A second evaporation and weighing was conducted after which the technetium was converted to $NH_4TcO_4$ and weighed. It appears (Table II) that the dark red crystals formed on evaporating aqueous solutions of $Tc_2O_7$ correspond to $Tc_2O_7 \cdot H_2O$, or to anhydrous pertechnic acid, $HTcO_4$.

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## The Solubility of Bismuth in Mixtures of Bismuth Chloride with Other Chlorides

BY GEORGE CLEARY[1a] AND DANIEL CUBICCIOTTI[1b]

The solubility of cadmium in cadmium chloride has been shown to be greatly influenced by the addition of other chlorides.[2] The properties of the added salt that appeared to determine its effect on the solubility of the cadmium were the anion-to-cation ratio and the electropositiveness of the metal of the cation. The present study on bismuth was made parallel to that on cadmium to investigate the influence of added salt.

### Experimental

**Method.**—The method was similar to that used in the cadmium system.[2] Mixtures of about 10 g. of salt and 10 g. of metal were sealed into iron tubes by brazing with a high melting brazing alloy. The mixtures were equilibrated at 450° for one hour, quenched in water, and samples of the salt phase taken for analysis. These weighed samples of salt were leached with concentrated hydrochloric acid, which dissolved the salts and left a precipitate of the bismuth metal that had been dissolved in the salt. The bismuth precipitate was dissolved in concentrated nitric acid and then precipitated as BiOCl after the proper adjustment of the acidity and chloride concentration of the solution. The oxychloride was dried and weighed, and the composition of the salt phase calculated from its weight together with the weight of the sample and the original salt composition.

**Materials.**—Anhydrous bismuth trichloride was obtained from the J. T. Baker Co. The other anhydrous salts were prepared by heating the hydrate or the moist salt *in vacuo*.

### Results and Discussion

Two separate determinations of the solubility of bismuth in its chloride gave 47.3 and 47.8 mole per cent. bismuth in the final mixture at 450°. This compares favorably with the value of 46.6 mole per cent. given by Eggink[3] at 320°.

The effect of added salts on the solubility of the bismuth is shown in Fig. 1. It may be seen from the figure that cuprous chloride reduces the solubility more than zinc chloride and sodium chloride more than calcium chloride. Thus with salts of metals of about the same electropositiveness, the larger the anion to cation ratio, the less effective the salt in reducing the solubility of the metal. It can also be seen that sodium chloride reduces the solubility more than cuprous chloride and calcium chloride more than zinc chloride. For salts of the same anion to cation ratio, the more electropositive the metal of the cation, the more effective the salt in reducing the solubility.

These results are in accord with the data observed in the case of cadmium[2] and fit the hypothesis suggested concerning the structure of metal-in-salt solutions.

