

On the Rates of Oxidation of Silicon and of Silicon Carbide in Oxygen, and Correlation with Permeability of Silica Glass

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Published information regarding the rates of oxidation of silicon in dry oxygen in the temperature range 850° to 1200°C is reviewed. Likewise, investigations on the rate of oxidation of silicon carbide in oxygen in the temperature range 900° to 1600°C are discussed, and the data on this subject are reformulated to allow direct comparison with the data for silicon. On the assumption that the rates for both oxidation processes are governed by the rate of diffusion of oxygen through silica, theoretical rate constants are calculated from published experimental data for the permeation of oxygen through silica glass. The three sets of rate constants show very good agreement throughout the temperature ranges covered, and thus the underlying assumption is supported.

The dependence of the rates on the oxygen pressure is also discussed. Available data on this point are meager, however, and do not allow a definite conclusion concerning the pressure dependence.

A number of investigations concerning the thermal oxidation of silicon in oxygen have been published in recent years,¹⁻⁸ mainly in connection with the use of silicon in solid-state electronics. Likewise, several investigations have been carried out during the last decade concerning the oxidation of silicon carbide in oxygen,⁹⁻¹⁴ of particular interest to the ceramists.

In both cases, it has been found that the reaction is diffusion controlled. Since the protective oxide layer is silica on the metal as well as on the carbide, it would appear interesting to compare the experimentally observed reaction rates for silicon and for silicon carbide under corresponding conditions. Furthermore, it would appear of interest to attempt a correlation between rates of oxidation, and recent data for the permeation of oxygen through silica glass.^{15,16}

Several investigations have also been published concerning the thermal oxidation of silicon, respectively silicon carbide, in steam, and in steam-oxygen mixtures, but the present paper will be limited to a discussion of the reactions in dry oxygen.

FORMAL TREATMENT OF DIFFUSION—CONTROLLED REACTIONS

The discussion of the oxidation processes is based on the concept of diffusion-controlled reactions. A review on part of the theory of such processes appears necessary to permit a consistent treatment of the experimental data of the various authors. For simplicity the oxidation of a plane sheet ("infinite" in two dimensions) will be considered first. We assume that u moles of diffusing species react with one mole of silicon or silicon carbide, to give one mole of silica. The rate of increase of the silica film thickness s must be proportional to the diffusivity D of this rate-controlling diffusing species, proportional to the concentration gradient dc/ds of this species within the silica film, and furthermore proportional to the molar volume V_2 of silica and inversely proportional to the stoichiometry factor u . Thus we have

$$\frac{ds}{dt} = -\frac{V_2}{u} D \frac{dc}{ds} \quad (1)$$

Assume that the concentration of the diffusing species is c_1 in the silica at the silica-gas interface, and c_2 at the silica-metal (or carbide) interface. By partial integration we then have

$$s \frac{ds}{dt} = \frac{V_2}{u} \int_{c_1}^{c_2} D \, dc \quad (1a)$$

The integral of $D \, dc$ between fixed limits is a constant, hence we may write

$$s \frac{ds}{dt} = k \quad (1b)$$

and by a second integration

$$s^2 - s_0^2 = 2k(t - t_0) \quad (1c)$$

Usually (but not always) the condition $s_0 = 0$ for $t_0 = 0$ is satisfied, and eqn. (1c) reduces to the more familiar

$$s^2 = 2kt \text{ or } k = s^2/2t \quad (1d)$$

Eqns. (1c) or (1d) are directly applicable to most of the oxidation experiments on silicon, since these have been done on polished or single-crystal planes and to small film thickness only. The oxidation experiments on silicon carbide, on the other hand, have mostly been done on powdered or granular samples. The observed data are then usually expressed in terms of the "degree of reaction", *i.e.*, the fraction R of the initial material which has reacted after the time t (assuming $R = 0$ for $t = 0$). For small values of R a parabolic law similar to eqn. (1d) will be obeyed,

$$R^2 = 2k't$$

At higher degrees of reaction, a deviation from this simple parabolic law will occur as a result of the non-planar sample. In order to enable a quantitative treatment on this point, it is assumed that the particles are spherical and of

