netic entropies of these ions cannot be made with confidence on the basis of the evidence now available.

Accordingly, we shall ignore such corrections and take the entropy of Am^{+3}(aq.) to be the same as that of Pu^{+3}(aq.), except for a correction of −0.8 e.u. because of the smaller ionic radius of the tripositive ion of americium.[11] Whence

$$S[Am^{+3}(aq.)] = -30 - 0.8 = -30.8 \text{ e.u.}$$

The entropy of metallic americium probably is substantially different from that of plutonium since the two metals differ greatly in density,[4] and melting point.[4] The melting point of americium metal is closer to that of lanthanum or cerium than to plutonium. We also regard it as significant that the density of americium metal is about equal to that of the lighter rare earths (La or Ce, for example), multiplied by the ratio of the atomic weight of americium to that of the rare earths. The metallic radii and bonding in these metals are probably quite similar.

We estimate the entropy of Am(s) from the entropy of Ce(s), given by Latimer,[15] using his formula for the mass correction

$$S(\text{Am}) = S(\text{Ce}) + 3/2\ R \ln (241/140) = 13.8 + 1.6 = 15.4 \text{ e.u.}$$

There are no data on which to base a correction for magnetic entropy. We take:

$$S[Am^{+3}(aq.)] + S[3/2H_2(g)] - S[Am(s)] = -30.8 + 46.8 - 15.4 = 0.6 \text{ e.u.},$$

whence ΔF_{298} for reaction (5) is equal to

$$-163.2 \pm 2.7 - 0.6 \times \frac{298}{1000} = -163.4 \pm 2.7 \text{ kcal. and } E$$

for the substances at unit concentration, = (163.4 ± 2.7)/23.07 × 3 = 2.36 ± 0.04 v. Even if the estimated entropies are in error by several entropy units, the result will be affected by only a few hundredths of a volt.

The E (formal) value for the corresponding plutonium reaction is given by Brewer, *et al.*,[11] as 2.06 v.

Americium metal is thus substantially more electropositive than plutonium and is about as electropositive as the lighter rare earths, if we take the electrode potentials quoted by Yost, Russell and Garner[16] to be correct.

It seems to us that in many respects americium may be regarded as the first of the transuranium elements which is rare-earth-like in the metallic state. It is also the first in which the stability of the tripositive state is comparable to that of the rare earths.

Acknowledgment.—We wish to express our thanks to Mrs. Winifred Heppler and Mr. Herman Robinson, who provided technical assistance in making our calorimetric measurements, and to members of the Health Chemistry Group of the Radiation Laboratory for their efforts in providing adequate safeguards against the hazards of handling high levels of radioactivity. We also wish to thank Mr. John Conway and Mr. Milton Moore, who carried out all spectrographic analyses reported in this paper. The work described here was carried out under the auspices of the Atomic Energy Commission.

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(15) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938.

(16) D. M. Yost, H. Russell, Jr., and C. S. Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, 1947.

BERKELEY, CALIFORNIA RECEIVED OCTOBER 10, 1950

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

The Reaction between Oxygen and Thorium

BY PASCAL LEVESQUE AND DANIEL CUBICCIOTTI

A study of the oxidation of thorium has been made in order to make comparisons with the oxidations of other metals of group IVB of the Periodic table.

The reaction was studied in the range 250 to 700°. Above 450°, the temperature of the sample was found to rise considerably above the temperature of the furnace; below 450°, the oxidations were found to be essentially isothermal. From 350 to 450°, the oxidation curves were linear in time. The rate constants for the linear oxidation were measured and the energy of activation calculated to be 22 kcal. per mole. From 250 to 350°, the oxidation proceeded according to the parabolic law and the energy of activation for the reaction was calculated to have a value of 31 kcal. per mole.

The oxidation of a metal at high temperatures will follow a linear law if the oxide formed scales off.[1] If the ratio of molal volume of oxide to metal is greater than unity and the oxide is strongly adherent, the metal oxidizes according to the parabolic law.[2] The rate-determining step of the parabolic reaction is assumed to be diffusion through the growing coating of oxide on the metal surface.[3,4] Titanium[5] and zirconium[6] have been found to follow the parabolic law over a wide range of temperatures.

The present study was made to compare the behavior of thorium with other metals of group IVb. The reaction was found to follow the parabolic and the linear laws in different temperature ranges.

