The Oxidation of Beryllium at High Temperatures[1]

BY DANIEL CUBICCIOTTI

It has been shown that the reaction of a gas with a metal at high temperatures may proceed according to one of several laws[2]

(I) the parabolic law $\quad w^2 = kt + C$
(II) the linear law $\qquad w = kt + C$
(III) the logarithmic law $\; w = \log (kt + C)$

where w is the amount of reaction in time t, and k and C are constants.

The parabolic law has been derived on the assumption that diffusion through the growing coating on the metal surface is the rate determining step of the reaction.[3,4,5] The species whose rate of diffusion determines the reaction rate may be ions of either sign or, in some cases, electrons.

In the search for metals that form protective coatings and oxidize slowly at high temperatures, beryllium is a logical subject for investigation since metals near it in the periodic table, i. e., aluminum and magnesium, have small rates of oxidation. Little work has been done on the oxidation of this metal. Terem[6] has studied the oxidation of the powdered metal. He observed no oxidation of the powder in air below 500°, and at 1000° he reports the oxidation of a powder sample to be 75% complete in fifteen minutes. The reaction of a powdered sample of metal may well be expected to proceed at a greater rate than that of a sheet sample because of the many sharp points of metal in the powder.

Experimental

Method.—The rate of oxidation of the metal was determined by measuring the decrease in pressure of oxygen in a closed bulb containing a sample of the metal. The apparatus used was similar to that used by Campbell and Thomas[7a] but modified for use at the high temperatures of the present work. Two silica glass bulbs of about 25 cc. capacity were connected by water-cooled, cemented rubber connectors to a pyrex manometer and a high vacuum system. The silica bulbs were situated in an electric muffle furnace whose temperature was maintained constant to $\pm 5°$ with a Wheelco Capacitrol. The temperature of the cell was measured with a chromel–alumel thermocouple independent of the regulating thermocouple. The manometer fluid was Amoil-S, a low vapor pressure liquid.

In a typical run, a sample of beryllium of about 1 cm.[2] area was placed in one bulb, the other left empty, and the whole system evacuated to about 10^{-5} mm. pressure. When the pressure in the system, cut off from the vacuum system, changed by less than 1 mm. per hour, the system was considered leak tight. Then the furnace was brought to temperature, oxygen let into both bulbs, and readings

taken on the manometer as the oxidation progressed. When the pressure difference between the bulbs reached about 0.07 cm., additional oxygen was bled into the bulb containing the sample so that the pressure of oxygen over the beryllium sample was constant (to ± 0.07 cm.) during the reaction. At the end of the run the pressure change in the system caused by a known volume of oxygen was measured. In that way the manometer readings could be converted into amount of oxygen consumed.

It was found that at the elevated temperatures silica reacted with beryllium touching it. Therefore, the metal sample was suspended with a platinum wire out of contact with the silica container.

The rate of evaporation of shiny beryllium at these temperatures was sufficient to allow appreciable quantities of the metal to distill while the furnace was brought to temperature. The distilled metal condensed out on cooler portions of the container and, in effect, increased the surface of metal later exposed to oxygen. It was found that the rate of evaporation and the amount of metal distilled could be reduced to a negligible value if the metal sample were coated with a thin film of oxide. Thus a coating was formed on each sample by heating it momentarily at about 600° in a bunsen flame.

The oxide film formed in this manner would have only little effect on the oxidation curves. The thickness of the film, estimated by extrapolating the data of Fig. 2 to 600°, would be about 10^{-7} g. of oxygen per sq. cm. for 0.1 min. and 2×10^{-7} g. for 0.4 min. of heating in the flame.[7b] Films of such thickness would be put on the metal in 10^{-3} to 4×10^{-3} min. at 840° and shorter times at higher temperatures. Thus the presence of the pre-formed oxide film corresponds, in effect, to errors of less than 10^{-2} min. in the time of starting of the oxidations.

