In a 1–1 salt there are as many cations as holes and so in the pure salt the holes are all filled. In a 2–1 or a 3–1 salt, one-half and two-thirds of the holes are empty. Therefore, the greater solubility of metal in a salt of large anion to cation ratio (item 2 above) is plausible since the concentration of holes in the salt depends upon the anion to cation ratio. The larger the cation the further the anions surrounding the hole are separated. Thus the metals with larger cations are more soluble (items 1 and 3 above).

The electrons transferred to the salt by the dissolved metal are in bands or zones of energy states belonging to the salt system as a whole. As the salt of a more electropositive metal is added the energy levels would be raised, making it more difficult for an electron from the metal to be transferred to the salt and in effect reducing the solubility of the metal (item 4 above).

The experimental facts seem to fit in with the picture suggested. A more detailed investigation of the correlation of solubility with electropositiveness of added salt should be made.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Reaction of Cerium with Oxygen

BY DANIEL CUBICCIOTTI[1]

The oxidation of cerium has been found to obey the parabolic law from 30 to 125°. Above 125° the reaction started parabolically but subsequently became linear. The parabolic portion became shorter as the temperature was increased. Cerium was the most rapidly oxidizing metal yet studied. The energy of activation of the parabolic reaction was the smallest yet observed.

The oxidations of certain metals,[2] namely, thorium, uranium and aluminum have been found to obey the parabolic law at low temperatures and the linear law at higher temperatures. Loriers[3] has reported that cerium oxidizes linearly at 300°. Since the ratio of molal volumes of oxide to metal is greater than unity, it would be expected that cerium would oxidize parabolically.[4] Thus the author supposed that the oxidation of cerium also undergoes the parabolic–linear transition. The present study shows that that supposition was correct.

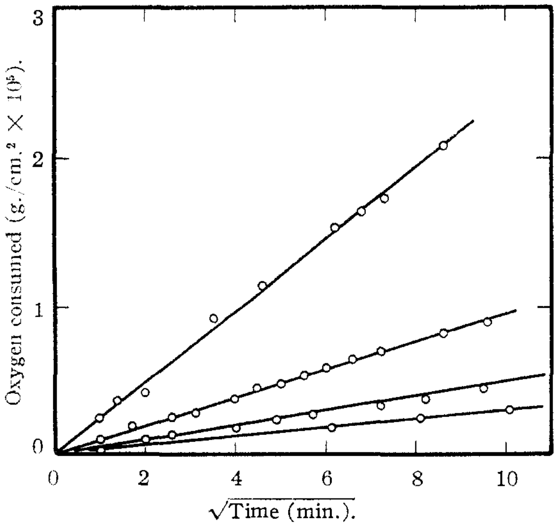

Fig. 1.—Parabolic plot of the oxidation of cerium at 30, 44, 68 and 125°.

Experimental

The method and apparatus were the same as those used for uranium.[2] Cerium metal was obtained from the A. D. Mackay Co., New York. It was stated to contain 92.6% cerium, 1.1% iron and the balance other rare earth metals. Two rectangular blocks each about 2.5 × 1 × 0.5 cm. were cut from the ingot obtained. These were abraded until the surface was free of pockets and salt inclusions. Immediately before each oxidation the surface was abraded with 400 emery cloth and washed with carbon tetrachloride. For each oxidation 120 minutes of preheating was allowed before the oxygen was admitted and the oxidation started. To clean the surface for the oxidation made at 30° the block was chilled so that it was always well below room temperature. This treatment probably only reduced the thickness of oxide initially present, and the oxidation of the clean metal may be more rapid than that observed.

Results

From 30 to 125° the oxidations were quite parabolic over a 100-minute interval. Figure 1 shows the type of data obtained in that temperature range on a parabolic plot.

Above 125° the oxidation started as a parabola but after a time became linear. This change may be seen in Fig. 2 where a linear plot of the higher temperature data is given. It may be seen that as the temperatures of the oxidations were increased the duration of the parabolic portion decreased. This effect in the cerium oxidation is more evident than in the case of uranium or thorium.