Experimental

Method. Above 350°.—The apparatus used was a modification of the one used in this Laboratory for studies of zirconium.[6] The oxidation was followed by observing the drop in pressure of oxygen gas in a closed system containing a sample of metal. Two silica glass bulbs were connected to a manometer containing amyl sebacate, a low vapor pressure oil, and through suitable stopcocks to a vacuum line and oxygen supply. The bulbs were heated in an electric muffle furnace whose temperature was maintained con-

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(1) U. R. Evans, *Trans. Electrochem. Soc.*, **91**, 547 (1947).

(2) N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 579 (1923).

(3) N. F. Mott, *Trans. Faraday Soc.*, **36**, 472 (1940).

(4) C. Wagner and K. Grünewald, *Z. physik. Chem.*, **40B**, 455 (1938).

(5) E. A. Gulbransen and K. F. Andrew, *A. I. M. E., J. of Metals*, **185**, 741 (1949).

(6) D. Cubicciotti, THIS JOURNAL, **72**, 4138 (1950); E. A. Gulbransen and K. F. Andrew, *A. I. M. E., J. of Metals*, **185**, 515 (1949).

stant to ±5° with a Leeds and Northrup Micromax. The temperature of the cell containing the sample was measured with a thermocouple located next to the silica bulb.

In a typical run a sample of thorium of about 2 cm.^{2} area was placed in one bulb, the other left empty, and the whole system evacuated to a few microns pressure. The furnace was brought to temperature, oxygen let into both bulbs, and readings taken on the manometer as the oxidation progressed. Except in a few runs the oxygen pressure was 45 cm. At the end of the run the change in the manometer caused by a known amount of oxygen, was measured. In that way the manometer readings could be converted into amounts of oxygen consumed.

Below 350°.—The technique was essentially the same as for the experiments above 350° except that Pyrex test-tubes were substituted for the silica bulbs. The sensitivity of the system was increased by using a differential capillary manometer and by increasing the area of the metal samples. The areas varied from 15 to 40 sq. cm. The largest were used at the lowest temperatures.

Materials.—The oxygen used was commercial 99.5% material and no additional purification of the gas was made. Cold rolled thorium sheet was obtained from the Westinghouse Electric Company. The thorium had been prepared by calcium reduction of thorium dioxide. When received the material was covered with a thin coating of oxide which was removed by abrasion with 2/0 emery paper. A typical analysis of the metal give:

Thorium, %	98
Thorium oxide, %	1.0 to 1.5
Calcium, %	0.04
Iron, %	0.03

Results

From 450° to 700°.—The oxidation curves in this temperature range were characterized by a sudden rise, which at the higher temperatures gave the curve a parabolic shape and at the lower temperatures an S-shape. The results obtained at several temperatures are shown in Fig. 1.

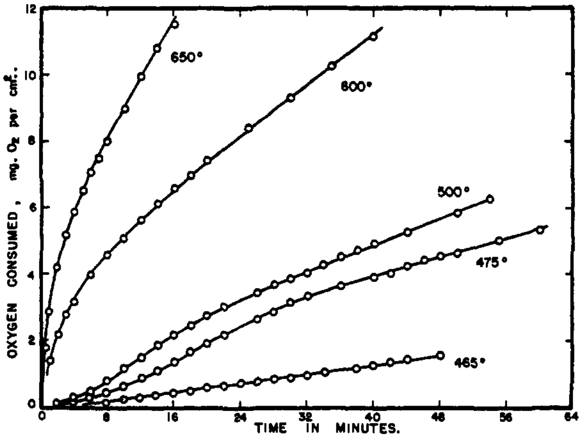

Fig. 1.—Oxidation curves (non-isothermal) for thorium at several initial temperatures.

From 600 to 700° the curves were parabolic; however, the parabolic rate constants for these oxidations were observed to decrease slightly with a temperature increase above 650°. Since the rate-determining step in a true parabolic oxidation is the diffusion of a species through the growing oxide coating, it is not likely that the rate would decrease with a temperature increase. Therefore, these oxidations were not considered to be true parabolic oxidations.

Below 600° the curves assumed an S-shape. Apparently an induction period occurred before the rise in the curve which altered the parabola to an S-shaped curve. With decreasing temperature, the S became more and more extended until it was no longer apparent at 465°.