X-Ray diffraction pictures of some of the metal samples were taken after oxidation. The sheet metal sample was rotated in the center of a powder camera. The CuKα radiation used penetrated the metal, and good diffraction patterns of both the metal and the oxide were obtained simultaneously.

Materials.—The oxygen used was the commercial 99.5% material. No additional purification of the gas was made since the impurities react with the metal much less rapidly than the oxygen.

Beryllium metal sheet of about 0.3 mm. thickness was supplied by the Atomic Energy Commission. Typical analysis of the materials gave

Be	97.2%
BeO	3.0%
Other metals (total)	0.7%

The material as received was covered with a heavy coating of oxide, which was removed by abrasion with emery paper. Each sample of metal was abraded with successively finer grades of emery paper ending with 4/0 and then flamed as mentioned above.

Results

The rate of oxidation of the metal was measured from 840 to 970° at 10 cm. pressure of oxygen and at 885° from 10 cm. to 72 cm. pressure. The oxidation curves were all found to obey the para-

(1) This research was conducted under the sponsorship of the Office of Naval Research.

(2) Gulbransen, *Trans. Electrochem. Soc.*, **91**, 573 (1947).

(3) Pilling and Bedworth, *J. Inst. Met.*, **29**, 529 (1923).

(4) Wagner and Grunewald, *Z. physik. Chem.*, **40B**, 455 (1938).

(5) Mott, *Trans. Farad. Soc.*, **36**, 472 (1940).

(6) Terem, *Bull. soc. chim.*, **6**, 664 (1939); *Rev. faculté sci. univ. Istanbul*, **8A**, no. 19, 22 (1943).

(7a) Campbell and Thomas, *Trans. Electrochem. Soc.*, **91**, 345 (1947).

(7b) A check was made that the oxidation at 600° did not proceed more rapidly than expected by extrapolating the data of Fig. 2. A sample of beryllium was abraded and heated in air at 600° for five hours. Its weight increase was $0 \pm 10 \times 10^{-6}$ g. per sq. cm. From an extrapolation of the data of Fig. 2 one calculates a weight increase of 5×10^{-6} g. Thus the extrapolation for this purpose seems justified.

bolic law (equation I) over at least the first 100 minutes. To show that the oxidation curves obeyed the parabolic law, graphs were made of the weight increase of the specimen (calculated from the manometer readings) *versus* the square root of time. For a parabolic oxidation such a graph is a straight line whose slope is the square root of the parabolic rate constant. The oxidation curves observed at several temperatures are presented in Fig. 1. The curves illustrate the type of data obtained and the agreement with the parabolic law.

The data obtained are summarized in Table I. The first column gives the average temperature of the oxidation, the second gives the average pressure, and the third, the parabolic rate constant k of equation I.

The last five runs of Table I demonstrate the effect of pressure on the rate constant. The pressure was varied over a sevenfold range; however, the rate constant was essentially the same for all but one of the runs. The rate constant of the run at 30 cm. pressure is about 20% larger than the others. This variation may be considered to be within the experimental error. The difference in surface roughness from one sample to the next may be sufficient in itself to account for a 20% deviation. Therefore, the rate constant may be said to be independent of the pressure.

The first four runs of Table I illustrate the magnitude of the temperature effect. These runs were not made at exactly the same pressure, but since the pressure effect is negligible, the difference in pressure may be overlooked. The 130° temperature range studied shows a fifteen-fold change in rate constant.

TABLE I

THE PARABOLIC RATE CONSTANTS FOR THE OXIDATION OF BERYLLIUM

Temp., °C. ± 5°	Oxygen pressure, m. ± 0.07 cm.	Parabolic rate constant, k, g.^{2}/cm.^{4} min. × 10^{11a}
970	8.1	18
900	9.8	4.1
860	10.6	1.0
840	12.7	0.85
885	10.1	1.6
885	16.0	1.6
885	30.0	2.0
885	40.0	1.6
885	72.0	1.6

^{a} g. is grams of oxygen consumed.

