[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Oxidation of Silicon at High Temperatures

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The oxidation of silicon was studied over the temperature range 950 to 1160°. The metal was found to oxidize very slowly even at high temperatures. From 1015 to 1020° the reaction proceeded according to the equation: amount of oxygen consumed $= k \log_{10} (1 + 0.4t)$, where t is time and k is a constant. An explanation of the logarithmic nature of the reaction is attempted in view of the vitreous nature of the oxide formed.

Recently, investigations have been made on the high temperature oxidation of the metals of group four of the periodic table. Work on titanium,[1,2] zirconium[3,4] and thorium[5] has already been reported. The present study of silicon was done to permit comparisons within the group.

Since the molal volumes of all the forms of silica are greater than that of silicon metal, the oxide should cover the metal and reduce the oxidation rate as the oxidation proceeds.[6] Thus the oxidation would be expected to follow the parabolic law ($w^2 = kt$) or the logarithmic law ($w = k \log (1 + at)$, where w is the amount of oxidation in time t, and k and a are constants).

McAdam and Geil[7] have already studied the rate of oxidation of silicon by an interferometric method of measuring the oxide thickness. They found the oxidation curve to be parabolic from 500 to 950°. The present study was made at higher temperatures by a different method and with somewhat different results.

Experimental

Method.—The apparatus was similar to that used in this Laboratory in studying the oxidation of zirconium.[4] The rate of oxidation was determined by measuring the decrease in the pressure of oxygen in a closed system. The change in pressure was observed with a differential manometer containing Amoil-S, a low density, low vapor-pressure oil. The manometer readings were converted to amount of oxygen consumed by the sample by determining the change on the manometer caused by a measured volume of oxygen.

From 950 to 1040° the reaction was carried out in silica-enclosed porcelain tubes. Porcelain tubes were used as reaction bulbs above 1040° to prevent gas from leaking through the silica. The high temperatures were obtained with an electric muffle furnace, controlled by means of a Wheelco Capacitrol to within ±5°. Vacua of the order of 10^{-4} mm. were obtained with a mercury diffusion pump backed by a mechanical pump. The system was considered to be leak-tight if there was less than 1 mm. change in the manometer 15 minutes after it was shut off from the pump. After the furnace had come to temperature, the sample was introduced by means of a magnet that pushed the sample into the reaction vessel.

During a typical run the system was evacuated and the furnace was heated to the desired temperature. The sample was dropped into the reaction tube and heated for 5 minutes under vacuum. A known pressure of oxygen was then admitted, the bulbs were shut off from the pumps, and the change in pressure was observed as a function of time for 100 minutes.

X-Ray diffraction pictures were taken of some of the oxidized samples. The samples were oscillated through an angle of 20° in a beam of CuK$_\alpha$ radiation and the diffraction patterns were obtained on a powder camera.

Materials.—Silicon lumps prepared by the carbon reduction of silica were obtained from the A. S. LaPine Company. A typical analysis on the metal gave: silicon 98%, iron 0.7, aluminum 0.5, calcium 0.3, other metals 0.5. A rectangular parallelepiped sample was prepared by embedding a rough piece of metal in plastic and cutting out the sample on a glassblower's silicon carbide wheel. The sample was then polished with 4/0 emery paper. The same sample was used for all runs reported; however, the oxidation of a second sample at 1080° checked within 25%. Commercial 99.5% oxygen was used.

Results

The oxidation was studied from 950 to 1160° at 20 cm. oxygen pressure. At 950° the data were found to fit a parabolic law and a logarithmic law equally well. Figure 1 shows the results of experiments from 950 to 1160° on a parabolic plot. The curves at 950° and 1160° may be called parabolic; the others are not.

