

Silica to Silicon: Key Carbothermic Reactions and Kinetics

The primary carbothermic reactions for the reduction of silica to produce silicon were defined and the reaction kinetics were determined. Most possible reactions between silicon oxide and carbon or carbon compounds were studied by a series of thermogravimetric analyses at temperatures up to 2000°C. Four key sequential reactions occur with SiC and SiO as intermediate reactants; two reactions involve SiO₂ and two involve SiO. Reaction rate versus temperature, activation energy, and preexponential factors were determined for each of six reactions involving SiO₂ or SiO. These kinetic studies show that SiO, when combined with either carbon or SiC, reacts in the gaseous state, and the sublimation of SiO is not the rate-limiting reaction for forming silicon. [Key words: silicon, silica, carbothermal reduction, reactions, kinetics.]

I. Introduction

SILICON has been produced commercially from silica for over 100 years. Yet, because of the experimental difficulties encountered at temperatures >1500°C, the key carbothermic reactions and the relative rates of those reactions had not been defined experimentally. Nor has there been general agreement on which reactions occur in commercial arc furnaces during formation of the silicon.

At least 17 possible reactions have been noted,¹ and two reaction schemes proposed. One scheme, proposed by Muller, advances reaction (a) as the silicon-forming reaction.² Another scheme, proposed by Schei, indicates that reaction (b) is the silicon-forming reaction:³⁻⁶

$$SiO(g) + SiC(s) \rightarrow 2Si + CO$$
 (a)

$$SiO_2 + 2SiC(s) \rightarrow 3Si + 2CO$$
 (b)

A computer simulation by Katkov *et al.* of the reduction of silicon oxides also indicated reaction (b) is the prime silicon-forming reaction.⁷

An experimental study was conducted in two steps by the authors to answer the key questions:

(1) Which of the many reactions that are thermodynamically possible are involved in the carbothermic reduction of silica to silicon?

(2) What are the kinetic parameters of these reactions?

II. Identification of Carbothermic Reduction Reactions

(1) Technical Approach

To identify those reactions that are involved in the carbothermic reduction of silica to silicon, thermogravimetric analysis (TGA) was coupled with both an evolved gas detection (EGD) technique and X-ray diffraction (XRD) of the residue. The XRD analyses were accurate within $\pm 20\%$. Daniel H. Filsinger and Daniel B. Bourrie Dow Corning Corporation, Midland, Michigan 48686

Before generating the experimental data, all the techniques had to be adapted for this study. One critical requirement for TGA analyses was the containment of the volatile SiO long enough to allow subsequent carbothermic reactions to take place. Procedures were developed for conducting hightemperature, >1600°C, thermal analyses at atmospheric pressure. Tantalum was identified as a nonreactive crucible material, and a crucible was designed to increase the residence time of any SiO produced. A nondispersive infrared CO detector was installed and standardized with known mixtures of CO and He. Procedures for computerized acquisition, display, and interpretation of thermoanalytical and evolved gas data were developed to facilitate data analyses. X-ray diffraction techniques were developed to analyze the residues.⁸

To study the reactions individually, most combinations of silicon oxide reacting with a carbon compound were investigated while varying the molar ratio of the reactants:

SiO + xC SiO + xSiC $SiO_2 + xC$ $SiO_2 + xSiC$

The carbothermic reduction of silicon monoxide, SiO, has been studied during the formation of silicon carbide, SiC.^{9,10} In both of these prior studies, silicon monoxide gas was purged through a packed bed of carbonaceous material which was heated to 1650°C. For this study, it was not practical to purge the TGA system with silicon monoxide gas; solid silicon monoxide was purchased and charged to the crucible. The existence of a truly unique solid compound which is silicon monoxide has been questioned by some authors. However, with the experimental procedure used for this study, the results would not change if a mixture of silica and silicon was used since the heating of such a mixture has long been known to result in the generation of silicon monoxide gas.¹¹⁻¹⁴ Subsequent experimental results indicate that, except for some minor absorption or interaction with the tantalum crucible, all of the silicon monoxide charged to the crucible vaporized upon heating.