uniform size, with initial radius r_0 . Furthermore, the ratio between the molar volumes of the reaction product and the starting material, $z = V_2/V_1$, enters into the calculation. The general mathematical solution to this problem was first given by Fischbeck,¹⁷ and again by Carter¹⁸ in a more convenient form for the present purpose. Carter's equation, slightly rearranged, may be written

$$z - (z-1)(1-R)^{2/3} - \{1 + (z-1)R\}^{2/3} = \frac{z-1}{z} \cdot \frac{2kt}{r_0^2} \quad (2)$$

where k is now the same constant as defined by eqn. (1b).*

For small values of R , eqn. (2) represents a linear relationship between R^2 and t which may be found, *e.g.*, by expanding the 2/3-power terms of eqn. (2) in series, retaining first and second order terms. This gives

$$R^2 = \frac{18 kt}{z^2 r_0^2} \quad (3)$$

The densities of SiC(cryst) and SiO₂(glass) may be taken as 3.17 and 2.20, respectively; this gives $V_1 = 12.6 \text{ cm}^3$, $V_2 = 27.3 \text{ cm}^3$, and $z = 2.16$. A numerical evaluation with this value of z shows that the values of R calculated from the simple parabolic expression (3) deviates less than 1 relative percent from the values calculated by the exact eqn. (2), up to $R \leq 0.4$. The values of R encountered in the experimental data to be discussed below are less than 0.25 throughout, and hence the simple parabolic equation will be adequate for the discussion.

Eqns. (2) and (3) are based on the assumption of spherical particles of uniform size with radius r_0 , whereas real silicon carbide have irregular shapes. The particles are characterized by a "grain size" d_0 which usually corresponds to the linear dimension of the sieve opening through which the grains have passed. The irregular grains will have a larger surface-to-volume ratio than the spherical particles with diameter $d_0 = 2r_0$, and this in turn affects the silica film thickness or the rate constant k calculated for a given value of R . The effect may be taken into account by introducing an empirical "shape factor" which is the ratio between the surface area (per unit volume) of the grains, and the surface area of the corresponding spheres with diameter d_0 . Wiebke¹⁴ gives the values 1.5 to 2.2 for this shape factor for silicon carbide particles; the average value 1.8 is used in the following. This shape factor enters squared into the denominator in eqn. (3). Introducing also the numerical value for z , the equation is transformed to

$$k = 0.020 d_0^2 R^2/t \quad (3a)$$

This equation will be used to evaluate k from corresponding values of R and t for silicon carbide. For the oxidation of silicon, eqn. (1d) is used. Length is expressed in cm throughout, and time in hours.

* The relation between the constant appearing in the final expression in Carter's paper,¹⁸ and the present k , is $k = z \times k_{\text{Carter}}$.

In establishing eqn. (1) above it was tacitly assumed for simplicity that the rate-controlling diffusing species are electrically neutral. This is generally not true; on the contrary it is definitely established that the transport of matter through inorganic solids in most cases take place by the motion of ions, coupled with the motion of electrons to preserve electroneutrality. The classical treatment of Wagner¹⁹ leads to the following equation:

$$s \frac{ds}{dt} = \frac{V_2(t_c + t_a)t_e \kappa \Delta G_T}{n_e F^2} \quad (4)$$

where t_c , t_a and t_e are the transport numbers of cations, anions and electrons respectively; κ is the conductivity of the silica, ΔG_T is the free energy change of formation of silica from the elements at the temperature in question, $n_e = 4$ is the valency of silicon, and F is the electro-chemical equivalent. In the present discussion, however, the oxidation rates will be correlated only with the net transport of oxygen through the silica. For this purpose, the detailed mechanism of the transport process need not be considered, and eqn. (1) is adequate.