The oxide coatings on the metal samples, when cooled to room temperature, were pearl gray in color and after long oxidations were granular in appearance. The X-ray diffraction patterns taken of several of the oxidized samples showed only those lines corresponding to beryllium metal and beryllium oxide given on cards 3632 and 3336 of the American Society of Testing Materials Set.[8]

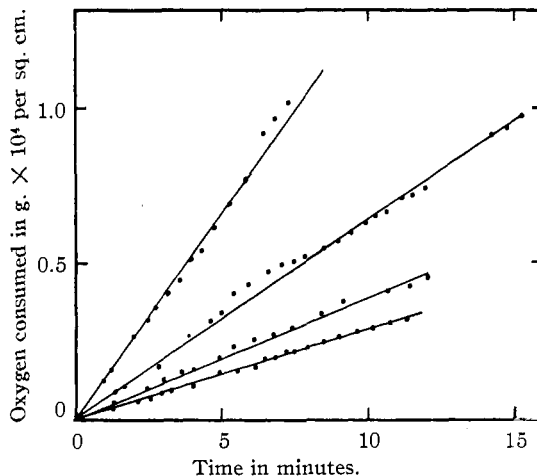(8) Am. Soc. Testing Mat., "Original Set of X-Ray Diffraction Patterns," 1942.

Fig. 1.—The oxidation of beryllium at 10 cm. oxygen pressure at 970, 900, 885 and 840°.

Thus, the normal beryllium oxide was formed on the metal.

Discussion

The most interesting aspect of the oxidation of beryllium is its very small rate compared to that found in the oxidation of other metals. Aluminum is reported to be highly resistant to oxidation at high temperatures[9]; however, its oxidation rate is much greater than that observed for beryllium in the present work. Gulbransen[2] has found the oxidation of aluminum from 350–450° to be parabolic with a rate constant of 10^{-12} g.^{2}/cm.^{4} min. at 450°. Extrapolating the present data, one finds that the rate constant of the beryllium oxidation reaches the value of 10^{-12} at about 750°. The beryllium rate is thus much smaller than the aluminum rate.

The oxidation rate of beryllium is also smaller than that of 50% Cr–50% Ni, a standard slow oxidizing alloy. At 900° the weight increase in one hour due to the oxidation of that alloy is about twice that found for beryllium.[10]

Price and Thomas[11] have suggested that because of its low electronic conductivity beryllium oxide should be effective as a coating to protect metals from oxidation. Beryllium in copper metal does reduce its oxidation rate markedly. The addition of 2.4% beryllium reduces the oxidation rate constant of copper[12] at 800° from 4.9 × 10^7 g.^{2} per cm.^{4} min. to 3.5 × 10^{-10}. The rate constant for pure beryllium is 2.6 × 10^{-12}, extrapolating the present data to 800°.

From the present data it is possible to calculate the energy of activation for the process of oxidation of beryllium. In Fig. 2 the logarithms of the observed rate constants are plotted against the reciprocal of absolute temperature. The observed

(9) Mears in "The Corrosion Handbook," edited by Uhlig. John Wiley and Sons, New York, N. Y., 1948, p. 617.
(10) Data from "The Corrosion Handbook," p. 696.
(11) Price and Thomas, *J. Inst. Metals*, **63**, 21, 28 (1938).
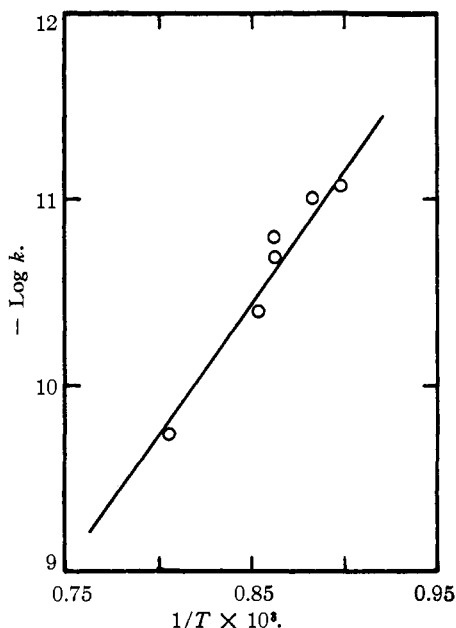(12) Data from "The Corrosion Handbook," p. 625.

