer Inc.). These samples were approximately 2.5 cm long segments of 1.9 cm diam rod coated on all surfaces. Similarly coated samples of Stackpole grade 2020 graphite were also obtained from Pfizer. To test the compatibility of these samples with sodium vapor, one sample of each was suspended in a Mo wire basket at the mid-region of the heated flow tube (about 13 to 18 cm from the sodium inlet).

Conditions for these experiments were selected in cooperation with JPL Task I scientists[22] to be an acceptable compromise between the exact Westinghouse values and those that could be achieved with existing apparatus at AeroChem. Experiments were chosen to be performed at 1200 and 1700 K, 0.5 atm of undiluted sodium, a linear flow velocity of at least 2.5 m s^{-1}, and an experiment duration of 0.5 h or longer. Table VII gives the experimental conditions that were in fact achieved. Test 1 fell somewhat short of the goals in pressure and duration and Test 2 a bit short in duration. The results of Test 2 were, however, conclusive and Test 3 repeated the conditions of Test 1, so it is felt that sufficient data were taken for the desired purposes. The cold trap designed to capture and freeze the Na vapor proved to be only partially effective and a cloud of small Na particles filled the reactor chamber. Test 1 was terminated at 16 min when the particle filter in the pumping line became clogged. The problem was most likely due to cooling the Na vapor too rapidly, and a higher temperature cold trap was used in the subsequent experiments. The Na dust in the chamber created somewhat of a cleanup hazard, requiring ≈ 24 h of surface passivation before the chamber could be opened to (moist) air.

Nonetheless, the experiments did provide good tests of the material in question. Two observations were immediately obvious. First, neither the pyrolytic coating nor any substrate graphite survived the test at 1150-1200 K. All samples were cracked and expanded approximately 10 to 30%. The results from the flow tube experiment at 1200 K correspond to those of the refluxing experiments

TABLE VII

FLOW TUBE CONDITIONS FOR Na/GRAPHITE COMPATIBILITY TESTS

Test	T K	P Torr	$\bar{v}$ $m\ s^{-1}$	Duration min	Sample[a]	Remarks
1	1700	50-150	20-6.4	16	A	Coating cracked and peeling, substrate graphite OK.
					B	Same as 1A.
2	1220	350	1.9	14	A	Extensive damage to coating and substrate.
					B	Same as 2A.
					C	Extensive damage.
3	1710	300	3.2	27	A	Coating cracked, substrate OK. Very little Na absorbed into sample.
					B	No damage visible, little Na absorbed into sample.
					C	Same as 3B.

[a] A = Pyrolytically coated graphite; Great Lakes Carbon Corp., HLM grade.

B = Pyrolytically coated graphite; Stackpole, 2020 grade.

C = Uncoated graphite; Airco-Speer, 580 grade.

performed in the Na vaporizer. The second observation was that the results are quite different at 1700 K. A total of five samples were exposed to Na vapor at 1700 K and none sustained structural damage. The uncoated graphite sample showed no evidence of absorbed sodium. The pyrolytic graphite coating, however, was extensively cracked in three out of four samples. Probably if the Na gets under the coating at any imperfection it separates from the substrate and cracks. It is unlikely that any large-scale reactor could be made without some such imperfections.

The primary implication of this work with regard to the Westinghouse arc-jet reactor is that the pyrolytically coated graphite reactor liner must be above 1200 K before exposure to the sodium flow.

VI. CONCLUSIONS

The main conclusions from this program are:

1. Flames of gaseous Na or K with $SiCl_4$ or $SiHCl_3$ are stable, high temperature, characterized by rapid kinetics, and produce free silicon.
2. Flames of gaseous Na or K with SiF_4 are characterized by much lower temperatures, slower kinetics, and produce free silicon only if the reactor is hotter than about 1000 K so that Na_2SiF_6 formation is prevented. Additional heat input would be necessary to separate the product Si from the NaF in the gas phase.
3. Silicon produced from the $Na/SiCl_4$ reaction can be separated from the byproduct NaCl(g) if the reactor temperature is above $\approx$ 1750 K and inert gas (argon) in the system is minimized.
4. Heat release measurements show the $Na/SiCl_4$ reaction to be mixing limited, thus allowing a well-stirred reactor to be compact in volume.
5. Sodium-graphite compounds form at $T \leq 1200$ K causing severe material problems. Similar problems are observed for pyrolytic graphite or silicon carbon coated graphite. At $T \geq 1700$ K these problems are not observed for graphite although the coatings still fail.

VII. RECOMMENDATIONS

With the completion of the experiments discussed in Section IV technical effort on the current program is ended. We are now in a position to produce relatively large samples (0.2-0.5 kg) of silicon, test separation/collection methods, evaluate reactor material properties, and measure impurity levels and sources in the silicon product. The following recommendations are made for extending the work performed under this contract.

1. It is recommended that the present program be continued to measure the overall rate of reaction producing silicon, the volumetric rate of heat release, and the extent of reaction. These data, measured as functions of pressure, temperature, reactor volume, etc., are necessary to evaluate the feasibility of a production process and to determine the effects of scaling on the process. Further studies should also be made of the particle impaction technique for separating the silicon product from the NaCl(g) and possible impurities.

2. It is recommended that the preliminary reactor material studies reported herein in Section V be continued to determine the suitability of various reactor materials in contact with Si, $SiCl_4$, and Na.

3. It is recommended that a more detailed study of alkali metal/silicon halide reactions be initiated using a high temperature fast flow reactor. This program would measure global reaction rate coefficients, but more importantly, would study the silicon nucleation and particle growth kinetics. This latter phenomenon cannot be modeled or computed with any reasonable accuracy. Therefore, experimental data are needed for process design. The data are also needed in the development of better theories and computer models for predicing the rate of such processes.

VIII. NEW TECHNOLOGY

No reportable items of new technology have been identified.

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