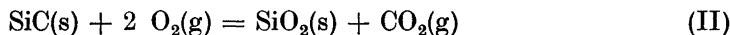
REVIEW AND CORRELATION OF EXPERIMENTAL OBSERVATIONS

The oxidation of silicon metal in dry oxygen proceeds according to the straightforward equation



Excepting the case of very thin films or low oxygen pressures,¹ all investigators of this process²⁻⁸ agree that the rate of the reaction is diffusion controlled. In analogy with other metal-oxide systems, Atalla *et al.*²⁰ suggested that the rate is governed by diffusion of silicon towards the oxide surface. In contrast to this, Ligenza and Spitzer⁴ by use of oxygen isotopes 16 and 18, showed that the rate of oxygen diffusion through the silica layer, and the rate of oxidation, were of similar magnitude. Jorgensen⁵ showed by means of marker experiments that the oxide growth occurs at the silicon-silica interface, and by application of an electric field across the silica film he was able to demonstrate that the rate determining diffusing oxygen species are oxygen ions.

The oxidation of silicon carbide in oxygen takes place according to the equation



Here again, all authors⁹⁻¹⁴ agree that the reaction is diffusion-controlled, but the nature of the rate-controlling species has not been established. There are in principle several possibilities; the rate may be controlled by diffusion of oxygen towards the oxide-carbide interface, or by diffusion of silicon, or carbon, or some carbon oxide, towards the oxide surface. If we accept as a hypothesis, however, that the rate is controlled by diffusion of oxygen also in this case, then a simple relationship between the experimentally observed rates for the two cases would be expected. More exactly, by comparing eqns. (I) and (II) it is seen that, at a given temperature and oxygen pressure, the rate of oxidation of silicon carbide would be expected to be one-half that of silicon.

Furthermore, if we venture the assumption that the silica formed on either silicon or silicon carbide is essentially equivalent to silica glass with respect

to its permeability to oxygen, then it should be possible to calculate by means of eqn. (1a) the rate constants for the oxidation processes from experimental data for this permeability.

Oxidation of silicon. Atalla³ and Ligenza and Spitzer⁴ give the following equation for oxidation of silicon

$$s^2 = 8.4 \times 10^{10} p^{4/5} \exp(-40\,000/RT)t \quad (5)$$

where s denotes film thickness in Å, p is oxygen pressure in atmospheres, and t is time in minutes. The basis of this equation is not quite clear. Atalla³ refers to Ligenza, while Ligenza and Spitzer⁴ refer to Atalla,³ and it appears that the original experimental data have never been published. Hence it is difficult to assess the reliability of this equation, which is stated⁴ to be valid in the temperature range 700 to 1100°C.

Some recent experimental data on the oxidation of silicon in oxygen are summarized in Table 1. The k value attributed to Jorgensen⁵ has been calculated from the slope of the

Table 1. Summary of published data on the rate of oxidation of silicon in 1 atm of dry oxygen. Last column gives k as defined by eqn. (1b).

Author(s)	Method	Basic equation	Temp. °C	Max. duration of runs, hours	Published rate constant		k cm ² h ⁻¹
					data	dimension	
Jorgensen ⁵	Film thickness by interference	$s^2 = 2kt$	850°C	110	s^2 vs. t	cm ² h ⁻¹ plot	1.25×10^{-11}
Deal ⁶	Weight increase	$w^2 = k't$	1000°C 1200°C	4 4	0.77×10^{-3} 3.51×10^{-3}	mg ² cm ⁻⁴ min ⁻¹ » » »	0.48×10^{-10} 2.18×10^{-10}
	Film thickness by groove-chord	$s^2 = k''t$	1000°C	4	1.48×10^{-4}	μ ² min ⁻¹	0.44×10^{-10}
Deal ⁷	Film thickness by interferometry	»	1200°C	4	6.95×10^{-4}	»	2.09×10^{-10}
Claussen and Flower ⁸	Film thickness by optical ellipsometry	$s^2 = k''t$	1200°C	3.5	7.6×10^4	Å ² min ⁻¹	2.28×10^{-10}

line for normal oxidation on Fig. 3 of his paper. The other values follow straightforward from the numerical values given by the authors, using the density 2.20 g/cm³ for silica to convert from weight to film thickness. The agreement between the weight and the thickness data of Deal^{6,7} is very satisfactory and lends confidence to his results, considering that the two sets of values are obtained by quite different methods. X-Ray and electron diffraction investigations of Jorgensen,⁵ density measurements of Deal,^{6,7} and the index of refraction observed by Claussen and Flower⁸ indicate that the product oxide was amorphous silica in all the experiments included in Table 1.