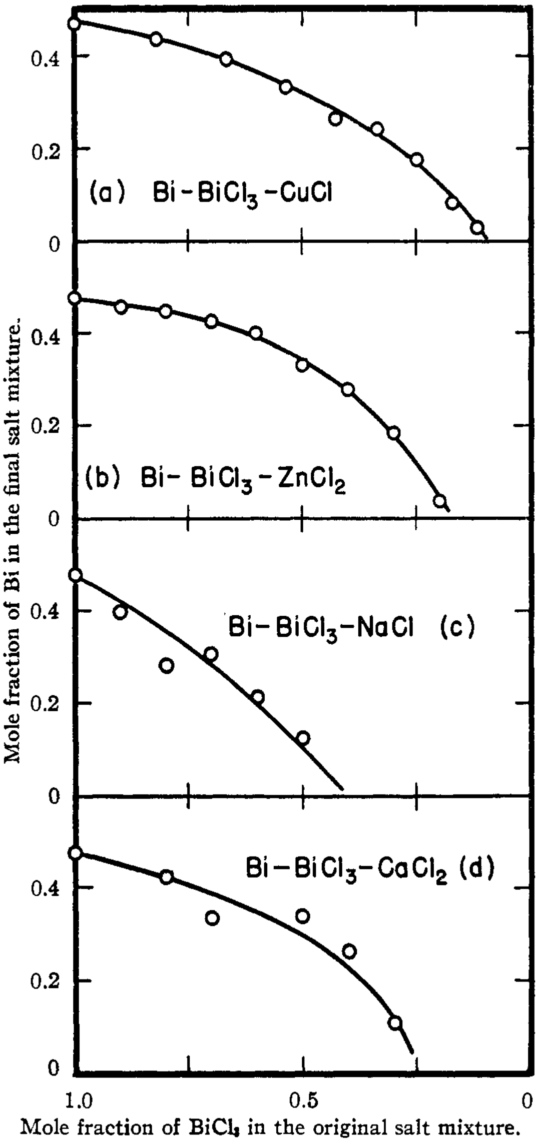

Fig. 1.—Influence of added salt on the solubility of bismuth in its trichloride at 450°.

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[1] (a) Sinclair Research Laboratories, Harvey, Illinois. (b) North American Aviation, Inc., Downey, Calif.

[2] D. Cubicciotti, THIS JOURNAL, to be published.

[3] Eggink, *Z. physik. Chem.*, **64**, 493 (1908).

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## The Oxidation of Calcium at Elevated Temperatures

BY DANIEL CUBICCIOTTI[1]

The ratio of molal volumes of calcium oxide to calcium metal is about 0.95. Since the ratio was less than unity, Pilling and Bedworth[2] expected the metal to oxidize according to the linear law. In their experiments, of long duration, the metal did oxidize linearly.

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[1] North American Aviation, Inc., Downey, Calif.

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

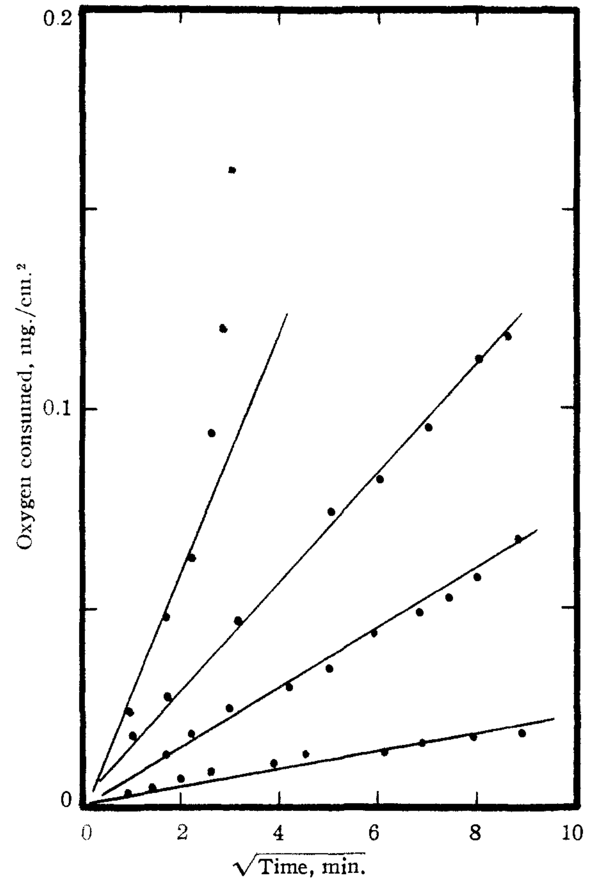

Fig. 1.—The oxidation of calcium at 330, 350, 385 and 435°; parabolic plot.

The oxide that forms initially is dark colored and appears to adhere to the metal. For that reason and because the ratio of volumes of oxide to metal is so close to unity the author felt that the initial portion of the oxidation curve might be parabolic. The present study shows that such is the case.