Preliminary data were obtained by heating reactants from 25° to 2000°C, monitoring the reaction by TGA and EGD, and analyzing the residues. These experiments defined the temperatures of interest for further study as well as provided data for a subsequent reaction rate study. For further experiments, the reactants were heated from 25°C to the temperatures of interest followed by rapid cooling of the residue. Analyses of these residues provided the information needed to identify the key reactions.

(2) Experimental Procedure

Thermogravimetric analyses were performed on a thermal analyzer* equipped with a 2400°C tungsten resistance furnace. The sample environmental temperature was monitored via tungsten-rhenium thermocouples located on the tungsten crucible holder platform. A tungsten gas exit tube was posi-

*Model 429 simultaneous thermal analyzer, Netzsch, Exton, PA.

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tioned 10 mm above the sample crucible extending through the top of the furnace; this allowed rapid escape of evolved noncondensables. The exit gas flowed through a 6-mm tube to an infrared analyzer[†] sensitized for CO in the range 100 ppm to 2%. Data were acquired, analyzed, and displayed with a laboratory automation system.[‡]

The TGA operating conditions generally did not vary for the data presented. Each sample was heated at a rate of 20° C/min under a flow of helium with <0.5 ppm oxygen content. The sample crucible, 7 mm in diameter, was supported in a vertical 38-mm tube with an average helium flow of 3 mm/s between the crucible and tube. All of the effluent was removed by a small conical hood directly over the crucible. The sample mixtures were made and stored in glass containers. The samples, ~100 mg, were tamped into the TGA crucibles using a pressure estimated at 70 kPa. In most cases, a light press-fit lid, with a 0.4-mm vent hole, covered the crucible.

The reagents, listed in Table I, were analyzed by X-ray diffraction. The results of the analyses revealed no extraneous crystalline material in the Si, SiC, SiO₂, or C, and no crystalline phases were found in the SiO.

(3) Thermal Analysis of Reactants

The starting materials—SiO, SiO₂, SiC, and C—were analyzed by X-ray diffraction both before and after TGA analysis. No weight or crystalline structure change occurred with SiC or C after heating to 2000°C.

The volatility of SiO under various experimental conditions is shown in Fig. 1. The TGA Run B of SiO in a crucible with a vented lid was typical of sample and operating conditions used throughout this investigation. SiO heated to 1620°C in a crucible with a vented press-fit lid and cooled at different rates of 10° and 500°C/min resulted in the formation of crystalline materials, 59 and 22 wt%, respectively. In both cases the crystalline phases formed were Si and SiO₂ in the cristobalite form. This may be the disproportionation:

$$2SiO \rightarrow SiO_2 + Si$$
 (c)

The type of SiO₂ used was characterized by X-ray analysis as α -quartz. A nonisothermal TGA analysis of SiO₂ resulted in a 6% weight loss (by evaporation) from 1700° to 2000°C. Further X-ray analysis of the fused α -quartz (mp 1710°C) gave no evidence that any crystalline phases were present after cooling. No significant response from the CO detector was observed during the heating of SiC (α or β), C, SiO, or SiO₂. These results demonstrated the gravimetric stability of the reactants with the crucible.

The reactants were of purified forms: carbon, in the graphitic phase; silica, in the form of α -quartz, α -silicon carbide; and silicon monoxide, which exhibited some silicon crystallinity but was essentially amorphous.

¹Model 202, Lira Mine Safety Appliance, Pittsburgh, PA. ³Model 3354B, Hewlett-Packard, Palo Alto, CA.



Fig. 1. TGA analyses of SiO with three environments.

(4) Identification of Carbothermic Reactions of Silica

Since the feed to arc furnaces is a mixture of silica and carbon, this study began with these reactants. Heating mixtures of SiO_2/C in 1:1 and 1:2 molar ratios via TGA resulted in a discontinuous weight loss in the TGA profile at 1720° and 1750°C, respectively (see Fig. 2). Additional weight loss then continued as the temperature approached 2000°C. The simultaneous monitoring of CO in the TGA exit gas showed a bimodal CO response with a minimum at 1720° to 1750°C. This indicated the likelihood of more than one reaction.