Evans and Chatterji² also studied the oxidation of silicon in dry oxygen, measuring the weight increase by means of a glass-spring balance. Their results for the oxidation rates are just about two powers of ten higher than those of the other authors. The conditions of their experiments appear to have been closely similar to those of the other investigators, but it should be noted that Evans and Chatterji² by X-ray analysis invariably

found significant amounts of cristobalite in their product oxide. Still it is puzzling that this difference should be accompanied by such a large difference in the measured rates. Alternatively, the discrepancy might be explained by assuming that there has been an error of one decimal place throughout the readings on their thermobalance (noting that the film thickness is squared in the expression for k).

Oxidation of silicon carbide. Some of the more recent information on the rate of oxidation of silicon carbide in oxygen is summarized in Table 2. The evaluation of the experimental data in this case involves some discussion of details which appear tedious, but unavoidable.

Table 2. Summary of published information on the rate of oxidation of silicon carbide in 1 atm of dry oxygen, re-evaluated to give $(2k)$ with k defined by eqn. (1b).

Author(s)	Method	Grain size designation	d_0 cm	Author's data used for present calculation	Temp. °C	Approx. duration of runs hours	$2k$ cm ² h ⁻¹	
Adamsky ¹²	Gas transport with CO ₂ absorption	200 μ average	0.023	Exptl. points from Fig. 1, (weight CO ₂ versus time) replotted	1200	3.3	6.71×10^{-11}	
					1300	3.3	2.92×10^{-10}	
					1400	3.0	5.10×10^{-10}	
Jorgensen, Wadsworth and Cutler ¹³	Thermogravimetry, quartz-spring balance	-325 +400 mesh	0.0044	Average slope of curves on Fig. 3	903	120	1.96×10^{-11}	
					$\alpha = 1^\circ 35'$	1135	120	1.38×10^{-10}
					$\alpha = 11^\circ 00'$	1215	120	2.31×10^{-10}
					$\alpha = 18^\circ 00'$	1502	60	8.66×10^{-10}
					$\alpha = 50^\circ 40'$	1555	50	1.04×10^{-9}
$\alpha = 55^\circ 40'$	1600	30	1.40×10^{-9}					
Wiebke ¹⁴	Gas transport with CO ₂ absorption	63 μm	0.0063	For $t=8h$ $R = 1.6\%$ » » » $R = 3.77\%$ » » » $R = 5.97\%$	1100	(20)	5.08×10^{-11}	
					1300	(20)	2.82×10^{-10}	
					1500	(10)	7.08×10^{-10}	

Adamsky ¹² has presented a plot of evolved amount of CO₂ (per gram SiC) as a function of time, for one run at each of the temperatures 1200, 1300, 1400, and 1500°C (his Fig. 1). The experimental values were taken from this plot and replotted as R^2 against t on a larger scale. None of the straight lines thus obtained go through the origin. For the three lower temperatures, the results correspond to a slight time lag before CO₂ begins to accumulate (presumably caused by the experimental arrangement rather than the reaction). The results have been corrected for this by means of eqn. (1c), with $s_0 = 0$ for $t_0 =$ the observed time lag. Adamsky gives the average particle size of his silicon carbide as 200 μ. For the other data of Table 2, the *maximum* particle size (sieve opening) has been adopted. In order to achieve comparable values for k , an estimated 15% has been added to the size stated by Adamsky, adopting 0.023 cm for his d_0 in the present eqn. (3a). The run at 1500°C indicates a very high rate of reaction at the start of the run, gradually diminishing to a normal value. Treatment of the data for this run according to eqn. (1c), with $s_0 > 0$ for $t_0 = 0$, shows that the rate did not yet obey the parabolic law at the end of the run. In line with this, a rate constant evaluated from the two last experimental points at 1500°C falls about 60 relative percent above the other data of Table 2 and has been omitted.

