solvent of higher dielectric constant than corresponds to the measured value for the solvent mixture, and the points on curves such as those shown in the figures are to the right of their "proper" place. Calculations similar to those of Ricci and Nesse show<sup>9</sup> that the "sorting" effect is much less for ethanol-water, and the points for this solvent mixture are closer to their "proper" place. If solvation parallels the solvent sorting effect, then solvation energies would contribute more to the solution process in dioxane-water mixtures, and the heat of solution would decrease. Such a decrease is observed for the 1-1 electrolytes in this solvent pair.

(9) R. M. Hall, Ph.D. Dissertation. The Ohio State University. 1956.

The increase in heat of solution in the other solvents requires a heat-absorbing process to overcome the heat of solvation. This could be found in breakdown of aggregates in the solvent by the introduction of ions, as suggested by Frank and Evans.<sup>10</sup> If the heat required for this "melting" process is greater than the energy gained in solvation, a net increase in heat of solution results; if on further addition of organic component the relative magnitudes of the two energies change, a maximum in  $\Delta H^0$  can be explained. This interpretation still leaves the behavior of the sulfates in dioxane-water anomalous as compared to the 1-1 electrolytes in this solvent pair.

(10) H. S. Frank and M. W. Evans, J. Chem. Phys., 13, 507 (1945).

# KINETICS OF THE OXIDATION AND NITRIDATION OF SILICON AT HIGH TEMPERATURES

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The kinetic behavior of silicon in oxygen, carbon dioxide, nitrogen and argon containing 0.2% by volume of nitrogen has been determined at  $1200-1400^{\circ}$  by means of a thermobalance. In oxygen and CO<sub>2</sub>, the rate laws were shown to be parabolic. Erratic behavior was observed in pure nitrogen with the formation of a volatile silicon nitride but at a low partial pressure of nitrogen in argon, volatilization was absent and a logarithmic rate law was shown to hold.

## Introduction

It is well known that the incorporation of small amounts of silicon into other metals can lead to a substantial improvement in the oxidation resistance of the alloy. Unfortunately silicon has a marked embrittling effect on other metals and is itself a hard and brittle material. However, its high intrinsic oxidation resistance in air has led recently to its suggested use in "cermets" (metal-refractories) in which pure silicon is the metallic constituent.

Comparatively little fundamental work has been carried out on the rate of reaction of silicon with oxygen and virtually none on the reaction with nitrogen. The latter reaction is of further importance since the product of the reaction, principally silicon nitride, Si<sub>3</sub>N<sub>4</sub>, is a promising high temperature special refractory.

Geil and McAdams<sup>2</sup> using an optical interferometric method found that silicon oxidized according to a parabolic rate law in the temperature range 500-950°. Brodsky and Cubicciotti,<sup>8</sup> using a volumetric absorption apparatus, measured the rate between 950-1160° and deduced a logarithmic rate law between these temperatures. However, their data at the extreme ends of this temperature range fitted a parabolic rate law equally well. Law<sup>4</sup> investigated the oxidation of silicon between 1000- $1300^{\circ}$ K. at pressures of oxygen in the region  $10^{-2}$ - $10^{-3}$  mm. His results demonstrated a parabolic rate law which was markedly pressure dependent.

(1) Culcheth Laboratories, U.K.A.E.A., Warrington, England.

No accurate work on the nitridation of silicon is known to the authors but it has been reported<sup>5</sup> that only silicon particles less than 0.1 mm. diameter can be nitrided completely in a reasonable time. Other workers<sup>6</sup> state that silicon powder reacts rapidly with nitrogen at 1350-1400° forming mainly Si<sub>3</sub>N<sub>4</sub>.

For the production of silicon nitride commercially, iron and alkaline earth fluorides are said to be valuable catalysts in promoting the silicon-nitrogen reaction. Nitrides other than  $Si_3N_4$  are said to exist but data for these are lacking.

This present work describes the kinetic behavior of silicon in oxygen and  $CO_2$  and in nitrogen and argon containing a trace of nitrogen at temperatures between about 1200-1400°.

