sorbancy of solutions of the beryllium-sulfosalicylate complex ion with dilution by means of this equation and the appropriate constants, and the accounting for observed absorbancies of solutions in which the mole ratios of sulfosalicylate to beryllium were greatly different than 2 to 1, were considered adequate reasons for the adoption of this equation.

The displacement of the phenolic hydrogens during complexation at this *p*H is, as indicated by Eq. 2, expected because of the increased acidity brought about by coördination of the phenolic oxygen atoms.

It is believed that considerable uncertainty is involved in the calculation of the lower ionic strengths used in the extrapolation to obtain $K$ since in the very low ionic strength region the complex ions contribute the main portion of the ionic strength.

The fact that an increase in $K$ is apparent for only a 5° increase in temperature indicates that by studying an appreciably larger temperature range $d \ln K/dT$ may be evaluated and an estimation of $\Delta H^0$ be made.

AMES, IOWA RECEIVED FEBRUARY 22, 1951

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

# The Kinetics of the Reaction of Germanium and Oxygen

BY RICHARD B. BERNSTEIN AND DANIEL CUBICCIOTTI

The rate of oxidation of germanium has been measured in the range 575 to 705°. The kinetics do not conform to any of the previously observed rate laws for metal oxidations but rather follow an equation of the form $Q = Q_\infty(1 - e^{-kt})$, where $Q$ is the quantity of oxygen consumed by the metal in time $t$; $Q_\infty$ and $k$ are constants. $Q_\infty$ varies approximately inversely to the oxygen pressure in the range 2 to 40 cm. and the rate constant, $k$, is temperature dependent. A mechanism is proposed in which the oxidation rate is controlled by the rate of evaporation of germanium monoxide. This rate of evaporation is in turn governed by the extent to which the surface is covered by impervious germanium dioxide.

Of the two oxides reported for germanium the monoxide is considerably more volatile than the dioxide.[1] This order of volatility may be contrasted with that of the majority of other metals which have volatile oxides, such as tungsten and molybdenum, where the higher oxide is the more volatile. The kinetics of the germanium oxidation have been found to be unusual because of this volatility.

## Experimental

The apparatus was similar to that used previously[2] for metal oxidations. The system was operated at essentially constant pressure and was capable of detecting changes of the order of a few micrograms of oxygen.

In a typical experiment, the sample was placed in the silica reaction tube, which was then evacuated to about one micron. A furnace, preheated and controlled to the appropriate temperature, was placed around the silica tube. After the sample was heated for 10 to 15 minutes *in vacuo*, oxygen was admitted to the desired pressure. The decrease of pressure in the reaction bulb, as observed with an oil manometer, gave a measure of the oxygen consumption. The change in pressure during a run was at most 2% of the total pressure. At the conclusion of each run the sensitivity of the system was determined by adding a measured amount of oxygen.

The germanium, obtained from the A. D. Mackay Company, was fused *in vacuo* and then polished with emery paper, finishing with number 4/0. The resulting rectangular parallelepiped was used for several runs; between runs it was repolished and weighed. The sample was generally found to have lost weight at the end of a run.

After oxidation the sample was coated with a thin blue film; the samples that were most extensively oxidized had a light-colored powdery film in addition. There was a deposit of white powder on the walls of the silica bulb near the sample and often a thin deposit of brown material at the cold end of the tube. When this brown film was heated in air, it seemed to evaporate and oxidize to a cloud of white powder which was unaffected by further heating.

X-Ray diffraction patterns were obtained from the edges of blocks of metal and oxidized specimens. The patterns of the germanium showed spots corresponding to all the interplanar spacings of germanium.[3] The patterns of oxidized samples also showed lines corresponding to germanium dioxide.[3] No extra lines were found in any of the patterns.

The brown substance was assumed[4] to be the germanium monoxide reported by Dennis and Hulse.[1] It was obviously more volatile than the white germanium dioxide since it was found in the cold part of the silica tube while the dioxide was found deposited in the hot zone of the tube. Apparently, the germanium monoxide evaporated from the metal surface during the oxidation. Most of it was then oxidized in the tube to the dioxide which deposited on the hot walls, while some of the monoxide diffused to the cold walls and deposited there as the brown material.

The fact that the weight losses of the samples were not due to evaporation of germanium itself was determined by evaporation experiments carried out with unoxidized samples in a $10^{-6}$ mm. vacuum at 800°. In a period of four hours the weight loss was less than 0.1 mg. per sq. cm.

