

bury and Powell. For these reasons we do not doubt either the results of T. W. J. Taylor, or those of Dusenbury and Powell.

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Chemistry of Technetium. I. Preparation of Technetium Heptoxide

BY G. E. BOYD, J. W. COBBLE, C. M. NELSON AND W. T. SMITH, JR.¹

In the study of the chemistry of technetium it was necessary to establish the formula of the compound formed on heating the element in dry oxygen at 400–600°. Fried and co-workers² have suggested the product of this reaction may be TcO_3 . However, elemental rhenium, when burned under these conditions gives Re_2O_7 .³ We were first led to the view that the oxidation product in reality was Tc_2O_7 by the observation that the titer of a standardized Ce(IV) solution was not changed upon adding milligram quantities of the compound. Furthermore, the absorption spectrum (Fig. 1) of an aqueous solution of the oxide was found to be identical before and after its treatment with alkaline H_2O_2 suggesting that the technetium was already Tc(VII).

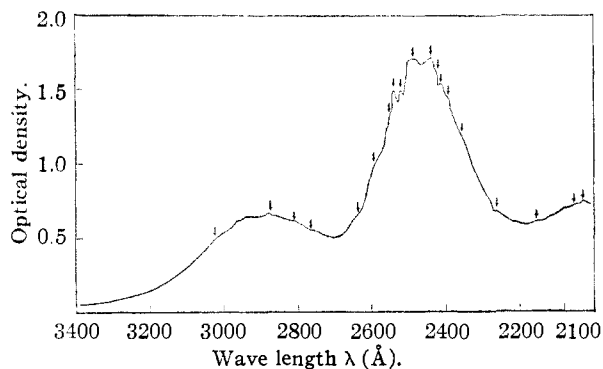


Fig. 1.—Ultraviolet absorption spectra of $3 \times 10^{-4} M$ NH_4TcO_4 vs. H_2O at 25° determined with Beckman model DU spectrophotometer using variable slit width and constant sensitivity; source: H_2 discharge lamp. Molar extinction coefficient at 2470 Å. = 4000.

Quantities of technetium metal⁴ were burned and the light yellow crystalline oxide (m.p. $119.5 \pm 0.1^\circ$) formed was purified by repeated sublimations into cooler portions of the quartz reaction tube. An aqueous solution containing a known quantity of the compound was prepared by sealing off an aliquot in a small quartz tube, weighing and

breaking the same, and then reweighing its parts after the oxide had dissolved completely. The oxide, which is very hygroscopic, dissolved to give a pink solution whose color disappeared with dilution. A potentiometric pH titration was performed using 0.05 *f* ammonium hydroxide. The titration curve, which was characteristic of a strong monobasic acid, showed but one inflection point. The entire neutralized solution was taken to dryness in a platinum dish at 95° and the weight of technetium salt was determined. Pure NH_4TcO_4 is non-hygroscopic and shows no decomposition when kept in air at 100° for several hours. Analytical results from two experiments are given in Table I where a comparison with the titers for Tc_2O_7 and TcO_3 , respectively, is made.

TABLE I
EVIDENCE THAT THE FORMULA OF THE YELLOW OXIDE OF TECHNETIUM IS Tc_2O_7

Wt. of oxide, mg.	Milli-moles ^a as Tc_2O_7	M.e. as Tc_2O_7	Milli-moles as TcO_3	M.e. as TcO_3	M.e. OH ⁻ required	M.e. NH_4TcO_4 found
157.7	0.5087	1.017	1.073	2.146	1.019	1.020
70.11	0.2262	0.4524	0.4769	0.9538	0.4561	0.4564

^a The theoretical isotopic weight of 99.0 given by Metropolis and Reitinuer (NP-1980, USAEC, March, 1950) was used in the calculations. Although fission product Tc^{99} may contain small quantities of other isotopes, the amounts will be such as to give a negligible error.

It was concluded that the correct formula for the light yellow oxide produced by heating technetium metal in dry oxygen at 400–600° is Tc_2O_7 .

The intense ultraviolet absorption (Fig. 1) of pertechnetate ion in aqueous solutions may be employed for the spectrophotometric determination of Tc(VII). Beer's law was found to hold rather well up to concentrations of $10^{-3} M$ for wave lengths near both maxima (*i.e.*, 2470 and 2890 Å.). As little as 10^{-8} g. of technetium may be detected, which sensitivity compares quite favorably with that obtained spectrochemically.⁵ A third absorption band in the far ultraviolet in addition to those previously measured² at longer wave lengths is suggested (Fig. 1).