Jorgensen, Wadsworth and Cutler, ¹³ using a thermobalance, determined the degree of reaction by measuring the weight increase of the sample. In an attempt to take into account the effect of the non-planar (powdered) sample, they derived the equation

$$[1 - (1 - R)^{1/2}]^2 = 2k_f t / r_0^2 \quad (6)$$

(where k_J has been used here to denote the constant of this equation). The inexactness of this equation has been discussed by Carter¹⁸ who presented the solution given as eqn. (2) above. It has been necessary to refer to eqn. (6) here because the experimental results of Jorgensen *et al.*¹³ are presented in the form of a plot of the left-hand side of eqn. (6) against time. Now, it was also indicated above that up to $R \leq 0.4$, a simple parabolic equation is adequate, while the maximum value encountered in the work of Jorgensen *et al.* is $R \simeq 0.25$. Hence their results are most simply re-evaluated by deriving the simple parabolic law corresponding to eqn. (6). This limiting law is found to be

$$R^2 = 18 k_J t/r_0^2 \quad (6a)$$

Comparison with eqn. (3) gives

$$k = z^2 k_J$$

The quantity k_J may be evaluated directly from the graph of the left-hand side of eqn. (6) against time, Fig. 3 of Jorgensen *et al.*¹³ Introducing also the particle size $d_0 = 0.0044$ cm and the shape factor 1.8, the desired rate constants are found directly from the slopes of the straight lines on that graph:

$$2k = 7.10 \times 10^{-10} \text{ tg } \alpha$$

In determining the angle α , it is noted that Jorgensen *et al.* observed an increase in the rates after some hours' oxidation. The data for the three lowest and the three highest temperatures have been evaluated by passing the best straight line through the experimental points for each temperature, ignoring the slight breaks in the curves as originally drawn. The angles α of these "best" lines and the resulting values of $2k$, are given in Table 2. For the runs at 1275, 1300, and 1327°C, the breaks in the original curves are so marked that it was found impossible to fit any straight lines, hence these runs have been omitted from Table 2.

Wiebke¹⁴ investigated the rate of oxidation of silicon carbide by weighing the sample before and after the run, by analysis of the amount of silica in the sample after the run, and by absorbing the CO_2 in the effluent gas. The latter method is assumed here to give the most accurate results, and the average of the reported values of R obtained by this method for green silicon carbide in 8 hours' oxidation have been used to calculate $2k$ by means of eqn. (3a) above.

Nakatogawa⁹ investigated the rates of oxidation of green and of black silicon carbide by measuring weight changes. His plots of s^2 versus t give good straight lines; but his results indicate a temperature dependence of the rate which is very much in excess of that of other investigators, and hence Nakatogawa's data have been omitted in Table 2. Erwin¹¹ also investigated the oxidation of silicon carbide, but his experimental data are not sufficient for the calculation of reliable rate constants.

Concerning the increase in rate after a certain initial period, as observed by Jorgensen *et al.*¹³, it should be mentioned that a similar behaviour was also observed by Nakatogawa⁹ and by Erwin¹¹ in the temperature range 1100 to 1300°C; hence the effect is probably not merely incidental. Jorgensen *et al.*¹³ ascribe the effect to the transition of the oxide from vitreous silica to cristobalite, with evidence from X-ray diffraction. Adamsky¹² found no evidence of crystallinity in his oxides by X-ray diffraction, but then his runs were of much shorter duration. Wiebke¹⁴ gives no information as to the structure of the product oxide.

Permeation of oxygen through silica glass. Norton^{15,16} has investigated the rate of permeation of oxygen gas through a thin-walled silica glass bulb, keeping a constant pressure of oxygen on the outside of the bulb while the inside was connected to a mass spectrometer. In Norton's first paper¹⁵ it is stated that a plot of the experimental values of $\log P$ versus $1/T$ yielded a good straight line, and a set of smoothed numerical values are presented. In his second paper,¹⁶ a few more experimental points have been added which indicate that the good straight line was partly fortuitous, whereas it appears that the absolute value of the permeability at 1100°C is fairly well established.