## Results

The reaction was studied from 575 to 705° at oxygen pressures from 2 to 40 cm. The data are shown in Figs. 1 to 4. In these figures the points show the experimentally observed data. These oxidation curves do not follow any of the usual theoretical oxidation equations, *i.e.*, the linear, parabolic or logarithmic laws.[5] Furthermore, the amount of oxidation is a function of the oxygen pressure, in contrast to the pressure independence of the usual metal oxidation.

It is possible to express the oxidation curves accurately by the equation

$$Q = Q_\infty(1 - e^{-kt})$$

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[1] L. Dennis and R. Hulse, THIS JOURNAL, **52**, 3553 (1930).

[2] D. Cubicciotti, *ibid.*, **72**, 2084, 4138 (1950).

[3] Am. Soc. Testing Met., "X-Ray Diffraction Patterns," 1942, Second Supplementary Set, 1950.

[4] A sample of this brown material, obtained as a sublimate on heating the metal in 0.1 mm. of oxygen, was found to have the composition $GeO_{1.04}$. The analysis was made by measuring the uptake of oxygen at 1 atm. and 1000°. A sample of germanium subjected to this method of analysis, as a check, took up 96% of the amount of oxygen calculated for the dioxide. Therefore, the brown material had the composition of GeO.

[5] For a discussion of the types of oxidation laws see: E. A. Gulbransen, *Trans. Electrochem. Soc.*, **91**, 573 (1947).

in which $Q$ is the amount of oxygen consumed in time $t$, $k$ a constant that depends on temperature, and $Q_\infty$ a pressure dependent constant that represents the total amount of oxygen consumed after long times. In Figs. 1, 2 and 3 the solid curves are calculated from equations of this type. Since the numerical results are not considered of fundamental significance they are not tabulated here.

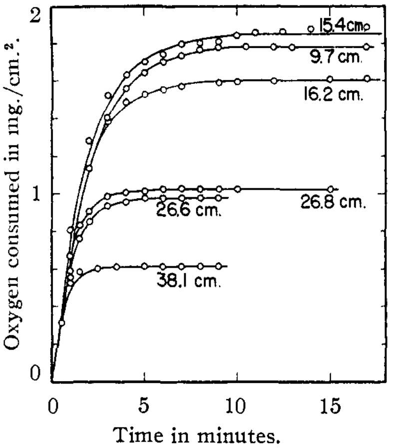

Fig. 1.—Germanium oxidation curves at 703°: the points are experimental data. The curves are calculated from the exponential equation. Numbers on the curves are the oxygen pressures.

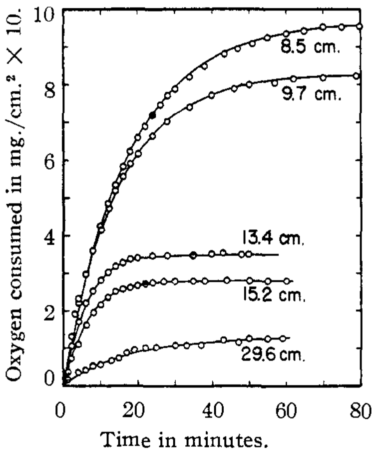

Fig. 2.—Germanium oxidation curves at 650°: the points are experimental data. The curves are calculated from the exponential equation. Numbers on the curves are the oxygen pressures.

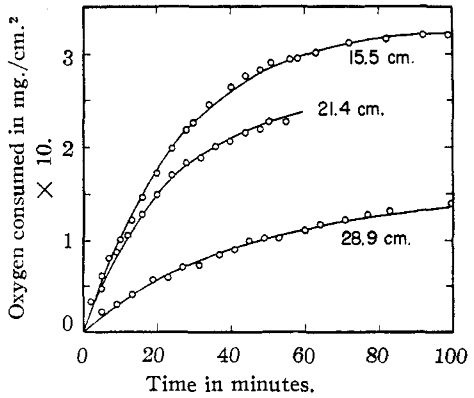

Fig. 3.—Germanium oxidation curves at 615°: the points are the experimental data. The curves are calculated from the exponential equation. Numbers on the curves are oxygen pressures.