These results indicated that the reaction studied was more complex than those ordinarily encountered in the oxidation of metals. An explanation was sought in the possibility that the sample did not remain at a constant temperature during the oxidation. The large heat of oxidation of thorium, 330 kcal. per mole, could cause a considerable temperature rise in the sample if it were not dissipated rapidly. Therefore, the oxidation rate measured may have been that of a reaction whose temperature increased continuously. A small thermocouple was placed in a hole drilled in a thorium sample. The temperature of the sample near the site of the reaction was observed during the oxidation. It was found that in an oxidation started at 500°, as shown in Fig. 2A, the temperature of the sample rose more than 300° above the temperature of the furnace at the same time that the oxidation curve rose steeply. At 450°, the oxidations seemed to be approximately isothermal for about 20 min. as shown in Fig. 2B.

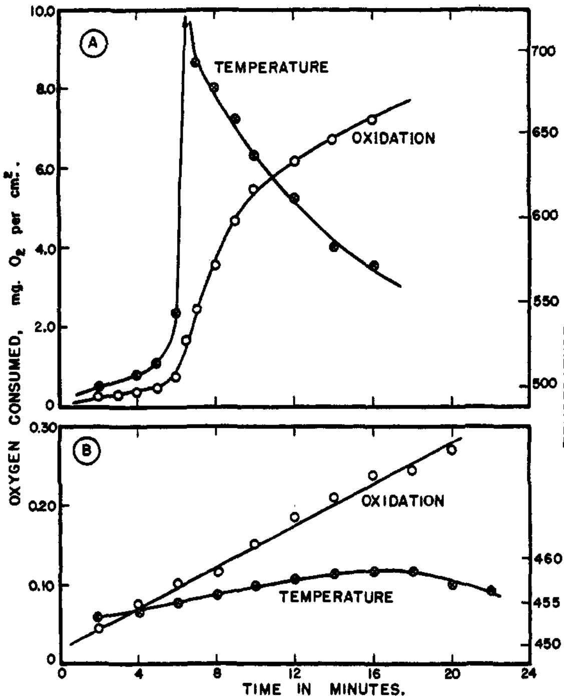

Fig. 2.—Temperature of sample during oxidation: A, initially 500°; B, initially 450°.

In view of these experiments it was concluded that the parabolic and S-shaped curves shown in Fig. 1 resulted from complex oxidations at rapidly changing and unknown specimen temperatures. The sharp rise in the S-shaped oxidation curves corresponded to a sudden temperature increase, as shown in Fig. 2A. At higher starting temperatures the

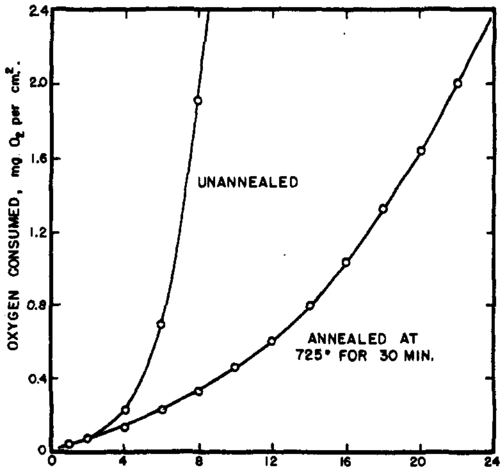

Fig. 3.—Effect of annealing on the oxidation of thorium at 475°.

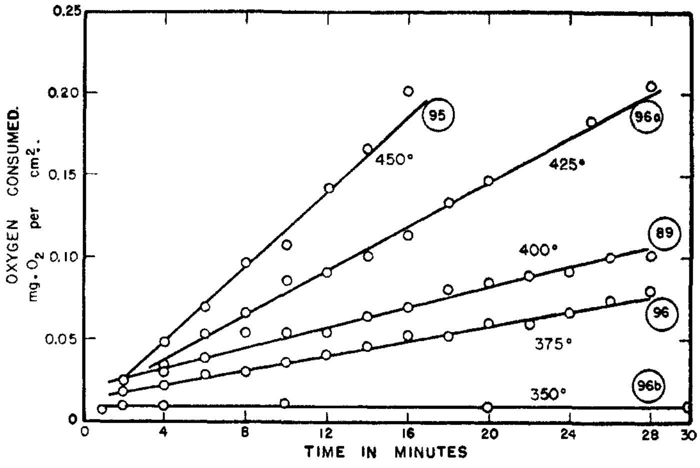

Fig. 4.—Linear oxidation curves for thorium at several temperatures. Circled numbers are run numbers.

rapid rise occurred at the beginning of the oxidation causing the curves to be parabolic. Thus the experiments above 450° measured the burning of the metal rather than its isothermal oxidation.