To learn more about the reactions that may have taken place, the TGA residue in both final and intermediate forms was qualitatively and quantitatively analyzed for crystalline components by X-ray powder diffraction. The intermediate TGA residues were obtained by repeating the experiments and terminating the heating program at the point of initial discontinuity with immediate and rapid cooling of the sample.

In both cases, with 1:1 and 1:2 molar silica to carbon, the XRD analysis showed the intermediate residue was silicon carbide in both α and β forms and also unreacted silica. This may have resulted from two possible reactions when there is an excess of silica:

$$3SiO_2 + 3C \rightarrow SiC + 2CO + 2SiO_2$$
 (d)

$$3SiO_2 + 6C \rightarrow 2SiC + 4CO + SiO_2 \qquad (e)$$

To confirm this, silica and carbon were mixed 1:3 molar and heated by TGA. The weight loss in reaction (f)

$$SiO_2 + 3C \rightarrow SiC + 2CO$$
 (f)

was essentially identical to the theoretical loss of carbon monoxide while XRD analysis of the residue confirmed that only silicon carbide was present. The TGA weight loss profile showed no perturbation in the simulation. The CO response coincided with the TGA and was monomodal indicating there was but a single reaction. This confirmed that reaction (f) is the stoichiometric molar ratio of SiO₂ and C. These results

Table I.	Analyses	of Reagents
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Reagent	Source	X-ray analysis		
Si	Hemlock Semiconductor Corp., Hemlock, MI; IVO190, lot S-03759	Si		
SiC	Cerac Pure, Milwaukee, WI; S-1058, lot 1587, 7 μ m average	α-SiC		
SiC: β form	Produced via SiO + 2C (see Table II)	75% β -SiC, 2% C (graphite), remainder α -SiC		
SiO	Cerac Pure, Milwaukee, WI; S-1064, lot 1858, 325 mesh	No crystalline phases detected		
SiO ₂	Cerac Pure, Milwaukee, WI; S-1061, lot 2957, 325 mesh	a-quartz		
C: graphite	Cerac Pure, Milwaukee, WI; G-1059, lot 480, 325 mesh	Graphite		



Fig. 2. TGA analyses of SiO₂ reaction with C.

also confirm that when there is an excess of silica, the process involves two reactions, (d) and (e), with silicon carbide as the intermediate reactant.

This series of experiments revealed that silicon carbide formation occurs upon initial heat-up of the reactants. But when silica was present in excess of carbon, further weight loss with carbon monoxide evolution was detected. Since only two condensed phases were present, and as the initial TGA curves progressed to higher temperatures, considerable loss of weight occurred. This weight loss is believed to be the loss of silicon monoxide and carbon monoxide:

$$2SiO_2 + SiC \rightarrow 3SiO + CO$$
 (g)

This explains why little residue remained when the equimolar mixture of silica and carbon reached 2000°C. The formation of silicon carbide below 1720°C left a 2:1 ratio of quartz and silicon carbide to form the SiO and CO volatiles. Furthermore, the analysis of the CO evolution above 1720°C had a lesser amount of area to the peak than did the initial reaction. This suggests that CO was not the major component of the weight loss. The rule of mixtures[§] also dictates that, based on the total carbon present, only a small amount of CO can account for the weight loss and that the silicon present as the dioxide and carbide also would have had to vaporize at temperatures where the vapor pressures are very low.

Likewise, this same reaction sequence apparently took place when SiO₂ and C were mixed 1:2 molar. The SiC that formed reacted with the excess SiO₂, but since excess SiC was present, a SiC residue would be expected after TGA measurement to 2000°C. This was observed. The remaining residue was >90% β -SiC with a small amount, ~2%, of Si. Furthermore, the weight remaining was 30%, comparing closely with the theoretical 23% for SiC with the path:

$$3SiO_2 + 6C \rightarrow 2SiC + 4CO + SiO_2 \tag{e}$$

$$2SiO_2 + 4SiC \rightarrow 3SiO + CO + 3SiC$$
 (g')

Consequently, it was learned that carbon does not reduce SiO_2 directly to Si but through an SiC intermediate.

The higher-temperature reaction of SiO_2 and SiC was likewise studied from 1560° to 1760°C by heating SiO_2 and SiC at various molar ratios in a manner similar to that for SiO_2 and carbon.

