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, $HTcO_4$.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE AND
THE UNIVERSITY OF TENNESSEE KNOXVILLE, TENNESSEE

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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.

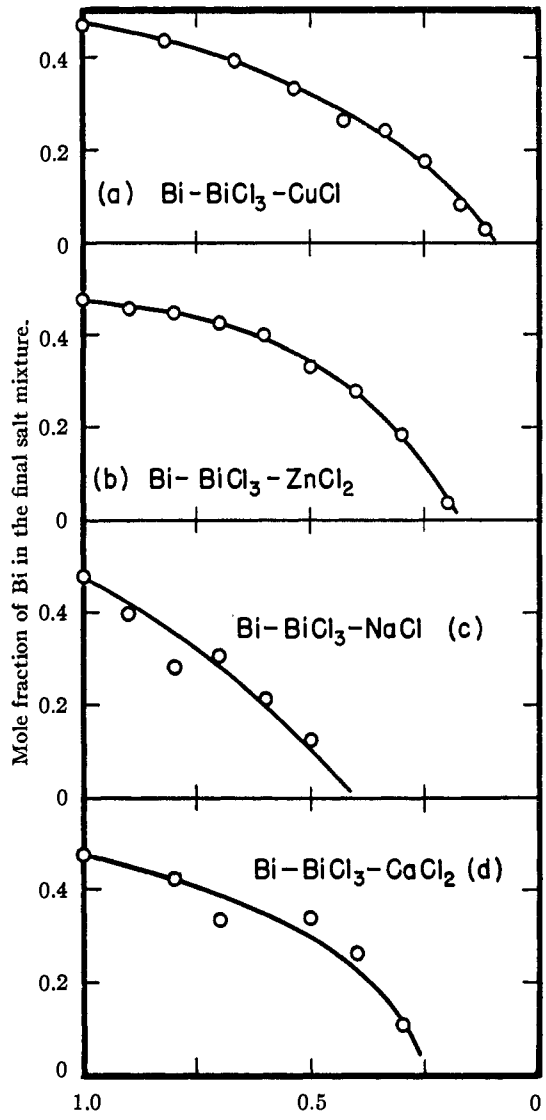

Fig. 1.—Influence of added salt on the solubility of bismuth in its trichloride at 450°.

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ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILLINOIS

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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).

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.

(1) North American Aviation, Inc., Downey, Calif.
(2) N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 529 (1923).