The metal samples as received were very brittle. If heated in a vacuum of a few microns at temperatures from 700 to 950°, the metal became ductile. The annealing treatment retarded oxidations near 475° but did not affect those above or below that temperature. Figure 3 shows the oxidation curves at 475° of a sample before and after annealing at 725° for 30 min. Annealing at 700° for 30 min. had no appreciable effect on the oxidation of a sample at 600° or at 450°. The results of other experiments on annealed samples showed that only in the case of S-shaped oxidation curves did annealing alter the curve; then it delayed the rise. That is, annealing delayed the rise in oxidation of those non-isothermal oxidations in which the rise in sample temperature occurred a few minutes after the oxidation started. A possible explanation of this annealing effect may be that in the annealing process the thermal conductivity of the sample was improved. The conduction of the heat of the oxidation away from the surface would have been facilitated and the oxidation at the surface would have been retarded by occurring at a lower temperature.

The oxide coating formed on the metal was black at the beginning of the oxidation but became white and flaky as the oxidation proceeded. At 500°, the oxidation was stopped at various stages and the color of the oxide observed. It was found that the formation of the white oxide on the black occurred at the same time that the sudden rise in the oxidation took place. X-Ray diffraction pictures were taken of metal samples at different stages of oxidation to determine the nature of the black coating found in the beginning of all oxidations. The diffraction patterns, formed by diffraction of CuKα radiation from a stationary edge of the sample, showed only those lines corresponding to thorium metal and thorium dioxide.[7] Thus the normal oxide, ThO_2, was formed on the metal and the black color was possibly due to the solution of thorium in the normal dioxide. The black oxide was very adherent especially when formed at high temperatures, above 800°.

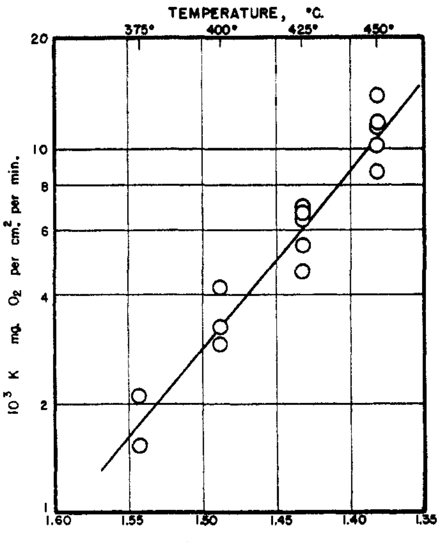

Fig. 5.—Variation of the linear rate constant with temperature.

From 350 to 450°.—Since the oxidations below 450° were isothermal, they were taken to indicate a "true" rate of oxidation of the metal. These oxidations were linear for about 20 minutes and obeyed the equation

$$w = kt$$

where w is the amount of reaction in time t. Figure 4 shows the results of several oxidations in this temperature range. Deviations from linearity were observed in some oxidations at 450° after about 25 min. of reaction. Those deviations were probably due to a slight temperature rise in the sample. The values of the rate constant in the temperature range 350 to 450° may be obtained from Fig. 5. At 375° the amount of oxidation was small and difficult to measure with the apparatus used in that temperature range. A run was made at 375° in the more sensitive apparatus used in lower temperature range. That oxidation was slightly curved at the beginning but became linear. Such behavior probably reflects the transition of the reaction from linear to the parabolic found below 350°. The linear rate constants of the two oxidations at 375° were the same within 15%.

Figure 5 shows the logarithm of the constant plotted against the reciprocal of absolute temperature. From the slope of the line, the energy of activation for the reaction was calculated to be 22 kcal. per mole.