### Experimental

The method was the same as that used previously in this Laboratory.[3] For the rapid oxidations a 500-cc. bulb was added to the system outside the furnace. The sample was a cube approximately 1 cm. on edge of electrolytic calcium, 99% pure, obtained from the A. D. Mackay Co., New York. Before each oxidation, the sample was abraded under carbon tetrachloride with 2/0 emery paper. The samples were heated for 100 min. *in vacuo* before oxygen was admitted to start the reaction.

### Results and Discussion

The oxidation was studied for 100 min. from 330 to 475° at 20 cm. oxygen pressure. Typical oxidation curves are shown in Figs. 1 and 2. The curves obtained from 330 to 435° are shown in Fig. 1 on a parabolic plot. The oxidations below 435° obeyed the parabolic law for at least 100 min. At 435° the curve was not parabolic beyond the first five minutes.

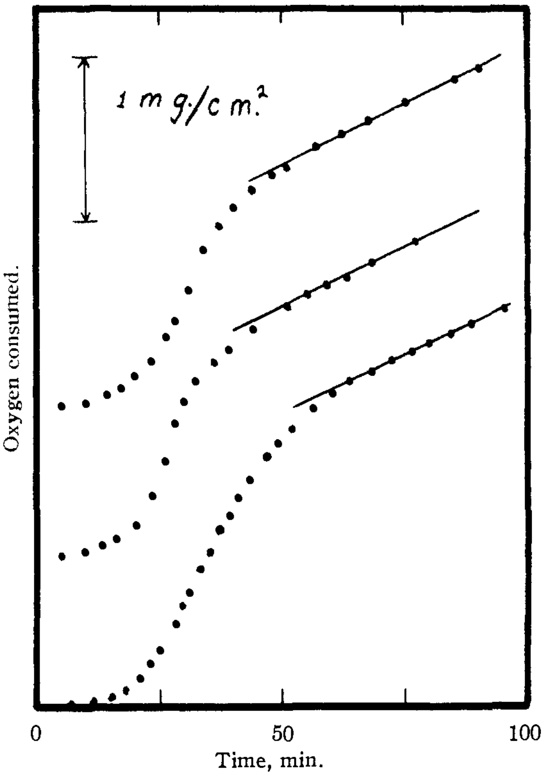

Fig. 2.—The oxidation of calcium at 425, 460 and 475°.

The results above 425° are shown in Fig. 2. The oxidations had an induction period followed by a rapid rise to an approximately linear shape after about 50 min. The induction period presumably corresponds to the formation of the first, adherent film. The linear portion is expected since the volume ratio is less than unity. However it is difficult to understand the sudden rise in the curves.

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

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[3] D. Cubicciotti, THIS JOURNAL, to be published.

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## Cactus Alkaloids. II. Condensation of Mescaline with Formaldehyde by the Eschweiler–Clarke Reaction

BY JOSÉ A. CASTRILLÓN

In previous work in this Laboratory[1] a tetrahydroisoquinoline base was obtained in an attempt to synthesize trichocereine, *i.e.*, N-dimethylmescaline, by methylation of mescaline with formic acid–formaldehyde. This base has now been characterized as N-methyl-6,7,8-trimethoxy-1,2,-3,4-tetrahydroisoquinoline. It is a new compound related to the *anhalonium* alkaloids, and can be expected to occur in nature, since it may be derived from anhalinine by an N-methylation or from anhalidine by an O-methylation.

Only one reference to cyclization during the Eschweiler–Clarke reaction with phenethylamines has been found in the literature,[2] though the cyclizing action of formaldehyde with the aid of a

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[1] L. Reti and J. A. Castrillón, THIS JOURNAL, **73**, 1767 (1951).

[2] J. S. Buck and R. Baltzly, *ibid.*, **64**, 2263 (1942), report that attempts to prepare 3,4-dimethoxyphenethylbenzylmethylamine from benzylhomoveratrylamine by this method, gave unsatisfactory results, probably owing to partial cyclization.