To study the suspected reaction, excess SiO_2 was mixed with SiC in a 2:1 molar ratio and heated in the TGA. As was found when equimolar SiO_2 and carbon reacted, forming SiC with excess SiO_2 , a continuous weight loss profile resulted with simultaneous CO evolution and essentially complete loss of the sample from the container. This corroborated that the 2:1 molar SiO₂ and SiC proceeds as presented in reaction (g). Additionally, the same materials were mixed in ratios of 1:1 and 1:2 SiO₂ to SiC, allowing an excess of SiC to be present during the evolution of the volatiles, SiO and CO. Again there was a considerable loss of reactants, and the excess SiC was expected to be found as a residue. XRD confirmed this reaction path by identifying SiC and also a considerable quantity of Si in the residue. Silicon is most likely being formed from the reaction of SiO with the excess SiC.

Some investigators have proposed that SiC may directly reduce SiO_2

$$SiO_2 + 2SiC \rightarrow 3Si + 2CO$$
 (h)

with a further loss of weight where the formed Si can react with the unreacted SiO_2 to form SiO:

$$SiO_2 + Si \rightarrow 2SiO$$
 (reverse of (c)) (i)

This is not likely. It will be shown by TGA that silicon is formed under high concentrations of SiO in the presence of SiC and at a temperature of 1700°C. The formation of SiO from SiO₂ and SiC begins at a temperature more than 100°C lower, ~1560°C.

The 2:1 molar SiO₂ to SiC TGA with α -SiC was repeated with the β form to determine any differences in reactivity, products found, or other characteristics. The resulting weight loss curves were nearly identical for both α and β forms. Thus, at least under these experimental conditions, there was no observed difference in reactivity.

As each pair of reactants was studied in various molar concentrations, dual or consecutive reactions were projected. Experiments presented thus far indicate the stoichiometric reaction for SiO_2 with C and SiC results in the formation of SiC and SiO. These two intermediates are suspected to further react to form Si.

Thus the next pair of reactants to be mixed and heated were SiO and SiC. SiO is a solid material at room temperature which permitted it to be mixed and added to the crucible with the other solid reactants. Upon heating, the weight loss began at $\sim 1200^{\circ}$ C and ended at 1700°C with SiC remaining in the crucible. The SiO was clearly subliming and not reacting with the SiC. XRD analysis of the residue revealed SiC and Si. The amount of SiO was increased in steps until a 1.8 mol excess of SiO was found to be necessary for 100% conversion of SiC to Si, reaction (j):

$$SiO(+1.8SiO) + SiC \rightarrow 2Si + CO(+1.8SiO)$$
 (j)

This is in agreement with the results of the prior computer simulation of reduction of silicon oxides.⁷

There was concern that possible alloying of silicon with the tantalum crucible would drive reaction (j) to the right. This reaction was also studied using a boron nitride crucible. The reaction rate at 1725°C, 49.2×10^{-4} s⁻¹, was within 2% of the average rate obtained with tantalum crucibles. Therefore, unless tantalum and boron nitride have identical reaction rates with silicon, the tantalum crucible had no significant effect.

As with the previously discussed reaction of SiO₂ with SiC, the β form of SiC was mixed and reacted with 2.8 mol of SiO. As before, both forms of SiC behaved similarly, yielding nearly identical TGA weight loss versus temperature profiles as well as near 100% yields of Si formation and weight residues based on the SiC charge.

The last pair of reactants studied was SiO with carbon. While this is not a likely predominant reaction in arc furnaces, it may occur in the hot zone with any unreacted carbon. The TGA experiments included heating mixtures of SiO and graphite in 1:1 and 1:2 molar ratios.

Equimolar SiO and C, mixed and heated, evolved CO at \sim 1550°C and this continued until the weight stabilized at 1920°C. The trace of CO versus temperature showed a bi-

⁸Excess or deficient elements are determined by comparing total elemental analysis with the sum of the elements in known components of a mixture.

modal peak with a minimum at 1730°C between peaks. An XRD analysis of the residues following a TGA measurement to 1730°C revealed 22% β -SiC and 3% Si. Based on the results of the previous combination of reactants, SiO and SiC, this was expected. Consequently, SiO was reacting with carbon to form SiC which then reacted with the excess SiO to form Si, i.e., reactions (k) and (j).

$$2SiO + 2C \rightarrow SiC + CO + SiO$$
 (k)

$$SiO + SiC \rightarrow 2Si + CO$$
 (i)

Thus, SiC was found to be an intermediate to reaction (k) which yields silicon.