Fig. 2.—The dependence of the logarithm of the rate constant on reciprocal of absolute temperature.

points fall very close to a straight line, as seen from the figure. The largest deviation from the straight line drawn corresponds to a 20% deviation in the rate constant. Such a deviation may be considered within experimental error as mentioned above. Because the oxidation curves were all parabolic and the log K vs. $1/T$ plot is linear, it is reasonable to state that the same mechanism for oxidation holds over the temperature range studied. The activation energy for this oxidation process determined from the slope of the line of Fig. 2 is 62 kcal. per mole.

Since the oxidation curves are parabolic, the rate determining step in the oxidation process is the diffusion of some species through the growing oxide film.[3,4,5] Thus the activation energy observed should correspond to the activation energy of diffusion through the oxide. Barrer[13] has tabulated the activation energies of diffusion of some ions through salts. Those values are all less than 50 kcal. per mole. Gulbransen[2] has given the activation energies observed in the oxidation of several metals obeying the parabolic law at high temperatures. The largest activation energy of his data is 45.7 kcal. per mole. It appears that the activation energy observed in the present study is exceptionally large for the type of reaction considered.

The species that can diffuse through the beryllium oxide scale are $O^=$, Be^{++}, and e^-. In view of its relatively large size, it is not likely that the $O^=$ ion diffuses sufficiently rapidly to account for any large fraction of the reaction rate. Of the other species, it is not possible at present to decide which has the smaller rate and is thus rate determining in the reaction. The further study of the mechanism of the reaction should prove interesting in view of the high activation energy and small rate.

Summary

The rate of the reaction between beryllium metal and oxygen gas has been studied from 840 to 970°. The oxidation was found to proceed according to the parabolic law with much smaller rate constants than for other similar reactions. The energy of activation for the reaction was found to be 62 kcal. per mole.

(13) Barrer, "Diffusion in and Through Solids," Cambridge University Press, Cambridge, England, 1941, p. 274.

Azeotropy in the System Phosphoric Oxide–Water

BY GRADY TARBUTTON AND M. E. DEMING

Although Tilden and Barnett[1] reported vapor density measurements which they interpreted to indicate that metaphosphoric acid (88.75% P_4O_{10}) exists in the vapor state as the dimeric molecule $H_2P_2O_6$, Balareff[2] has reported data that indicate that the meta acid dissociates on vaporizing. He found that the residue from the distillation of metaphosphoric acid in a gold vessel contained 89 to 93.4% phosphoric oxide. It should be noted that the materials investigated by Tilden and Barnett[1] contained about 90% phosphoric oxide, which is significantly greater than the phosphoric oxide content of metaphos-

phoric acid. Balareff[2] concluded that the rate of loss of water by metaphosphoric acid and the eventual composition of the acid apparently depend on the temperature and duration of heating and on the partial pressure of water vapor in the system.

Zagvozdkin, Rabinovich and Barilko[3] measured the "dehydration" pressure of orthophosphoric acid (72.4% P_4O_{10}) at temperatures between 150 and 300°, and determined the amounts of ortho-, pyro- and metaphosphoric acids in the residues. They reported that the residue obtained at 300° contained a total of 88.68% phosphoric oxide, composed of 96.10% meta- and 4.62% ortho-

(1) W. A. Tilden and R. E. Barnett, Trans. Chem. Soc. (London), 69, 154–160 (1896).

(2) D. Balareff, Z. anorg. Chem., 102, 34–40 (1917).

(3) K. I. Zagvozdkin, Yu. M. Rabinovich and N. A. Barilko, J. Applied Chem. (U. S. S. R.), 13, 29–36 (1940).