The permeability P corresponds to the integral in eqn. (1a) (with $c_1 = \text{solubility}$ and $c_2 = 0$), hence the rate constant for oxidation of silicon should be given by the relation

$$k = V_2 P \quad (7)$$

if the correlation between oxygen permeability and oxidation rate holds.

The units for P used by Norton are cm^3 gas (S.T.P.) per sec for 1 mm thickness per cm^2 area per cm mercury difference of gas pressure. (It is noted that, in choosing the dimensions for the permeability, it has already been presupposed that the rate of permeation is directly proportional to the gas pressure. This need not concern us for the present since the experimental data were obtained for gas pressures of the order of magnitude one atm.) Some more comments on the pressure dependence are given in a subsequent section.) In order to conform to eqn. (7), the permeability data have to be converted to $\text{mole} \cdot \text{h}^{-1} \cdot \text{atm}^{-1} \cdot \text{cm}^{-1}$. The numerical relation is $P = 1.221 \times P_{\text{Norton}}$. Introducing also the numerical value of V_2 we should have the relation

$$k_{\text{Si}} = 2 k_{\text{SiC}} = 27.3 P = 33.3 P_{\text{Norton}} \quad (7a)$$

Instead of going by way of the numerical values, it has been preferred here to perform the comparison graphically.