#### Experimental

(i) Materials.—Silicon of purity 99.95% was obtained from the Morgan Crucible Co. The silicon was melted in from the Morgan Crucible Co. The silicon was melted *in* vacuo in a thoria-lined alumina crucible, cast and roughly machined to size. Final polishing was carried out with metallurgical emery paper, ultimately with 4-O grade to give a mirror finish. The final specimens were small rectangular blocks weighing approximately 1-2 g. Oxygen, oxygen-free argon and oxygen-free nitrogen were obtained in cylinders from the British Oxygen Co. Pure carbon dioxide was obtained from the Carbon Dioxide Co. Apparatus.—The reaction of silicon with the various gases was determined by means of a thermobalance. A platinum-

was determined by means of a thermobalance. A platinumwound resistance furnace was used with an impervious mullite reaction tube mounted vertically. Temperature control was maintained to  $\pm 5^{\circ}$  over a three inch central zone by means of a mechanical controller operated by a Pt/Rh thermocouple. Connections to the mullite tube were made in

<sup>(2)</sup> G. W. Geil and D. J. McAdams, J. Research Natl. Bur. Standards, 28, 593 (1942).

<sup>(3)</sup> M. B. Brodsky and D. Cubicciotti, J. Am. Chem. Soc., 78, 3497 (1951).

<sup>(4)</sup> J. T. Law, This JOURNAL, 61, 1200 (1957).

<sup>(5)</sup> J. F. Collins and R. W. Gerby, J. Metals, 7, 612 (1955).

<sup>(6)</sup> A. G. Nasini and A. Cavallini, IX Cong. Intern. Quim. Pura Aplicada, 3, 280 (1934).

Pyrex glass with Araldite cement and these joints were water cooled.

The balance consisted simply of a precision glass spring (obtained from Still and Cameron, London) suspended from the inside of a ground glass joint above the furnace. The sensitivity of the spring was approximately 43 mg./cm. extension under a load of one g.; Hooke's law was obeyed over exten-sions of several cm. The entire spring was virtually maintained at room temperature and the specimens were suspended in the hot zone of the furnace by a fine silica rod; a small silica stirrup was used to support the silicon sample. The weight changes were obtained by measuring the changes in spring extension with a travelling microscope focused on a fine datum mark on the spring. Weight changes of better than 0.1 mg. could be observed without difficulty.

The usual arrangements were made for evacuating the fur-

The usual arrangements were made for evacuating the fur-nace tube and for flowing dry gases through the system. The procedure for making a measurement was as follows: The furnace was brought to temperature and the ground glass joint removed. The spring with its silica rod and silicon sample suspended from it was carefully attached to the hook. Whilst a rapid stream of argon was flowing through the furnace tube, the joint and spring assembly were lowered into position. This could be done in a few seconds and the furnace was then evacuated.

The travelling microscope was focused on the mark on the spring to obtain the initial reading. The appropriate gas was admitted and the weight gains followed by adjusting the microscope at suitable intervals to coincide with the datum mark; initially, readings were taken every minute and for longer intervals after the first hour. Many runs were extended over 24 hours.

## Results

(i) Oxygen.—The rate of reaction of silicon with pure dry oxygen at one atmosphere and temperatures of 1201, 1255, 1303, 1360° was deter-mined over periods of 24 hours; the results fit a parabolic law, *viz.*,  $(\Delta m)^2 = kt + c$  satisfactorily as shown in Fig. 1. At all temperatures the initial rate of reaction was somewhat higher than the overall parabolic rate curve which explains why the linear plots do not pass through the origin. The reaction product was invariably transparent cristobalite as shown by X-ray analysis. The stable silica phase in this region is tridymite but this particular variety appears to be difficult to form. It seems likely that part of the silica may be vitreous but this is not detected easily.

The activation energy for this process is calculated from the Arrhenius equation, viz.

$$\frac{\mathrm{d}\,\ln\,k}{\mathrm{d}\,T} = \frac{\Delta E^*}{R\,T^2}$$

where k is the parabolic rate constant and  $\Delta E^*$ the activation energy.

The graph of log k against 1/T is shown in line a of Fig. 2. From the slope of this line the activation energy is 43 kcal.

