# A STUDY OF THE REDUCTION OF POTASSIUM HEXACYANOMANGANATE(III) WITH POTASSIUM METAL IN LIQUID AMMONIA

by

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# I. INTRODUCTION

In a research project at the University of Kansas, Robert N. Hammer (1) had succeeded in obtaining a yellow product from the reduction of potassium hexacyanomanganate(III) by means of potassium metal in liquid ammonia. This product changed color immediately upon exposure to air, and exhibited other strong reducing properties. A search through the literature revealed that no manganese complex of this color and possessing such reducing properties had ever been reported previously. It was concluded therefore, that this was a new compound which probably contained manganese in a very low oxidation state. In Hammer's work the reduction product was not positively identified, nor was the oxidation state of the manganese in it definitely established.

The investigation reported herein was undertaken to study the nature of the yellow reduction product. The specific objectives were (a) to establish the identity of the compound and (b) to determine the oxidation state of the manganese therein.

The problem was approached in four ways:

(a) The combining ratio of the reactants was studied. The stoichiometric ratio of the reactants required for the reduction process suggested an equation for the reaction and a formula for the reduction product.

(b) The reduction product was analyzed directly. Since Hammer had encountered difficulty in the analysis of this compound, it was decided to try first various methods of analysis on known mixtures of potassium, manganese, and cyanide. From these studies a scheme of analysis was developed which was suitable for the accurate determination of these elements in a complex. These methods were applied to the analysis of the reduction product. Data from such determinations established an empirical formula for the reduction product.

(c) The reducing power of the yellow product was measured. Whereas direct analysis is the best criterion for establishing the composition of a new complex compound, a measurement of its reducing power (or oxidizing power) is equally important in determining the oxidation state of the metal. These measurements supplemented and were consistent with the direct analytical data.

(d) The magnetic susceptibility of the product was measured. Although, in general, magnetic measurements in themselves do not give direct indication of structures or formulas, they should be in approximate agreement with other experimental data. The magnetic measurements obtained supported the analytical data.

In the exploratory work of Hammer, techniques had been devised and an apparatus had been designed for carrying out the reduction. Therefore, the necessary alterations of the apparatus were minor and the difficulties encountered in the preparation of the reduction product were comparatively few.

# II. HISTORICAL REVIEW

## A. Preparation of the Lower Cyanomanganates.

In acid solution the most stable oxidation state of manganese is the divalent ion, and in basic solution the most stable state is tetrapositive manganese as the dioxide. However, in complex compounds, of which the cyanomanganates are the most typical, it is the tripositive state which is the most stable with respect to oxidation or reduction.

In these compounds, oxidation states above three are both rare and unstable. By treating an 80 per cent solution of potassium cyanide with a saturated solution of potassium permanganate, Yakimach (2) obtained an interesting eight-coordinated cyanomanganate of tetrapositive manganese, $K_4Mn(CN)_8$. The crystals were hydrolyzed almost immediately in water. Also, they were decomposed by concentrated acids, by alcohol, or by heating.

Cyanomanganates containing the central atom in an oxidation state less than three can be air oxidized to yield the complex containing manganese in the tripositive state. Therefore, they may be referred to as the lower cyanomanganates. The stable cyanomanganate(III) ion, $Mn(CN)_6^{=}$, is often used as a starting material for preparing cyanomanganates containing manganese in lower oxidation states.

1. Preparation of cyanomanganates containing dipositive manganese.

a. Sodium and potassium hexacyanomanganate(II).

Potassium hexacyanomanganate(II), $K_4Mn(CN)_6 \cdot 3H_2O$, can be prepared by the reduction of a solution of potassium hexacyanomanganate(III), $K_3Mn(CN)_6$, with potassium amalgam (3). It is more commonly prepared, however, by the well known method of Eaton and Fittig (4) and Descamps (5), which was later improved by Christensen (6) and Straus (7). In this method a solution of manganese(II) acetate is added to a concentrated potassium cyanide solution. An amber solution of the hexacyano complex results, from which the dark blue $K_4Mn(CN)_6 \cdot 3H_2O$ can be crystallized. If prepared in a nonoxidizing atmosphere its solution is almost colorless, but darkens upon exposure to air. From studies of dialysis coefficients, Brintzinger and Jahn (8) report that the hexacyanomanganate(II) ion holds six molecules of water when in solution, whereas the blue crystals hold but three molecules.

The glistening dark blue color of freshly precipitated $K_4Mn(CN)_6 \cdot 3H_2O$ changes to a dull lavender hue when the product is washed with alcohol and dried. This change in color has been attributed to partial dehydration of the compound. When dried in an almost pure nitrogen atmosphere the solid becomes superficially brown, a change which

is believed to be due to the formation of a higher oxide of manganese (1,9). Although $K_4Mn(CN)_6 \cdot 3H_2O$ is unstable in air, it is stable in a solution of excess cyanide ion.

