bilities of the various ligands necessitated the use of different solvents. However, in all the systems studied, the free energy changes which occur when the complexes are formed are small, and the differences among them even smaller so that one is not justified in trying to relate these differences to structural differences in the various complexes.

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Preparation of Vanadium Monoxide

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A compressed, intimate mixture of vanadium trioxide and finely divided vanadium is heated in a vacuum at 1750° for one hour. Evidences of conversion are changes in physical and chemical properties, chemical analysis and X-ray examination. Vanadium monoxide has a specific gravity of 5.55 (25°/4), hardness 8–9 on the Mohs scale, and a medium gray color. It dissolves slowly in hot dilute hydrochloric acid, forming a violet or blue solution; hydrofluoric acid acts faster, and nitric acid dissolves it readily under evolution of nitric oxide.

Vanadium monoxide, VO, was prepared from vanadium pentoxide containing 99.80% V_2O_5, 0.08% SiO_2 and spectroscopic traces, or less than 0.01% of manganese, copper and calcium.

The pentoxide, contained in a porcelain boat and placed in a tubular electric furnace, was reduced in a current of purified hydrogen, first for one hour slightly below the melting point, 658°, and subsequently for one hour at 1000°. Complete reduction to vanadium trioxide, V_2O_3, is thereby obtained, as shown by the weight loss, determined after cooling in hydrogen.

Vanadium trioxide was then further reduced to metallic vanadium with calcium hydride, 100 mesh, 87.7% CaH_2, by the method of Meerson, Kats and Khokhlova.[1] The mixed powders, with 50% excess of calcium hydride, were pressed into an armco iron boat and heated in a hydrogen atmosphere for one hour at 1025–1175°. The reaction product was freed from calcium and magnesium compounds with cold, dilute hydrochloric acid (1:10), washed with water, and dried in a vacuum. It consisted of fine, gray particles, size one micron or less, mostly metallic vanadium as shown by the percentage analysis: 87.59 V (not including V in VO), 11.00 VO, 0.98 H_2, 0.28 C, 0.10 Fe and 0.01 Mn.

To convert this product into the monoxide it was thoroughly mixed with an amount of vanadium trioxide, 200 mesh, calculated from the equations

$$V + V_2O_3 = 3VO; \quad C + V_2O_3 = 2VO + CO;$$
$$2VH_x + 2V_2O_3 = 6VO + XH_2$$

By compressing the mixture in a steel cylinder at 70,000 lb./sq. in., the particles were brought in close contact. The resulting disc was placed in a covered platinum crucible supported by a fireclay crucible, and surrounded with an inverted 3 inch Pyrex tube connected to a liquid air trap and a vacuum pump. Under vacuum the crucible was heated with a water cooled induction coil until the platinum started to melt (1755°), and held at this temperature for about one hour, before being allowed to cool to room temperature. During the heating period the Pyrex tube was cooled with a strong air blast. A dark deposit of negligible weight was formed on the inside walls of the Pyrex tube; by spectrographic analysis it was found to contain gold, silver, copper, platinum and vanadium; all but the last one coming from the platinum itself.

The melting points of vanadium and vanadium trioxide are 1710 and 1970°, respectively. The vanadium was, therefore, melted with some attending vaporization, favoring contact and reaction with the solid trioxide.

The yield was a gray, porous, sintered disc of smaller dimensions than the original. Changes in some physical properties, given in Table I, indicate the formation of a new compound. The color changed from dark gray to medium gray.

TABLE I

PHYSICAL PROPERTIES

	Color	Specific gravity	Hardness Mohs scale
Mixture	Dark gray	5.13	V: 6–7
Yield	Medium gray	5.55 (25/4)	8–9

The specific gravity of the yield was determined by the pycnometer method at 25°. The hardness of the product is remarkable, exceeding that of metallic vanadium. It was determined with Vickers and Rockwell testers, and converted to the Mohs scale.

By chemical and spectrographic analysis the composition was found to be 99.68% VO, 0.13% SiO_2, 0.10% FeO, 0.03% CaO, 0.02% Al_2O_3, 0.01% CoO, less than 0.01% Pt, Cu, Ag, Sn.

X-Ray examination confirms the composition VO.

The powdered yield dissolves slowly in warm dilute hydrochloric acid, forming a blue or violet solution, characteristic of a hypovanadous salt. Vanadium trioxide gives a green solution under the same conditions. The yield dissolves faster in hydrofluoric acid, and readily in nitric acid with evolution of nitric oxide.

WASHINGTON 25, D. C.

(1) G. A. Meerson, G. A. Kats and A. V. Khokhlova, *J. Applied Chem. (U.S.S.R.)*, **13**, 1770 (1940), [C. A., **35**, 4712 (1941)].