The author desires to take this opportunity to express his obligations and thanks to Professor Louis Kahlenberg under whose direction and guidance the present work was undertaken and prosecuted.

LABORATORY OF PHYSICAL CHEMISTRY.
UNIVERSITY OF WISCONSIN,
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A NEW METHOD FOR THE PREPARATION OF VANADIUM TETRACHLORIDE.[1]

BY A. T. MERTES.

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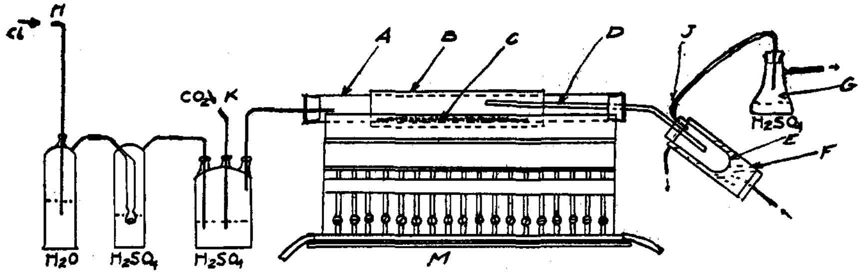
The usual methods for the preparation of vanadium tetrachloride involve the fractional distillation and separation of vanadium tetrachloride from a mixture with other chlorides. This fractionation requires time and results in losses, due not only to the imperfect separation of the fractions, but to the inevitable loss of vanadium tetrachloride due to its decomposition.

The writer had occasion to prepare a considerable amount of vanadium tetrachloride and believes the following method to be superior to any given in the reference works or journals. It is essentially the action of chlorine upon ferrovanadium, and takes place as follows:

$$FeV + 7Cl = FeCl_3 + VCl_4.$$

Dry, air-free, chlorine is passed over heated ferro-vanadium contained in a reaction tube. Vanadium tetrachloride distils over while the ferric chloride remains in the tube. The accompanying sketch shows the arrangement of apparatus.



The reaction tube *A*, is made of hard glass about 5 cm. in diameter and about 150 cm. long. A sheet iron jacket, *B*, 8 cm. in diameter, surrounds this tube and leaves an air space of about 1 cm. between it and the glass. This permits of a uniform and slow heating of the tube—the heat being easily regulated by the combustion furnace, *M*. The ferro-vanadium is crushed to about 4 mesh and placed in the reaction tube at *C*. An inclined delivery tube, *D*, extends into the receiver *E*, which is sur-

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[1] Extract from thesis for the degree of E.M., Colorado School of Mines, Golden, Colorado. The writer wishes to thank Dr. Herman Fleck. who suggested this method.

rounded by water in the condenser F. A current of water keeps the condenser sufficiently cool. The volatil lower chlorides of vanadium escape through the tube J and are absorbed by concentrated sulfuric acid in the filter flask G. Excess of chlorine or unabsorbed gases pass out through the side aperture to a hood or drain pipe. Chlorine is obtained either by generation with a mixture of manganese dioxide, salt and sulfuric acid, or from a tank of liquid chlorine. Since the flow of chlorine need not be rapid—2 to 3 bubbles a second—the chlorine can be generated very satisfactorily. The gas passes through a wash bottle containing water, then through one containing concentrated sulfuric acid, and then into a three-necked Woulf's bottle also containing concentrated sulfuric acid. A tube dipping below the acid serves for the introduction of carbon dioxide and to trap the chlorine. To start the preparation, the air in the reaction tube and condenser is removed by passing a current of carbon dioxide for some time. Chlorine is then allowed to replace the air in the purifying apparatus. When all air has been displaced, the train is connected up and the furnace started. The heat is brought up slowly while a stream of chlorine is passed, displacing the carbon dioxide.

Fifty to 100 grams of ferro-vanadium are sufficient for a charge, since the ferric chloride formed will fill the reaction tube and may be carried over into the condenser with the vanadium tetrachloride.

In order to preserve vanadium tetrachloride indefinitly it was found best to dissolve it in carbon tetrachloride. In case any ferric chloride contaminates the vanadium tetrachloride obtained by the above method, it can easily be removed, since it is insoluble in carbon tetrachloride.

BEHAVIOR OF THE HYDRONITROGENS AND THEIR DERIVATIVES IN LIQUID AMMONIA. V. ELECTROLYSIS OF A SOLUTION OF AMMONIUM TRINITRIDE IN LIQUID AMMONIA.

By A. W. Browne and M. E. Holmes.

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The electrical conductivity of hydronitric acid in aqueous solution has been determined by Ostwald,[1] by Hantzsch,[2] and by West.[3] Hittorf[4] has investigated the behavior of ammonium trinitride in aqueous solution toward the electric current. Peratoner and Oddo,[5] and Szarvasy[6] have electrolyzed aqueous solutions of hydronitric acid and of sodium trinitride, with a view to investigating the possible formation of poly-

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[1] See Curtius and Radenhausen, *J. prakt. Chem.*, [2] **43**, 207 (1891).

[2] *Ber.*, **32**, 3066–88 (1899), p. 3072.

[3] *J. Chem. Soc. London*, **77**, 705–7 (1900).

[4] *Z. physik. Chem.*, **10**, 593–620 (1892).

[5] *Gazz. chim. ital.*, **25**, II, 13 (1895); **30**, II, 95 (1900); *Chem. Zentralbl.*, **1895**, II, 864; **1900**, II, 660.

[6] *J. Chem. Soc. London*, **77**, 603 (1900).