From 250 to 350°.—The oxidation of the metal was observed from 250 to 350° at 21 cm. pressure. The oxidation

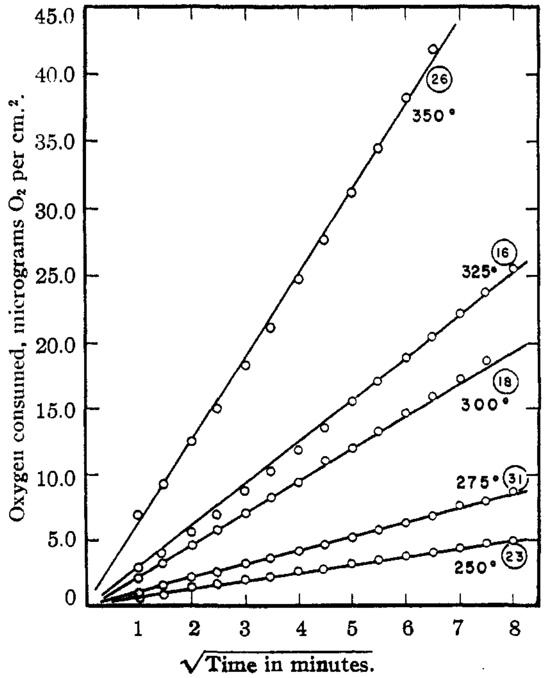

Fig. 6.—Parabolic oxidation of thorium from 250 to 350°.

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(7) Am. Soc. Testing Mat. "X-ray Diffraction Patterns," Original Set, 1942, cards 1769, 2258; First Supplementary Set 1944, Card 2995.

curves in this temperature range were all found to obey the parabolic law

$$w^2 + kt + c$$

over at least the first 80 min. Figure 6 is a parabolic plot of results of several experiments in this temperature range. The data obtained are shown in Fig. 7.

The energy of activation for the process of oxidation between 250 and 350° was calculated from the slope of the line of Fig. 7 to have a value of 31 kcal. per mole of thorium.

The oxidized specimens in this temperature range were always black or deep purple. The X-ray diffraction pattern of one such sample showed the structures of thorium dioxide and thorium metal.

Discussion

Over the whole range of temperatures studied the oxidation of thorium was found to go from a parabolic reaction at low temperatures to a linear reaction at higher temperatures and finally to a non-isothermal burning of the metal at 500° and above.

Gulbransen[8] has observed the transition from parabolic at lower temperatures to linear at higher temperatures in the case of aluminum. In the present oxidation of thorium the parabolic reaction is presumably due to a diffusion through the adherent layer of black oxide observed. The activation energy for this reaction is the 31 kcal. per mole observed for the parabolic oxidation. Above 350° the oxidation becomes linear and diffusion through the layer of black oxide is apparently no longer rate-determining. The rate-determining step of the linear reaction, which is independent of time, may be the conversion of the black material to white thorium dioxide. The white dioxide was found to flake off and would thus leave an essentially constant area of black oxide exposed to the oxygen.

A self-accelerated rate of oxidation, such as observed in the thorium oxidation above 450° has been reported by Pilling and Bedworth[2] in the oxidation of calcium. They observed a sudden rise in the linear oxidation after several hours of reaction and attributed it to a temperature rise of the sample caused by the heat of oxidation. In the present work the rise in temperature of the specimen was observed to occur simultaneously with the increase in oxidation rate and with the change from black to white oxide. The change in color of the sample would reduce its emissive power and cause the temperature of the sample to increase. The color change may be the start of the process of temperature increase and consequent oxidation rate increase.

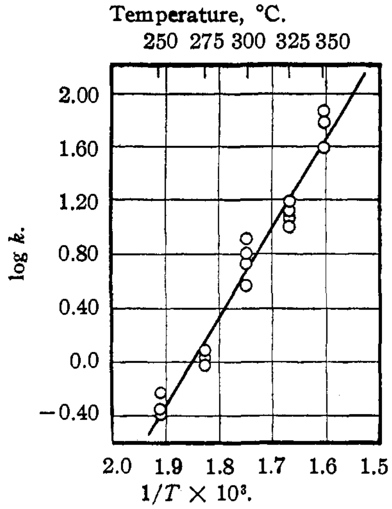

Fig. 7.—Variation of the parabolic rate constant with temperature.

It is possible to compare the oxidation rate of thorium with those of titanium[5] and zirconium at 300° as reported by Gulbransen[6] since all three metals oxidize parabolically at that temperature. The parabolic rate constants are 0.15×10^{-12} g.²/cm.⁴ min. for titanium, 3.1×10^{-12} for zirconium and 5.0×10^{-12} for thorium. Thus the oxidation rates increase uniformly with atomic number in that group of the periodic table.

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(8) E. A. Gulbransen, *Trans. Electrochem. Soc.*, **91**, 595 (1947).