The rate constants obtained are shown in Fig. 3 as the logarithm of the constant *versus* reciprocal of absolute temperature. The left hand line and abscissa represent the linear oxidations and the right hand ones represent the parabolic. From the slopes of the straight lines one can calculate the energies of activation for the two reactions. For the linear reaction the value is 14 kcal. per mole while for the parabolic it is 12 kcal. per mole.

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(1) North American Aviation, Inc., Downey, Calif.

(2) D. Cubicciotti, THIS JOURNAL, to be published.

(3) J. Loriers, *Compt. rend.*, **229**, 547 (1949).

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

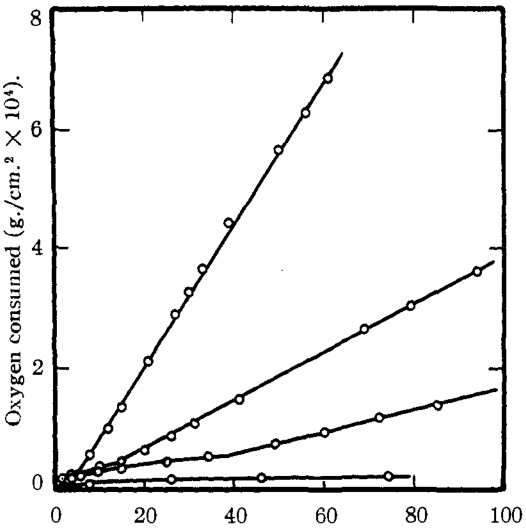

Fig. 2.—Linear plot of the oxidation of cerium at 125, 160, 170 and 190°.

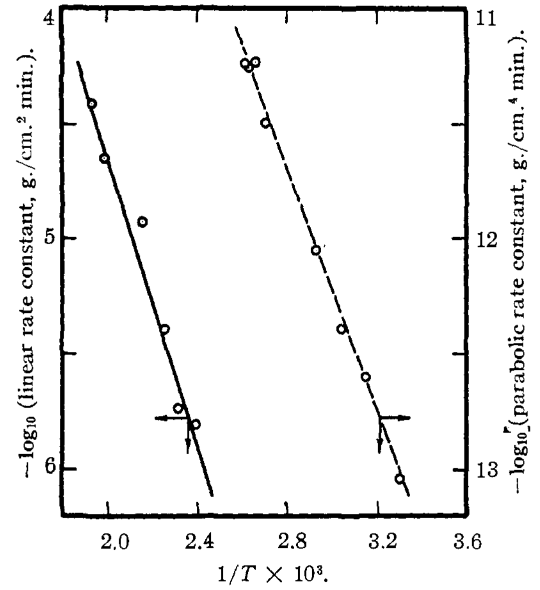

Fig. 3.—Activation energy plot of linear (full curve) and parabolic (dotted curve) oxidation constants for cerium.

Discussion

The oxidation of cerium is the most rapid of the known parabolic metal oxidations. At room temperature the parabolic oxidation rate constant is about 10^{-13} g.^{2}/cm.^{4} min. It is interesting to note the small activation energy of the parabolic reaction, 12 kcal. per mole. The usual values for such reactions range from 20 to 50 kcal. per mole.

Another interesting fact is that the activation energies of the linear and parabolic reactions are almost equal. This was true of the uranium oxidation[2] where the values were 22 and 24 kcal. per mole for the linear and parabolic reactions. For thorium[5] the values were somewhat more divergent, 22 and 31 kcal. per mole for the linear and parabolic reactions; however, they were still close. The approximate equality of the activation energies may indicate that the rate-limiting step in both types of reaction is diffusion through the oxide. In the parabolic reaction the rate-determining step is diffusion through a growing layer of oxide. In the linear reaction the rate-determining step may be diffusion through a layer of oxide of constant thickness. Such a rate-determining process would give rise to a linear oxidation with an activation energy the same as that of the parabolic reaction. If the oxide formed up to a certain thickness were adherent but that beyond non-adherent or porous, then diffusion would occur only through the adherent layer of thickness, and give rise to a linear oxidation. The change in adhesion of the oxide could be caused by a change in structure of the oxide.

Acknowledgment.—The author is grateful to the Office of Naval Research for supporting this investigation.

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[5] P. Levesque and D. Cubicciotti, THIS JOURNAL, 73, 2028 (1951).