Reaction (k) was confirmed by mixing 2 mol of graphite with solid SiO and heating to 2000° C. Again the CO was monitored but only a single peak was observed from 1450° to 1800°C. Table II summarizes the analyses of the reactions of SiO and XC. For the SiO/2C mixture, four independent weight loss analyses were within 3% absolute of the 41% theoretical conversion which is based on complete formation of SiC from the carbon charge. This verifies the stoichiometric reaction as

$$SiO + 2C \rightarrow SiC + CO$$
 (1)

This very high conversion rate was quite different from the reaction with SiO/SiC 2.8/1 molar ratio (including a 1.8 mol excess of SiO) for total conversion. Since no excess SiO was needed, this reaction does not appear to have a critical partial pressure of SiO for the formation of SiC.

(5) Discussion

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Based upon these data, four key reactions occur during the carbothermic reduction of silica within the temperature range studied, 25° to 2000°C. Note that the chemical equations are written so that the stoichiometry of these reactions is readily apparent. No implications of the mechanism or interaction of the reactants are made.

Two of these key reactions involve silica:

$$SiO_2 + 3C \rightarrow SiC + 2CO$$
 (f)

 $2SiO_2 + SiC \rightarrow 3SiO + CO$

The remaining key reactions involve silicon monoxide:

$$SiO + 2C \rightarrow SiC + CO \tag{1}$$

$$SiO + SiC \rightarrow 2Si + CO$$
 (a)

The apparent individuality of the various combinations of these reactions has caused much of the confusion in the literature. The intent of this study was to provide a comprehensive set of experimental evidence for consecutive reactions occurring during the carbothermic reduction of silica.

For example, the formation of SiO from SiO_2 and C is not a separate reaction, but a combination of reactions (f') and (g'):

$$\frac{1}{3}SiO_2 + C \xrightarrow{1550^\circ - 1750^\circ C} \frac{1}{3}SiC + \frac{2}{3}CO$$
 (f')

+
$$\frac{2}{3}$$
SiO₂ + $\frac{1}{3}$ SiC $\xrightarrow{1625^{\circ}-1900^{\circ}C}$ SiO + $\frac{1}{3}$ CO (g')

$$SiO_2 + C \rightarrow SiO + CO$$
 (m)

The fact that two reactions occur is indicated by the two peaks in the evolved CO curve shown in Fig. 3. Analysis of the residue of a 1:1 molar ratio of SiO_2 to graphite heated to 1610° and 1720°C revealed the formation of SiC.

Reaction (b) is the silicon-forming reaction claimed in Schei's model.³⁻⁶ This study indicates that reaction (b) is not an individual reaction but the net result of reactions (g'') and (a'):

$$SiO_2 + \frac{1}{2}SiC \rightarrow \frac{3}{2}SiO + \frac{1}{2}CO$$
 (g")

$$+\frac{3}{2}SiO + \frac{3}{2}SiC \rightarrow 3Si + \frac{3}{2}CO$$
 (a')

$$SiO_2 + 2SiC \rightarrow 3Si + 2CO$$
 (b)

Data from these experiments agree with portions of the model proposed by Müller:²

$$SiO(g) + 2C(s) \xrightarrow{152/C} SiC(s) + CO(g)$$
 (1)

+ SiO(g) + SiC(s)
$$\xrightarrow{1500}$$
 2Si(l) + CO(g) (a)

+
$$\operatorname{SiO}_2(l)$$
 + $\operatorname{Si}(l) \xrightarrow{1823^{\circ}C} 2\operatorname{SiO}(g)$ (i)

$$SiO_2 + 2C \rightarrow Si + 2CO$$
 (n)

This model uses the reflux of silicon to explain the need for high temperatures in commercial submerged arc furnaces:

$$Si(l) \xrightarrow{1980^{\circ}-3030^{\circ}C} Si(g) \xrightarrow{3030^{\circ}-1980^{\circ}C} Si(l)$$
 (0)

Reaction (o) provides the mass transfer needed for reaction (i) to provide sufficient SiO.

