

### THE PREPARATION OF TECHNETIUM METAL

Sir:

Element number 43, technetium, which was discovered by Perrier and Segre<sup>1</sup> has now been prepared in metallic form from two separate samples of technetium compounds which were obtained from Dr. G. W. Parker of Clinton Laboratories, Oak Ridge, Tennessee. Both original samples were reported to be the ammonium "per" salt, probably  $\text{NH}_4\text{TcO}_4$  and were shown by spectrographic analysis to contain negligible amounts of impurities.

The first sample was obtained from Oak Ridge as a pink deposit, weighing 119 micrograms, on a platinum plate. Hydrogen sulfide was passed, for a period of one hour, over a pink solution of the solid in 100 microliters of 4 *N* hydrochloric acid in a microcone placed in a water-bath at 80°, and a brownish, flaky precipitate formed slowly. This was centrifuged, washed and dried *in vacuo* at room temperature. A sample of this sulfide which was submitted for analysis gave an X-ray diffraction pattern which has not yet been interpreted.

The sulfide was transferred to a thin-walled quartz capillary (i. d. 0.15 mm., wall thickness 0.015 mm.) which was attached to a vacuum line in such a manner that hydrogen could be admitted onto the heated sulfide and then removed by pumping.

When the compound was treated with hydrogen at 1000° for three two-minute intervals with intervening evacuation a black cindery mass resulted and a yellow material sublimed out, presumably sulfur. The black material was transferred to an X-ray capillary and submitted for X-ray analysis. It was reported by Dr. R. C. L. Mooney to be technetium metal, isomorphous with rhenium, osmium and ruthenium.<sup>2</sup>

The second sample of technetium was obtained as a pink sirup in a sealed quartz tube. The sirup, which was reported to contain *ca.* 200 micrograms of technetium, was dissolved in 100 microliters of 4 *N* hydrochloric acid as before. This time when hydrogen sulfide was passed over the heated solution a black precipitate immediately formed. This compound gave no X-ray diffraction pattern.

On treatment of the dried solid with hydrogen at 900°, a substance was formed yielding an X-ray diffraction pattern totally unlike that obtained before. The product was then treated with hydrogen at 1000° and the pattern obtained was again different but may have contained some metal. Finally, it was treated with hydrogen at 1100° and a silvery, sintered mass was obtained which proved to give the same pattern as the first metal obtained.

Technetium metal does not dissolve in hydrogen peroxide-ammonium hydroxide mixture or in hydrogen peroxide alone as does rhenium metal, nor does it dissolve in hydrochloric acid.

(1) Perrier and Segre, *J. Chem. Phys.*, **5**, 712 (1937).

(2) Mooney, *Phys. Rev.*, **73**, 1269 (1947).

The patterns obtained at 900 and 1000° may be due to lower sulfides of technetium and these compounds will be investigated further.

The disparate results on the precipitation of the technetium sulfides may be due to the fact that two distinct oxidation states were involved.

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### PREPARATION OF CARBON MONOXIDE<sup>1</sup>

Sir:

Because of the wide interest in carbon monoxide as an intermediate in the synthesis of isotopically labeled organic compounds, and in view of the recent report by Kummer<sup>2</sup> on the preparation of  $\text{C}^{14}\text{O}$  by an exchange reaction with  $\text{C}^{14}\text{O}_2$ , I am prompted to describe a method which, because of its extreme simplicity, is applicable not only to the preparation of isotopic carbon monoxide, but also to the ordinary laboratory preparation of this gas. It consists simply in heating a mixture of calcium carbonate and zinc dust, whereupon the following reaction occurs



This reaction was reported many years ago by Kinnicutt<sup>3</sup> and Schwartz,<sup>4</sup> but appears to have been overlooked, since the only subsequent reference found is a brief mention by Mellor. Investigation revealed that at 700–750° a mixture of dry, powdered calcium carbonate with twice the theoretical quantity of zinc dust<sup>5</sup> gives a quantitative yield of carbon monoxide of high purity. For small-scale preparations (1–10 mM.) it was found convenient to heat the reactants in a quartz tube attached to an evacuated system of known volume, the rate and extent of gas evolution being measured by means of a manometer. In a typical run, 10 mM. of calcium carbonate and 20 mM. of zinc yielded 216 ml. N.T.P. of gas consisting of CO, 99.1%; CO<sub>2</sub>, 0.9%; H<sub>2</sub> and H<sub>2</sub>O, traces; as determined by mass-spectrometric analysis. Larger-scale preparations (up to 5 liters) have been made at atmospheric pressure by heating the reactants in a Pyrex test-tube and collecting the gas by displacement of a liquid (water or oil).

The rate of gas evolution is easily controlled by varying the temperature of the reaction vessel. The reaction doubtless depends upon dissociation of calcium carbonate, since the more stable barium carbonate gives no trace of carbon monoxide under the same conditions.

(1) This work was sponsored by the Sun Oil Company, Philadelphia, Pa.

(2) Kummer, *THIS JOURNAL*, **69**, 2239 (1947).

(3) Kinnicutt, *Am. Chem. J.*, **5**, 43 (1883).

(4) Schwartz, *Ber.*, **19**, 1141 (1886).

(5) An excess of zinc is necessary because some distills at the temperature employed.