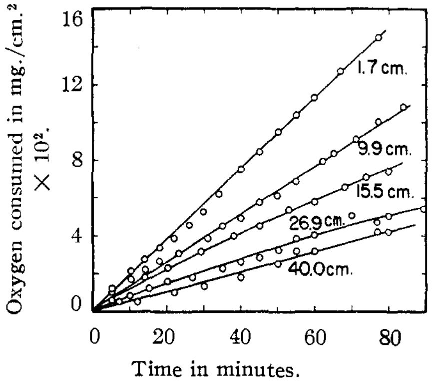

Fig. 4.—Germanium oxidation curves at 577°: the numbers on each curve are the oxygen pressures.

From the figures it may be seen that $Q_\infty$ shows a noticeable trend with pressure. Very roughly $Q_\infty$ depends inversely upon the oxygen pressure. The weight losses showed a similar decrease with increasing pressure; they were largest at the high temperatures, becoming as high as 1 mg. per sq. cm.

The parameter $k$ appeared to be dependent on temperature but independent of pressure. The values at each temperature scattered over a wide range, presumably because of the difficulty in reproducing the surface of the sample from run to run. However, as a test of the reproducibility, measurements were made at 650° and 15 cm. using an entirely different apparatus with a different size reaction vessel. The values of $k$ and $Q_\infty$ agreed within 40%. There appeared to be no significant trend of $k$ with pressure. The temperature variation of $k$ was large enough to show above the scatter at each temperature. Thus, the average values of $k$ at 615 and 703° were 0.034 and 0.87 min.$^{-1}$, respectively, representing a 25-fold change over this temperature range.

## Discussion

The mechanism of the germanium oxidation must be radically different from the diffusion mechanism responsible for the usual parabolic or logarithmic oxidation. The most significant differences from the normal oxidations are the loss in weight of the sample, the pressure effect and the form of the oxidation curve itself.

A mechanism that accounts for the experimentally observed facts is as follows. The metal is assumed to be initially covered by a layer of the monoxide. The majority of the oxygen consumption is attributed to the oxidation of germanium monoxide that has evaporated from the surface of the sample. The rate of evaporation of the monoxide is decreased during the reaction by the formation of an impervious film of germanium dioxide, which eventually stops the evaporation. The pressure dependence of $Q_\infty$ arises from the pressure dependence of the rate of evaporation of the germanium monoxide.[6] Increasing the oxygen pressure decreases the rate of evaporation thus reducing the total amount of monoxide evaporated before the process is halted by the layer of dioxide.

The reactions to be considered are

$$GeO(s) + {}^1/_2O_2 \longrightarrow GeO_2(s) \text{ slow, surface reaction} \quad (1)$$

$$GeO(s) \longrightarrow GeO(g) \text{ slow, evaporation competing with eq. (1)} \quad (2)$$

$$GeO(g) + {}^1/_2O_2 \longrightarrow GeO_2(s) \text{ rapid, in hot zone} \quad (3)$$

Let $[GeO]_s$ and $[GeO_2]_s$ be the surface concentrations in moles per cm.$^2$ of each species and $Q$ the number of moles of oxygen consumed per cm.$^2$ of sample. We assume that the rate of the surface reaction (1) is first order in $[GeO]_s$. Thus, $R_1 = d[GeO_2]_s/dt = k_1[GeO]_s$. The rate of evaporation is $R_2 = k_2f(p)[GeO]_s$, in which $f(p)$ is an approximately inverse pressure dependent factor. If it is assumed that the amount of oxygen needed to cover the sample with dioxide is negligible, the rate of consumption of oxygen is $dQ/dt = R_3 = k_2 f(p) \cdot [GeO]_s = b[GeO]_s$. Since the surface is covered only by GeO and $GeO_2$, then $d[GeO_2]_s = -d[GeO]_s$ and $[GeO]_s = [GeO]^0_s e^{-k_1t}$. Thus $dQ/dt = b[GeO]^0_s e^{-k_1t}$. When $t = 0$, $Q = 0$; so, $Q = b[GeO]^0_s (1 - e^{-k_1t})/k_1$ or, $Q = Q_\infty (1 - e^{-kt})$.

Thus the mechanism proposed accounts for the experimentally observed facts. The exact form of the oxidation curve is derived. The weight loss of the specimens is accounted for on the basis of evaporation of the monoxide. The pressure dependence of $Q_\infty$ originates in the pressure dependence of the evaporation rate. The temperature dependence of the parameter $k$ arises because $k$ is the rate constant for the conversion of the monoxide to the dioxide on the surface of the sample and would be expected to have a large temperature dependence.