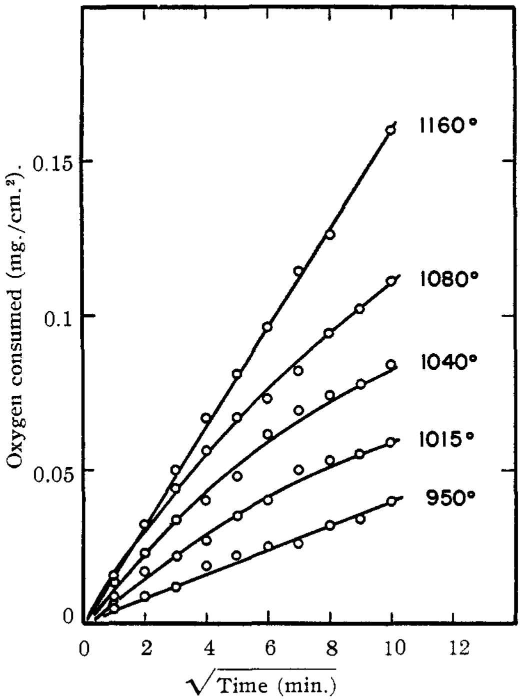

Fig. 1.—Parabolic plot of the silicon oxidation data.

Above 950° the shapes of the curves suggested that the oxidations followed a logarithmic equation. Thus, the data above 950° were fitted to an equation of the form $w = k \log_{10} (1 + at)$. In this equation a is a temperature independent constant that serves to render the quantity at dimensionless. The magnitude of a was determined by finding that value which gave the best fit to the experimental

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(1) W. A. Alexander and L. M. Pidgeon, *Can. J. Research*, **28B**, 60 (1950).

(2) E. A. Gulbransen and K. F. Andrew, *AIME, J. of Metals*, **185**. 741 (1949).

(3) E. A. Gulbransen and K. F. Andrew, *ibid.*, **185**, 515 (1949).

(4) D. Cubicciotti, THIS JOURNAL, **72**, 4138 (1501).

(5) P. Levesque and D. Cubicciotti, *ibid.*, **73**, 2028 (1951).

(6) N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 529 (1923).

(7) D. J. McAdam and G. W. Geil. *J. Research Natl. Bur. Standards*, **28**. 593 (1942).

data at all temperatures. A value of $a = 0.4$ was chosen; however, the equation is rather insensitive to the value of a.

In Fig. 2 the data at several temperatures are shown on a logarithmic plot. The curves below 1160° follow the logarithmic law. At 1160° the curve does not fit the logarithmic law well; however, to compare the results with those of other temperatures the data were expressed by a logarithmic law. At 950° the data fit the parabolic and logarithmic laws equally well.

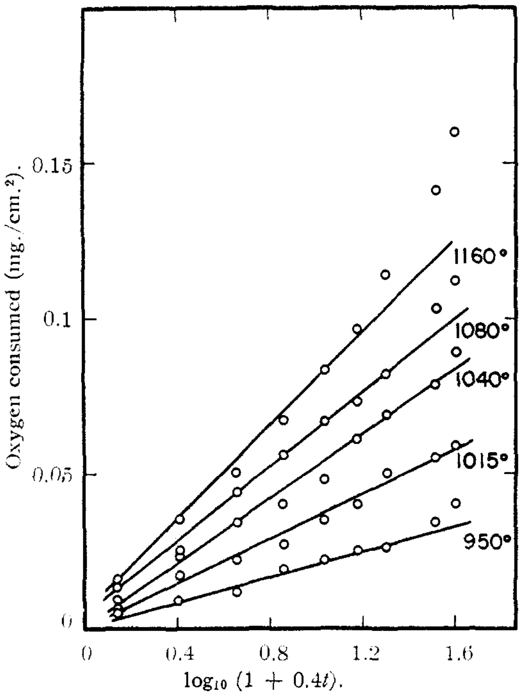

Fig. 2.—Logarithmic plot of the silicon oxidation data.

Figure 3 gives the results of all the oxidations plotted as the logarithm of the rate constants, k, of the logarithmic oxidations as a function of the absolute temperature. The straight line drawn in the figure gives an activation energy of 26 kcal. per mole.