(ii) Carbon Dioxide.—The reaction with dry carbon dioxide at one atmosphere was determined at 1212, 1301 and 1372°; as with oxygen the results fit a parabolic law. This graph is shown in Fig. 3. The initial rate is again faster than the over-all rate. The reaction product was translucent and rather deeply blue tinted but appeared by X-ray to be principally silica, although some carbon or silicon carbide may have been present.

From the graph of log k against 1/T for this reaction (line b in Fig. 2), the activation energy is 32 kcal.

(iii) Nitrogen.—Several runs were made in pure nitrogen at one atmosphere between 1200 and 1410°. The weight gains were erratic (Fig. 4)



Fig. 1.—Parabolic plots for the oxidation of silicon: ٠. 1360°; ●, 1303°; ▲, 1255°; ■, 1201°.



Fig. 2.-Logarithm of the rate versus inverse absolute temperature plots for the reaction of silicon with: oxygen; A, carbon dioxide.







Fig. 4.—Reaction curves of silicon with nitrogen at 1 atm. pressure:  $\bigcirc$ , 1410°;  $\blacktriangle$ , 1354°;  $\blacksquare$ , 1251°,  $\triangle$ , 1402°,  $\checkmark$ , 1308°,  $\blacklozenge$ , 1200°.



Fig. 5.—Reaction curves of silicon with argon gas containing nitrogen: ■, 1372°; ●, 1308°; ▲, 1208°.



Fig. 6.—Δm versus log (1 + t) curves for silicon with argon gas containing nitrogen: ■, 1372°; ●, 1308°; ▲, 1208°.

and at the higher temperatures the silicon appeared to gain and lose weight successively.

The product was the fibrous white nitride  $Si_3N_4$  (as determined by X-ray); there was evidence of some volatilization since fine whiskers were found on the supporting silica rod, about a centimeter away from the specimen. The temperature co-efficient of the nitridation could not, of course, be determined but an inspection of the results as plotted graphically suggests that the effect of temperature on the rate is relatively small.

(iv) Argon Containing 0.2% Nitrogen.—The effect of nitriding at a low partial pressure of nitrogen was studied by using argon which normally contains about 0.2% by volume of nitrogen. At the three temperatures studied, *viz.*, 1208, 1308 and 1372°, the reaction proceeded quite smoothly and regular weight gains were found (Fig. 5). The results also have been plotted according to the logarithmic rate law, *viz.* 

# $\Delta m = k \log \left(1 + t\right)$

and these are shown in Fig. 6. The reaction product was a dense white adherent scale of  $\hat{S}i_8N_4$ . There was no evidence of the volatilization which had occurred in pure nitrogen.

The temperature coefficient, as with nitrogen, appears to be small.

#### Discussion

(i) Oxidation in  $O_2$  and  $CO_2$ .—Apart from the faster initial rate due to atomic surface roughness the parabolic oxidation behavior in pure oxygen suggests that the oxide film grows by the diffusion of some species through it, the most probable being the inward diffusion of oxygen which could be molecular, atomic or ionic. The diffusion of molecular oxygen through the lattice is unlikely, whilst diffusion through "micro-cracks" would tend to lead to a logarithmic rate law rather than a parabolic one. The electrical properties of silica are ambiguous; recently Cohen<sup>7</sup> has determined the electrical conductivity of fused quartz at these high temperatures. One sample showed electronic behavior with values of the order of  $10^{-4}$ mho/cm. for the conductivity in the temperature range 1000-1400° and, moreover, relatively insensitive to temperature. Another sample showed anomalous electrical behavior with essentially ionic conduction. Cohen attributed these marked differences to the presence of traces of metallic oxide impurities. Since our silicon samples contained trace impurities film growth by diffusion of oxygen ions is clearly possible. Equally, of course, a slight solubility of dissolved oxygen (in the silica lattice) could account for film growth by diffusion of neutral oxygen atoms inwards; this process would probably be pressure dependent.

The results generally confirm the observed parabolic behavior of Geil and McAdams<sup>2</sup> and Law<sup>4</sup> working under different conditions of temperature and pressure. The results of Cubicciotti and Brodsky<sup>3</sup> indicated that a parabolic rate law applied at the two extreme temperatures of 950 and 1160° but not in between; from these extreme values an apparent activation energy of 45 kcal.