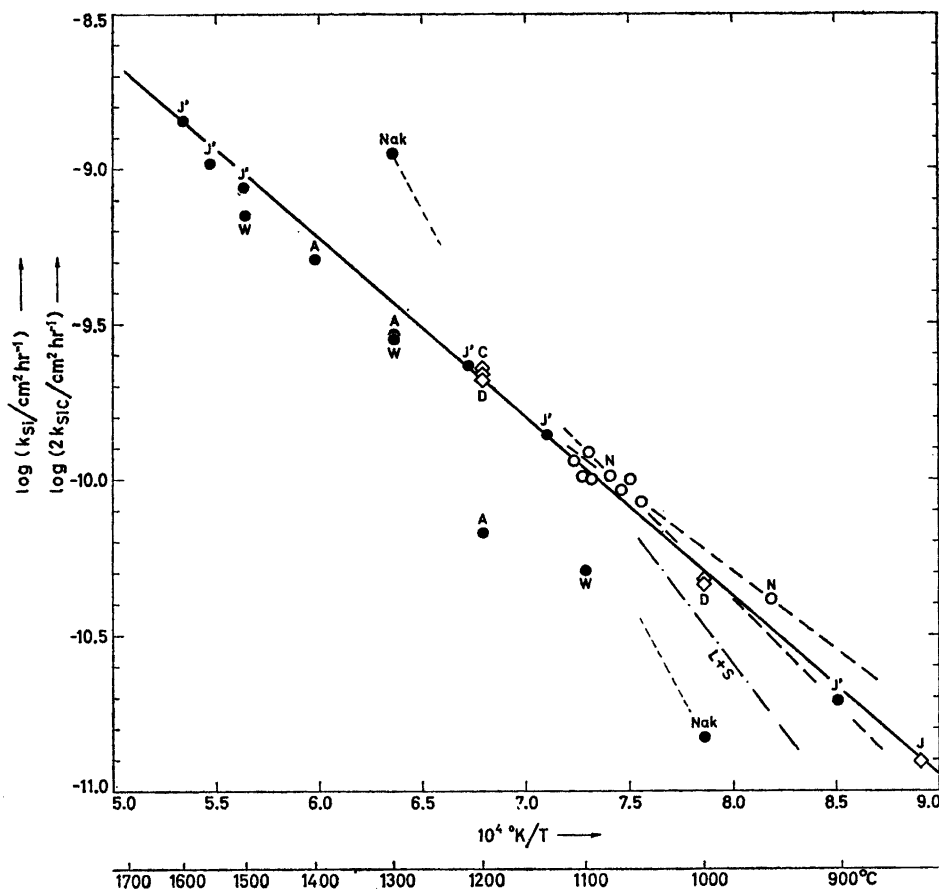


Fig. 1. Logarithm of the rate constants plotted versus reciprocal temperature. Diamonds: k for oxidation of silicon. Filled circles: $2k$ for oxidation of silicon carbide. Open circles: k calculated from data for oxygen permeability of silica glass. Letters directly above or below points indicate source of data: J: Jorgensen,⁵ D: Deal,^{6,7} (2 exptl. points at each letter). C: Claussen and Flower,⁸ A: Adamsky,¹² J': Jorgensen, Wadsworth and Cutler,¹³ W: Wiebke,¹⁴ Nak: Nakatogawa⁹ (the points for his highest and lowest temperature only). L + S: Ligenza and Spitzer⁴ and Atalla³ (line evaluated from (5)). N: Norton,¹⁶

DISCUSSION

The rate constants of Tables 1 and 2 are plotted in Fig. 1 as $\log k_{\text{Si}}$ and $\log (2 k_{\text{SiC}})$ versus $10^4/T$. The points from the permeability data have been taken directly from Fig. 4 of Norton's second paper, shifting the points by an amount of $\log 33.3 = 1.523$ along the ordinate, *cf.* eqn. (7a). The two dashed lines through the points represent the smoothed values given by Norton in his first and second paper, respectively. The highest and lowest points from Nakatogawa⁹ have been included to indicate his observed slope. The absolute values of the rate constants from Nakatogawa's results may be lower than indicated by these points, since there is some doubt as to his estimation of the surface area of his carbide.

Excepting the few discordant results, Fig. 1 demonstrates an almost striking agreement between the rate constants for silicon, the doubled rate constants for silicon carbide, and the theoretical rate constants from the permeability data.

Some deviation is noted for the lowest point from Adamsky¹² and from Wiebke¹⁴ for silicon carbide, while the points for higher temperatures from these authors fall well in line with the rest. For illustration it may be noted that, *e.g.*, the points from Wiebke¹⁴ for silicon carbide at 1300 and 1500°C would have fallen exactly on the straight line of Fig. 1 if the value of the shape factor for this case had been chosen as 1.6 instead of 1.8. It should be emphasized that, apart from the slight arbitrariness introduced by the choice of shape factor for the carbide, no arbitrary assumption or parameter has been introduced in the present treatment. If the mechanisms for oxidation of silicon, for oxidation of silicon carbide, and for permeation of oxygen through silica, were not essentially the same, there would be no reason to expect that the rate constants for the three cases would even be of the same order of magnitude. In fact, at the outset of this investigation, the writer did not expect to find much of a correlation, but Fig. 1 strongly supports the view that the three processes are interrelated in the way proposed in the first part of this paper.

Pressure dependence. While Fig. 1 gives a representation of the temperature dependence of the rates at one atmosphere pressure of oxygen, it will be of interest to consider also the dependence on the oxygen pressure. Norton^{15,16} found that his measurements indicate direct proportionality between permeation and oxygen pressure. From this, he concludes that the diffusing species are molecules, not ions, a conclusion which is in contradiction to the observations of Jorgensen⁵ on the oxidation of silicon, if the mechanism for the two cases is the same. Norton states¹⁶ that permeation of oxygen as ions would lead to a square-root dependence on pressure, but the present writer is not convinced that this must necessarily be true. We may schematically write the reaction to form oxygen ions



from which an equilibrium constant K may be formulated

$$c_{\text{O}^{2-}(\text{excess})} = K \sqrt{p_{\text{O}_2}} \cdot c_{\text{e}}^2 \quad (\text{8})$$

A square-root dependence follows only if the concentration of electrons is put equal to a constant but this probably represents an oversimplification.