Table II. Analysis of Reactions of SiO and C

(g)

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	Initial		Intermediate		Final residue, 2000°C	
Reactants	Mole ratio	(°C)	Material	Temp (°C)	Reactants (wt%)	XRD
SiO ₂ /C	1/1	1300	11% β-SiC 5% SiO2	1720	<11	None
	1/2	1300	27% β-SiC 5% SiO ₂ 3% C	1730	30	97% β-SiC 2% Si
	1/3	1400			42	73% β-SiC 12% C
SiO ₂ /SiC	1/1	1500			29	42% Si 36% <i>B</i> -SiC
	1/2	1550			50	71% β-SiC 29% Si
	2/1	1520			8	
SiO/SiC (lid)	1/1	1500			72	92% β-SiC 4% Si
	2.8/1	1500	20% Si 8% TaSi ₂ 4% β-SiC	1800	22	>90% Si
SiO/C	1/1	1470	22% β-SiC 3% SiC	1720	42	70% β-SiC 19% Si
	1/2	1450			40	75% SiC β:α/3:1 2% C

III. Kinetic Analysis

(1) Analytical Approach

The second objective of this study was to determine the effect of reaction conditions, such as temperature and stoichiometry, on the reactions. Kinetic or rate data can be determined by thermoanalytical techniques employing either isothermal or nonisothermal heating. The rate data, with nonisothermal heating, are obtained over a temperature range with only one heating excursion for a single specimen. However, the calculation of the reaction rate at a given temperature is based on a few or even a single discrete experimental value.

The isothermal heating mode allows the determination of the extent that a reaction follows a chosen rate expression. Reaction conversion and yield may also be determined by analysis of the residue after each isothermal measurement. This information is necessary when applying rate data to batch and continuous processes. Another advantage of the isothermal heating mode is the minimization of the thermal equilibrium time lag encountered between the sample and the thermocouple when heating or cooling. The multitude of experimental data points available with the isothermal mode also provides a superior statistical data base.

Reactions (a), (b), (l), (m), (n), (o), the basis for deriving the kinetic data, all result in the forming of one or more gases and a weight change. The extent of the reaction or conversion is determined by continuously measuring the weight at a given temperature. Reaction (a), SiO + SiC \rightarrow 2Si + CO, poses a special problem, as an excess of SiO is required to convert the SiC to Si and CO. Weight measurement alone will not distinguish between the SiO loss due to sublimation and the CO formed. An IR detector calibrated specifically for quantitative measurements of CO can follow the reaction and provide comparable reactant weight data as is done with the thermobalance. However, if the IR analysis is used in the nonisothermal mode, the effluent gas stream from the TGA to the IR detector would sense the rising temperature because the gases would be continuously expanding. Thus, the measurement of weight change would be considerably less precise. For this and other reasons, an isothermal thermogravimetric evolved gas detector (TGA/EGD) approach was taken to determine rate data.

Comprehensive reviews describe the method for determining kinetic data from isothermal weight responses.^{15,16} Various mathematical models of these methods have been classified by Flynn and Wall¹⁷ as (a) integral methods, (b) difference differential, (c) methods applicable to initial rates, and (d) nonlinear or cyclic heating rate.

However, they all take the general form

$$da/dt = ak \tag{1}$$

$$k = A \exp(-E/RT) \tag{2}$$

and if the heating is nonisothermal

$$T = T_0 + bt \tag{3}$$

where a is the weight fraction reacted, b is the heating rate, k is the rate constant at temperature T, A is the preexponential factor, E is the activation energy, R is the gas constant, and T_0 is the starting temperature.