(7) J. Cohen, J. Appl. Phys., 28, 795 (1957).

is obtained which is in reasonable agreement with the presently determined value of 43 kcal.

Law obtained an activation energy of 36 kcal. for the growth of silica formed at 1000-1300 °K. with low gas pressures. His films were in the so called "thin film" region of 100-1000 Å. where the mechanism is almost certainly different from the present work on relatively thick films of the order of 100,000 Å.

The results for silicon in  $CO_2$  show that whilst the rates are similar to those for oxygen, the absolute values are significantly faster with a lower activation energy of 32 kcal. Whilst the principal product of the reaction is silica given by the equation  $Si + 2CO_2 = SiO_2 + 2CO$ , small amounts of free carbon or silicon carbide may be formed by such reactions as  $Si + CO_2 = SiO_2 + C$ , and  $2Si + CO_2 = SiO_2 + SiC$ .

Presumably traces of these other products could be incorporated in the silica lattice and thus modify the diffusion behavior.

(ii) Nitridation in  $N_2$  and Argon with a Trace of  $N_2$ .—The growth of nitride films on silicon is by a mechanism distinctly different from that of silica films. In pure nitrogen, the rate law could not be determined since volatilization of nitride was occurring simultaneously. The smooth nitriding reaction in argon with a trace of nitrogen was not accompanied by volatilization. Since the only important difference is that of nitrogen partial pressure, it is possible that traces of another more volatile nitride than  $Si_3N_4$  was being formed in pure nitrogen, e.g.,  $Si_2N_3$ . The results would then imply that the dissociation pressure of this higher nitride was greater than about one mm. but less than 760 mm. in this temperature range for a hypothetical reaction

 $6Si_2N_3$  (volatile) =  $4Si_3N_4 + N_2$ 

This explanation is very tentative since no other nitride than  $Si_3N_4$  was detected and the properties of other nitrides are virtually unknown.  $Si_3N_4$ is, of course, appreciably volatile itself but only at substantially higher temperatures.

The logarithmic growth of the nitride film in argon containing a trace of nitrogen can be interpreted by assuming that nitrogen diffuses through minute cracks or faults in the growing film. As the film thickens the path for the nitrogen gas becomes increasingly tortuous and eventually becomes almost completely blocked. It is assumed that no ionic or atomic diffusion occurs within the lattice proper of the nitride. There is some support for this in that the temperature coefficient of the reaction rate is small or zero. It seems reasonable to suppose at these temperatures that the surface reaction between silicon and nitrogen is extremely rapid and that the over-all rate of reaction would be governed by the supply of nitrogen. The very low temperature coefficient would suggest that gaseous diffusion through microcracks in the nitride was the controlling step, rather than a diffusion process in the lattice itself.

The logarithmic growth clearly shows why complete nitriding of silicon powder would depend critically on the particle size, since once an initial film of nitride had formed rapidly, subsequent growth would be extremely slow. Collins and Gerby<sup>5</sup> state that in the production of commercial silicon nitride only particles less than 0.1 mm. in diameter can be nitrided completely in a reasonable time. A simple calculation from the present results confirms this value. A variety of catalysts have been described for this reaction, *e.g.*, iron. A simple explanation is that during nitriding the iron in the ferrosilicon is unaffected but becomes incorporated as an intimate mixture in the nitride film; differences in thermal expansion alone would give a less perfect film and hence facilitate nitrogen permeation.

#### Conclusions

At temperatures between about  $1200-1400^{\circ}$  silicon oxidizes in oxygen and CO<sub>2</sub> at one atmosphere according to a parabolic rate law.

In pure nitrogen, at similar temperatures, the nitridation is irregular and volatilization of, presumably, a silicon nitride occurs.

In nitrogen at a partial pressure of about 1.5 mm. the reaction follows a well-defined logarithmic rate law.

Acknowledgments.—Thanks are due to the Morgan Crucible Co. Ltd., London, for financial support of this work and for X-ray determinations. The authors are grateful to Dr. O. Kubaschewski for useful discussion.