It should be remembered that a net transport by means of diffusion of ions requires a concentration gradient for the oxygen ions in the silica, *i.e.*, an anion excess at the out-

side of the silica layer and/or a deficit at the inside. A theoretical evaluation of the pressure dependence would have to be based on some concept regarding the type of defect structure, including the deficit or excess electrons. In this context, the treatment of Wagner¹⁹ for the oxidation of metals (*cf.* eqn. (4) above) might possibly be applied also to the corresponding cases of permeation of gases through ionic solids. For the present, however, only an empirical approach will be attempted, to see whether the scanty experimental data that exist can give any information.

Experimental evidence in the case of silicon is almost missing. Ligenza *et al.*^{3,4} give a dependence of the $4/5$ power of the oxygen pressure (*cf.* eqn. (5)) but as previously noted, the experimental evidence for this is unknown.

The dependence of the rate of oxidation of silicon carbide on the oxygen pressure has been studied quite extensively by Jorgensen *et al.*²¹ Here again, some discussion of details in their presentation is necessary. Their results in this case are presented in terms of rate constants k_J evaluated from an equation similar to eqn. (6) above. The values of this k_J are plotted as functions of oxygen concentration in moles per liter (their Fig. 1) and as functions of the logarithm of this oxygen concentration (their Fig. 2). Straight lines are fitted through the points on the latter figure, and this is taken by the authors as evidence that the rate constants follow an equation of the form $k_J' = A \log c_{O_2} + B$, where A and B are functions of temperature. As an alternative approach, their data will be reconsidered in terms of an equation of the form $k = C \times p^m$ (analogous to eqn. (5)).

Supposedly the same experimental data are presented on their Figs. 1 and 2,²¹ but a check indicates that substantial discrepancies exist between the points on the two graphs, particularly for the lower temperatures. Not knowing which of the sets of data (sets of points) is the more reliable, both have been included in the reconsideration. It is furthermore noted that the text to both figures states that the rate constants are given in reciprocal seconds, whereas a comparison with their earlier paper¹³ shows that the unit must be reciprocal hours throughout. On this basis the k_J values taken from both figures have been converted to $2k$ of the present notation, and the oxygen concentrations have been converted to oxygen pressures. The resulting data are given on a log-log scale in Fig. 2, where the values for 1 atm taken from the straight line in Fig. 1 are also included. It is seen that the rather scattered points are in reasonable agreement with a square-root dependence, represented by the straight lines which have tentatively been fitted through the points. The agreement is particularly good for the line at the highest temperature, where the internal consistency of the three sources of data is also quite good.

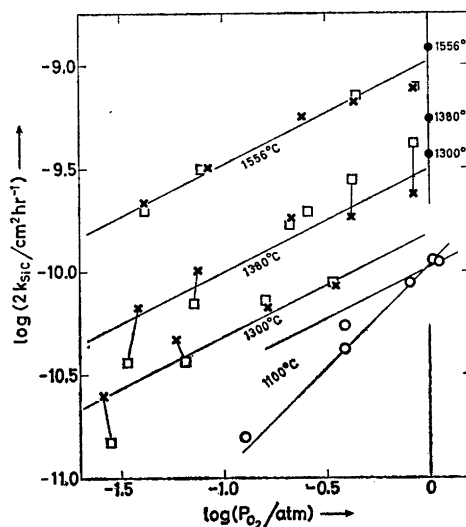


Fig. 2. $\log(2k_{\text{sic}})$ versus $\log p_{O_2}$, from data of Jorgensen *et al.*²¹ Squares: From experimental points on their Fig. 1. Crosses: Same from their Fig. 2. Points for the same temperature and approximately the same pressure have been joined by thin lines. Filled circles: Taken from solid line of present Fig. 1. Open circles: From oxygen permeability data of Norton,¹⁴ experimental points on his Fig. 5 converted by means of eqn. (7a).

Included in Fig. 2 are also the points for the pressure dependence of oxygen permeation through silica glass, taken from Fig. 5 of Norton's second paper¹⁶ and converted by eqn. (7a). It is seen that, although the points show some scatter, they indicate a pressure relationship closer to the first power than to the square root. More data are needed, however, for the pressure dependence of the permeability as well as of the oxidation rates, before this point can be settled.

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