

60 cc. of pyridine was added slowly to the well-stirred solution. A dark red oil was thus precipitated, and toward the end of the addition a light yellow solid began to separate. On thorough cooling in an ice-bath the red oil solidified (dry weight, 148 g.). Without drying the product or breaking up the lumps the pyridine compound was stirred into a solution of 300 g. of potassium cyanide in 500 cc. of water. Noxious gases were evolved and the material rapidly dissolved to give a solution which was first green and then yellow-brown. The mixture was heated on the steam-bath and stirred for one-half hour, filtered from a certain amount of black material, and evaporated on the water-bath until a large crop of amber-colored crystals had separated. After cooling, the material was collected and washed with a small amount of potassium chloride solution. The crystals collected in this way were usually contaminated with a considerable amount of black material, but the latter is not soluble in water and is easily removed. The crude product was dissolved in warm water, the solution was treated with animal charcoal, filtered, and to it there was added one to two volumes of alcohol. The potassium molybdocyanide soon separated in the form of golden-yellow crystals of great purity; yield, 100 g. Further evaporations of the cyanide mother liquor yielded, after two or three recrystallizations, 9 g. more of the pure product.

**Potassium Molybdicyanide Solution,  $K_2Mo(CN)_8$ .**—Oxidation to the pentavalent cyanide was carried out according to Olsson.<sup>20</sup> A solution of 4.4 g. of potassium molybdocyanide in 20 cc. of water and 10 cc. of 6 *N* sulfuric acid was titrated with a 10% solution of potassium permanganate until a pink color indicated complete oxidation. Fifty cc. of 10% silver nitrate solution was then added to precipitate the molybdicyanide in the form of the fine, brown-red silver salt. This was collected on a Büchner funnel washed with water, suspended in 50–100 cc. of water, and treated with 50 cc. of 10% potassium chloride solution. By shaking the mixture vigorously in a stoppered flask the silver salt was soon decomposed. The solution was filtered by suction from the silver chloride, clarified with animal charcoal and diluted to a volume of 250 cc. As the pentavalent molybdenum compounds are sensitive to light, the above operations were carried out in the dark-room.

The strength of the molybdicyanide solution was determined by electrometric titration with potassium ferrocyanide, and it was found to vary from 0.032 to 0.034 *M*. The solution was diluted to 0.030 *M* and stored in the dark. The fresh solution always contained a small amount of molybdocyanide, as revealed by the titration curve, and when exposed to the light of the laboratory the concentration of molybdicyanide decreased at the rate of about 0.2% per hour.

**Potassium Ferricyanide and Ferrocyanide Solution.**—These solutions were prepared by dissolving 0.03 mole of the salt in 200 cc. of water and diluting to 1 liter with the alcoholic buffer solution. The solutions decompose slowly and should be rejected after the second day.

**Procedure for the Determination of Critical Oxidation Potentials.**—The five reversible oxidation-reduction systems which were employed as reference systems are listed in Table X. Since the potentials of the complex cyanides vary considerably with dilution, it was essential to determine the normal potential under conditions comparable with those of the oxidation tests. For this purpose 20 cc. of the 0.03 *M* potassium ferrocyanide solution was added to 200 cc. of the buffer solution and titrated electrometrically with 0.03 *M* molybdicyanide solution, giving a curve from which the normal potential could be calculated. The potential of

<sup>20</sup> Olsson, *Ber.*, 47, 917 (1914).