Once the TGA/EGD weight data have been obtained for a given reaction and the residue analyzed to confirm the yield and conversion, the appropriate rate expression must be determined. For this study, an expression common to TGA-derived kinetics¹⁸ was first tested based on homogeneous first-order kinetics:

$$-d(W/W_0)/dt = k_1(W/W_0)$$
(4)

where W is the weight of reactants, W_0 is the initial weight of reactants, and k_1 is a rate constant. The well-known solution

to this first-order differential equation is

$$\ln W_0/W = k_1 t \tag{5}$$

or to test graphically, Eq. (5) becomes

$$n W/W_0 = -k_1 t \tag{6}$$

For cases in this study where nonvolatile products are formed, the weight of the reactants, W, is determined by decreasing the observed weight, W_{obs} , by the ratio of the molecular weight (MW) of the nonvolatile to volatile products, e.g.

$$SiO_2 + 3C \rightarrow SiC(s) + 2CO(g)$$

$$MW = W_{abs}[40/(2 \times 28)]$$

$$MW = W_{abs}[40/(2 \times 28)]$$

If the resulting plot of the ln of the weight of reactants versus time is linear, the expression is valid and the rate constant is the negative of the slope in units of s^{-1} . These values, temperature and respective rate constants, are then applied to the Arrhenius equation:

$$\ln k = A/T + B \tag{7}$$

This determines the activation energy and preexponential or frequency factor and allows the interpolation of the rate constants. The rate expression, Eq. (6), tested favorably for all six reactions studied. Hence no tests of other equations were attempted.

The rate constant k is correctly defined and referenced as a "constant" only if all parameters significantly affecting the rate are treated in the rate expression. There are obvious parameters not studied here which will most likely affect the rate, such as (a) mass, resulting in diffusion as rate limiting, (b) particle size, (c) surface area, (d) crucible geometry, (e) heat of reaction, and (f) heat of vaporization. While it would be impractical to account for the effects of all parameters, an attempt was made to hold many of these variables constant while studying the six reactions over a temperature range. The rates, activation energies, and frequency factors of the six reactions could then be ranked and compared with each other.

(2) Results and Discussion

Isothermal TGA analyses were performed over the temperature range from 1410° to 1800°C on each of the reactions:

$$SiO_2 + 3C \rightarrow SiC + 2CO$$
 (f)

$$2SiO_2 + SiC \rightarrow 3SiO + CO$$
 (g)

$$SiO + 2C \rightarrow SiC + CO$$
 (1)

$$SiO + SiC \rightarrow 2Si + CO$$
 (a)

$$SiO_2 + Si \rightarrow 2SiO$$
 (i)

$$SiO(s) \rightarrow SiO(g)$$
 (p)

The temperature range chosen was dictated by the reaction rate. Reactions (1) and (a) involving the reactant SiO required a minimum temperature for reaction; otherwise loss of SiO reactant occurred through sublimation. The maximum temperature was limited to the time necessary to obtain sufficient data for analysis. In several instances with heating at 100° C/min, >30% of the reaction occurred before the desired isothermal temperature was reached, leaving only a few minutes for the remaining reactants to convert. Each of the reactions was studied in its stoichiometric form to eliminate simultaneous reactions which would unduly complicate the rate expression.

The performance of the IR/CO quantification was measured using the reaction $SiO_2 + 3C \rightarrow SiC + CO$. This reaction was chosen because all the weight loss is attributed to CO evolution. Thus, a TGA weight loss curve and original sample weight reduced by CO detected by IR should be identical at time t. Comparing reaction rate values determined by



Fig. 3. Isothermal TGA analysis of reaction $SiO_2 + 3C \rightarrow SiC + 2CO$.

both techniques, a maximum deviation of 21% between the IR and the TGA technique was found. This deviation increased with an increase in reaction rate. Nevertheless, this performance was considered better than expected for the complexity of calculation and approximation of control parameters such as flow rate.

Figures 3 and 4 represent a typical isothermal TGA analysis for deriving reaction rates. Figure 3 is a conventional TGA plot indicating weight loss for each isothermal temperature studied along with a scale, on the right, indicating the reaction extent at any time t. Figure 4 represents the natural log of the weight of reactants versus time from which the rate constant is determined. The starting weights were not identical but were within 30 to 35 mg. Thus the right scale is an approximation of the extent of the reaction. It is not uncommon in kinetic studies to find a deviation from a rate expression after a reaction is partially completed. In this study, linear responses were typically found beyond reaction extents of 50%.