The oxidized samples had a blue-gray, glassy-looking coating. X-Ray patterns of the oxidized specimens showed intense spots at the angles expected for silicon metal[8] and occasional lines that could be attributed to one of the crystalline forms of silicon dioxide. However, no pattern had more than two such lines. Since the oxide layers were about 5,000 Å. thick, as estimated from the amount of oxidation, there was sufficient oxide present to give an X-ray pattern. One oxidized sample, after being heated overnight at 1200°, gave X-ray pattern lines that fitted the patterns of α-cristobalite[8] and quartz.[8] These X-ray results indicate that the oxides formed during the 100-minute oxidations were glasses.

Discussion

It is possible to compare the results at 950° with the work of McAdam and Geil.[7] Those authors report a parabolic oxidation with a film thickness of 2,000 Å. after 100 minutes while from the present work it is estimated that *ca.* 1,800 Å. of oxide formed in 100 minutes.

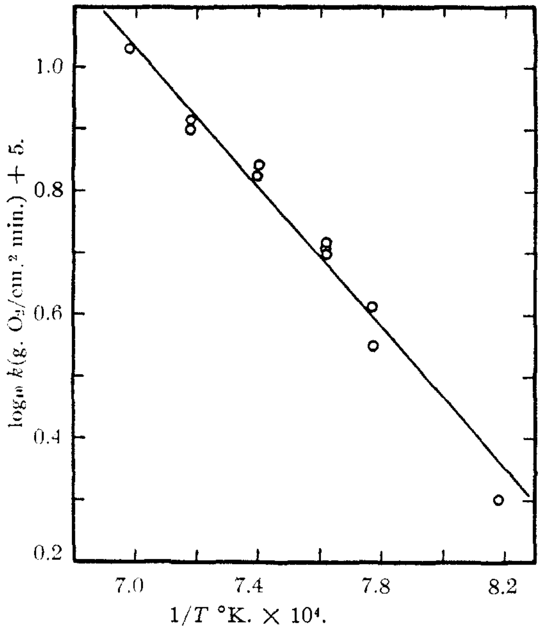

Fig. 3.—The variation of the logarithm of the logarithmic rate constant with the reciprocal of temperature.

A comparison of the rate of oxidation of silicon with that of other metals may be made at 950°. Silicon is a very slow oxidizing metal. At 950° in 100 minutes one square centimeter of metal consumes 0.04 mg. of oxygen, while beryllium may be estimated[9] to consume 0.1 mg. of oxygen and 1.6 mg. by the rather slow oxidizing metal nickel.[6]

A quantitative comparison of the oxidation rates of silicon with other metals of group four is not easily made because of the large difference in temperature at which the several oxidations are measurable. It is apparent, however, that silicon oxidizes much more slowly than any of the other metals of that group. The amount of oxygen consumed per cm.² of silicon at 950° is about the same as that consumed by titanium[2] at 500°. It has already been shown[5] that zirconium and thorium oxidize more rapidly than titanium. Thus in the series silicon, titanium, zirconium, thorium, the oxidation rate increases with increasing atomic weight of the metal.

The logarithmic form of the oxidation may be due to the vitreous nature of the oxide formed during the oxidation. Following the method of Tammann and Koster[10] one may relate the logarithmic oxidation with a vitreous oxide product. If the diffusion of some species through the growing oxide layer is rate determing, Fick's law states

$$\frac{dw}{dt} = D\frac{\partial c}{\partial x}$$

If the oxide coating is a glass rather than a crystalline solid, the diffusion paths through the oxide will be blocked in a statistical manner. Instead of the

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[8] Am. Soc. Testing Mat., "Original Set of X-Ray Diffraction Patterns," 1942, Card 1905 for silicon, 1010 for α-cristobalite, and 1612 for quartz.

[9] D. Cubicciotti, THIS JOURNAL, **72**, 2084 (1950).