Previously,⁶ relatively concentrated strongly acid technetium solutions had been found to show a pink coloration. In this work when a 1 *M* aqueous solution of Tc_2O_7 was slowly evaporated at room temperature over concentrated sulfuric acid, it became yellow, dark yellow, red and dark red; finally, long red-black crystals formed. These hygroscopic crystals were rapidly weighed (15 seconds) and then were allowed to absorb water from the atmosphere to form a dark red solution.

TABLE II
FORMULA OF RED-BLACK CRYSTALS RESULTING FROM THE ISOTHERMAL EVAPORATION OF AQUEOUS Tc_2O_7 SOLUTIONS

Tc_2O_7 hydrate, mg.	Weight of NH_4TcO_4 formed, mg.	Mol. wt. of hydrate	Hydrate formula
1st weighing, 98.1	108.5	327.4	$Tc_2O_7 \cdot (H_2O)_{0.97}$
2nd weighing, 98.5	...	328.6	$Tc_2O_7 \cdot (H_2O)_{1.03}$

(5) D. Timma, *J. Optical Soc.*, **39**, 898 (1949).

(6) E. E. Motta, G. E. Boyd and Q. V. Larson, *Phys. Rev.*, **72**, 1270 (1947).

(1) Department of Chemistry, University of Tennessee, Knoxville, Tenn.

(2) S. Fried, A. H. Jaffey, N. F. Hall and L. E. Glendenin, *Phys. Rev.*, **81**, 741 (1951).

(3) A. D. Melaven, J. N. Fowle, W. Brickell and C. F. Hiskey, "Inorganic Syntheses," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 188.

(4) The pure metal was produced from technetium separated from a "crude" tetraphenylarsonium perchlorate + pertechnetate precipitate dissolved in concentrated H_2SO_4 kindly supplied to us by G. W. Parker, leader of the "hot" laboratory group, Chemistry Division, ORNL. The details of the preparation will be reported in another communication.

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 $\text{Tc}_2\text{O}_7 \cdot \text{H}_2\text{O}$, 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 electropositivity 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 Eggink³ 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 electropositivity, 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 cadmium² and fit the hypothesis

(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).

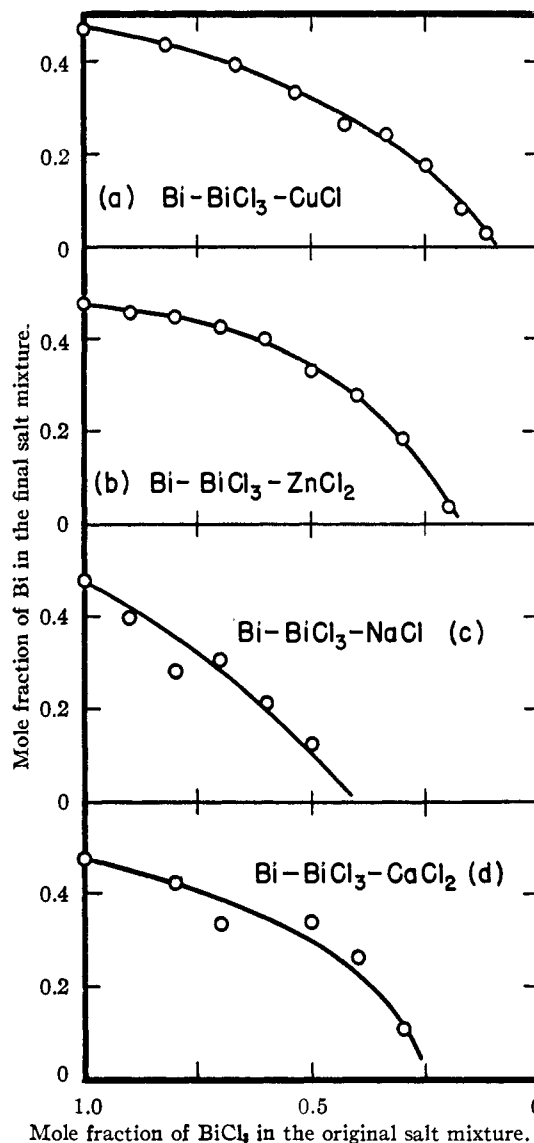


Fig. 1.—Influence of added salt on the solubility of bismuth in its trichloride at 450°.

suggested concerning the structure of metal-in-salt solutions.

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The Oxidation of Calcium at Elevated Temperatures

BY DANIEL CUBICCIOTTI¹

The ratio of molal volumes of calcium oxide to calcium metal is about 0.95. Since the ratio was less than unity, Pilling and Bedworth² 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).