The silicon-producing reaction SiO + SiC \rightarrow 2Si + CO required analysis with a vented tight-fitting lid to contain the volatile SiO to a temperature of ~1800°C where CO is first observed and the reaction proceeds. This reaction was also attempted with a loose-fit vented cover. Arrhenius plots of these two conditions resulted in parallel lines, with the loose cover reaction occurring faster over the 1700° to 1800°C range. This could be due to the decreased CO concentration with the loose fit cover.

The reactants in this study were also heated to 1660° C in both tantalum and boron nitride to determine if the crucible composition affects the reaction rate. The relative difference between the reaction rates was less than 5%. Since tantalum and boron nitride crucibles are not likely to have the same effect on the reaction rate, the crucible is not a significant factor in the reaction kinetics.

Typical Arrhenius plots for two reactions are shown in Fig. 5. The Arrhenius plots for all reactions at each tempera-



Fig. 4. Derivative of isothermal analysis of reaction $SiO_2 + 3C \rightarrow SiC + 2CO$.



Fig. 5. Typical Arrhenius plots for SiO and SiO₂ reactions: A, $SiO(s) \rightarrow SiO(g)$; G, $2SiO_2 + SiC \rightarrow 3SiO + CO$.

ture are presented on Fig. 6. The Arrhenius plot regression lines for both the vaporization of commercial SiO and the production of SiO by reacting SiO_2 with Si are remarkably similar in their reaction rates from 1410° to 1560°C; the rates measured at 1460° and 1510°C are nearly identical. These rates are the fastest for any of the reactions studied and were detected at the lowest temperature. This indicates that SiO, when combined with either carbon or SiC, reacts in the gaseous state.

The kinetic data, reaction rate versus temperature, activation energy, and preexponential factors determined for six reactions under specific experimental conditions are summarized in Table III and Fig. 6.

IV. Conclusions

Four key consecutive reactions occur during the carbothermic reduction of silica to silicon; two reactions involve silica and two involve silicon monoxide. Schei's model reaction for the formation of silicon is shown to be the net result of two separate reactions. Carbon does not reduce SiO_2 directly to Si



Fig. 6. Arrhenius plots for SiO and SiO₂ reactions: A, SiO(s) \rightarrow SiO(g); B, SiO₂ + Si \rightarrow 2SiO; C, SiO₂ + 3C \rightarrow SiC + 2CO; D, SiO + 2C \rightarrow SiC + CO (lid); E, SiO + SiC \rightarrow 2Si + CO (loose lid); F, SiO + SiC \rightarrow 2Si + CO (tight lid); G, 2SiO₂ + SiC \rightarrow 3SiO + CO; H, SiO(s) \rightarrow SiO(g) (lid).

Table III.	Summary	of Kinetic	Study 2	Results

Reaction	Crucible vent	<i>T</i> (K)	A	B	E_a (kJ/mol)	$Z(s^{-1})$
$SiO_2 + 3C \rightarrow SiC + 2CO$	Open	1733-1933	-4.68	18.82	390	108
$2SiO_2 + SiC \rightarrow 3SiO + CO$	Open	1833-2033	-4.18	17.55	348	106
$SiO + 2C \rightarrow SiC + CO$	0.4 mm	1733-1933	-5.69	23.76	472	1010
(2.8) SiO + SiC \rightarrow 2Si + CO	0.4 mm	1963-2073	-6.10	24.42	505	1010
	Loose lid	1998-2073	-6.99	25.10	505	1011
$SiO(s) \rightarrow SiO(g)$	0.4 mm	1833-2033	-4.06	13.79	340	106
	Open	1683-1833	-3.68	14.34	305	106
$SiO_2 + Si \rightarrow 2SiO$	Open	1683-1883	-4.18	16.95	348	107

but through a SiC intermediate. All the reactions are significant at the temperatures found in arc furnaces, typically 1400° to 3000°C.

Glossary

- A Preexponential factor, Arrhenius reaction equation
- Weight fraction reacted a
- b Heating rate
- Ε Activation energy
- EGD Evolved gas detection
- Rate constant at temperature Tk
- Melting point (temperature) mp
- R Gas constant
- TGA Thermogravimetric analysis
- Starting temperature T_0
- Initial weight of reactants W
- XRD X-ray diffraction

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