[10] G. Tammann and W. Koster, *Z. anorg. Chem.*, **123** 196 (1922).

linear concentration gradient, which leads to the parabolic law, the concentration of diffusion species would decrease exponentially along the diffusion paths, or

$$c = c_0 e^{-\alpha x}$$

where c is the concentration of the diffusion species at a distance x from its starting point. Thus, the concentration gradient would be

$$\partial c/\partial x = -c_0 k e^{-\alpha x}$$

Since the total thickness of oxide, x, is related to the amount of substance that has diffused, w, by a gravimetric factor $w = gx$, then

$$\mathrm{d}w/\mathrm{d}t = -Dc_0\alpha e^{-w\alpha/g}$$

Integrating

$$w = k \log(1 + at)$$

which is the logarithmic law for oxidation.

Acknowledgment.—The authors are grateful to the office of Naval Research for sponsoring this work.

CHICAGO 16, ILL. RECEIVED NOVEMBER 20, 1950

NOTES

Quaternary Salts of Halogenated Pyridines and Quinolines[1]

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Since certain quaternary salts of pyridine and quinoline have been reported to damage sarcoma cells *in vivo*[2] we have prepared similar salts of several halogenated pyridines and quinolines for screening against sarcoma in mice[3] and for correlation of biological effects and other properties with structure.

The quaternary salts listed in Tables I and II were prepared by reaction of a halogenated heterocyclic base with the appropriate organic halide at 30–40°. When the reactants alone did not form a homogeneous solution a small amount of chloroform was added to bring them into solution. The products usually precipitated as they were formed and the mixture was allowed to stand as long as seemed necessary to obtain a good yield. The rates of reaction varied greatly. For 6-chloroquinoline the reaction periods were: with glycerol-

TABLE I

HALOPYRIDINE DERIVATIVES

Salt from	Empirical formula	M.p., °C.[a]	Analyses, % Ionic Halogen Calcd.	Found[b]
2-Chloropyridine and				
β-Phenylethyl bromide	$C_{13}H_{13}BrClN$	193	26.76	26.50
Styrene bromohydrin	$C_{13}H_{13}BrClNO$	182	25.40	25.30
Phenacyl bromide	$C_{13}H_{11}BrClNO$	187	25.57	25.30
p-*t*-Butylphenacyl bromide	$C_{17}H_{19}BrClNO$	192	21.68	21.40
p-Fluorophenacyl bromide	$C_{13}H_{10}BrClFNO$	185–187	24.17	24.03
p-Chlorophenacyl bromide	$C_{13}H_{10}BrCl_2NO$	188–189	23.03	23.01
p-Bromophenacyl bromide	$C_{13}H_{10}Br_2ClNO$	194	20.41	20.42
p-Iodophenacyl bromide	$C_{13}H_{10}BrClINO$	193	18.23	18.00
m-Nitrophenacyl bromide	$C_{13}H_{10}BrClN_2O_3$	172	22.35	22.42
2-Bromopyridine and				
p-Fluorophenacyl bromide	$C_{13}H_{10}Br_2FNO$	174–175	21.30	21.08
p-Chlorophenacyl bromide	$C_{13}H_{10}Br_2ClNO$	201	20.41	20.44
p-Iodophenacyl bromide	$C_{13}H_{10}Br_2INO$	189	16.55	16.40
p-Phenylphenacyl bromide	$C_{19}H_{15}Br_2NO$	160–161	18.45	18.54
5,6,7,8-Tetrahydro-β-naphthacyl bromide	$C_{17}H_{17}Br_2NO$	207	19.44	19.54
3-Fluoropyridine and				
p-Fluorophenacyl bromide	$C_{13}H_{10}BrF_2NO$	189	25.36	25.29
3-Chloropyridine and				
p-Fluorophenacyl bromide	$C_{13}H_{10}BrClNO$	169–170	24.17	24.33

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(1) This investigation was supported in part by a research grant from the National Cancer Institute, of the National Institutes of Health, Public Health Service.

(2) Shear, *et al.*, in "Approaches to Cancer Chemotherapy," American Association for the Advancement of Science, F. R. Moulton, Editor, Washington, D. C., 1947, p. 236 ff.; *cf.* J. L. Hartwell and S. R. L. Kornberg, THIS JOURNAL, **68**, 1131 (1946).

(3) Results of screening tests at the National Cancer Institute are to be reported elsewhere.