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[6] Studies by Fonda (G. R. Fonda, see S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 78) on the evaporation of tungsten showed a pronounced dependence of the rate on the pressure of the argon or nitrogen added. The net rate of evaporation decreased with increasing external pressure in an approximately inverse manner.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

# Low Temperature Thermodynamic Properties of Sodium Hydroxide[1]

BY JOHN C. R. KELLY[2] AND PAUL E. SNYDER

The heat capacity of pure crystalline sodium hydroxide has been determined from 60 to 300°K. by use of a low-temperature adiabatic calorimeter. The sodium hydroxide used in this work was purified by mono-alcoholate formation. From the experimental data, smoothed values of the several thermodynamic functions were calculated at several temperatures. These calculations yield the value of 15.34 ± 0.1 entropy units for the entropy of this compound at 298.16°K.

## Experimental

**Purification of Sodium Hydroxide.**—Although no satisfactory method has been reported for the preparation of pure, anhydrous sodium hydroxide, the most promising approach is the reported solubility of the compound in absolute ethyl alcohol,[3] and the reported formation of a solid alcoholate which is easily decomposed at reduced pressures and slightly elevated temperatures.[4]

The starting material was Baker and Adamson special reagent grade sodium hydroxide containing approximately 1.1% $H_2O$ and 1.2% $Na_2CO_3$. One hundred gram quantities were dissolved in one liter portions of ethanol which had been dried and purified by the method of Kaufman and Dreger.[5] This solution was transferred to a dry, $CO_2$-free box wherein all further operations were performed. The solution was filtered under vacuum through a "fine" fritted glass disc in order to remove insoluble carbonates and halides. The resulting solution was pumped under mild heating conditions until a thick slurry of the mono-alcoholate was produced. This slurry was transferred to a "coarse" grade fritted glass disc and pumped free of the mother liquor. The alcoholate, appearing as white hexagonal crystals, was washed several times with purified alcohol to remove any last traces of water. The crystals were then transferred to a filtering flask and pumped under mild heating for approximately 30 hours in order to decompose the alcoholate.

Analysis of the product by the usual methods showed that the maximum limits of $Na_2CO_3$, $SiO_2$ and $Cl^-$ were 0.02, 0.02 and 0.005%, respectively. The minimum assay of NaOH was 99.84%. The low silica content indicated negligible pick-up from the glass vessels used in this preparation. The final product, as placed in the calorimeter, appeared as a fine, white, crystalline powder.

**Apparatus.**—The calorimeter used in this work is of the adiabatic type and was constructed along the lines described by Southard and Brickwedde.[6]

The thermometer used with the calorimeter was constructed in the usual manner.[7] A helix of 0.004 inch diameter platinum–10% rhodium wire was wound on a mica cross. The whole unit was then sealed in a platinum sheath. The thermometer was soldered in a well in the calorimeter with Woods metal. The thermometer also served as a heater during the heating periods. The potential drop across the thermometer as well as the current flowing was measured by means of a White double potentiometer with a range of 0–100,000 microvolts. To facilitate the work, the potentiometer was used as a null instrument by means of an effective fifth decade of the Lindeck–Rothe[8] type. As a matter of fact, the sensitivity of the combined system was such that a potential could be rechecked to a few-tenths of a microvolt.

Standardization of the entire system was made in terms of a one and a ten ohm standard resistance each of which had been calibrated at the National Bureau of Standards. The standard cell used with the potentiometer likewise was calibrated at the National Bureau of Standards.

**Temperature Scale.**—Since the platinum–10% rhodium resistance thermometer served as the fundamental tempera-

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[1] From a thesis submitted by John C. R. Kelly to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science in Chemistry. This work was performed under contract N6 ori-47, T.O. 8 between the Office of Naval Research and Carnegie Institute of Technology.

[2] Westinghouse Electric Corporation, Bloomfield, N. J.

[3] Gmelin, "Handbuch Anorg. Chem.", Vol. 21, J. Springer, Berlin, 1928, p. 121.

[4] Lescoeur, *Compt. rend.*, **121**, 889 (1895).

[5] Kaufman and Dreger, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 259.

[6] Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).

[7] Meyers, *Natl. Bur. Standards J. Res.*, **9**, 807 (1932).

[8] Brooks and Spinks, *ibid.*, **9**, 781 (1932).