The sodium salt is prepared in a similar manner.

b. Potassium tricyanomanganate(II). Potassium tricyanomanganate(II), $KMn(CN)_3$, is prepared by a slight variation of the above method. In a nitrogen atmosphere, the addition of potassium cyanide to a solution of manganese(II) acetate precipitates green $KMn(CN)_3$ (4,5,6,7). This precipitate dissolves very slowly in warm aqueous potassium cyanide solution to give the amber solution of the hexacyanomanganate(II). Although the green complex also is unstable in air, Goldenberg (9) found it could be preserved indefinitely in vacuo over sulfuric acid.

2. Preparation of cyanomanganates containing unipositive manganese.

a. Sodium and potassium hexacyanomanganate(I). Manchot and Gall have done some very important work in the preparation and identification of unipositive manganese compounds. In their first paper (10) they reported some indications of the existence of unipositive manganese in solution. Potassium hexacyanomanganate(II), prepared from manganese(II) acetate and potassium cyanide in the absence of air, was used as a starting material.

This complex, in sodium hydroxide solution, was reduced in an atmosphere of hydrogen by means of granular aluminum or Devarda's alloy. In the almost colorless solution streaks of yellow could be seen after addition of each particle of metal, and before long the entire solution had become intensely yellow. Since the reaction was exothermic, the temperature of the reduction was kept between 10° and 22°C by circulation of a cold brine solution through a cooling coil immersed in the reaction vessel. Below 10° the reduction was too slow, and above 22° decomposition was appreciable.

The yellow solution possessed strong reducing properties. When shaken with air, it was quickly decolorized. The solution readily evolved hydrogen upon boiling; even at room temperature, hydrogen was slowly liberated. Iodine was reduced to iodide, and litmus was immediately decolorized. Addition of hydrogen peroxide turned the entire solution blue. A mixture of anthraquinone with sodium hydroxide solution and alcohol became intensely red upon the addition of a few drops of the reduced solution. The yellow solution also reduced lead(II) and cadmium acetate solutions to finely divided precipitates of the free metals. The starting material, $K_4Mn(CN)_6$, exhibits none of these reducing properties. The bleaching of acidified indigo and

methylene blue solutions, and the reduction of ammoniacal silver nitrate, were much more rapid and intense than the effects produced by $K_4Mn(CN)_6$.

Two types of quantitative measurements were made on the yellow solution. The quantity of hydrogen evolved per unit weight of manganese in the sample was determined. The results of the determinations indicated that 44 and 46.3 per cent of the total manganese in the solution was in the unipositive state. The reducing power of the yellow solution was determined by measuring the quantity of iodine used in oxidizing the manganese to the dipositive state. The sample was placed in a measured volume of 0.1 N iodine solution containing 8 per cent of sodium hydroxide. After the solution had stood for one-half hour potassium iodide was added, the solution was acidified with hydrochloric acid, and the unreacted iodine was determined. The solution was then decomposed with sulfuric acid. Manganese was precipitated as the sulfide and dissolved with hydrochloric acid. It was then precipitated as manganese ammonium phosphate and ignited to the pyrophosphate. The results of three determinations showed 68.4, 72.0, and 80.2 per cent of the manganese in the yellow solution to be in the unipositive state.

Qualitatively, the existence of a unipositive

manganese complex in aqueous solution was convincingly demonstrated by these experiments. However, the quantitative aspects left something to be desired, since only 50 to 80 per cent reduction to the unipositive state could be demonstrated. Also, since the solid salt was not isolated, it was impossible definitely to determine the formula of the compound.

In their second paper (11), Manchot and Gall reported the isolation and definite identification of the reduction product. They prepared sodium hexacyanomanganate(I), $Na_5Mn(CN)_6$, in the following manner. $Na_4Mn(CN)_6$ was dissolved in a 2 per cent sodium hydroxide solution and reduced with granular aluminum in a hydrogen atmosphere. After the solution had become yellow, it was filtered into a concentrated solution containing sodium hydroxide and sodium cyanide, saturated with sodium acetate. A very fine white precipitate was separated from this solution by centrifugation and washed with alcohol. Treatment with alcohol or acetone dehydrated the salt, causing it to turn blue, but the white color was regenerated when water was added. The alcohol-moist precipitate was used for analysis. Manganese was determined as the pyrophosphate and sodium as the sulfate. The analyses gave sodium to manganese ratios of 4.97 and 5.01 to 1.

This salt exhibited the same reducing properties as the yellow solution from which it had been precipitated. A quantitative measurement of its iodine consumption gave 96.1 per cent of the theoretically expected for unipositive manganese. These data were taken to establish the composition of the white precipitate as a hydrate of $Na_5Mn(CN)_6$.

The corresponding potassium salt, $K_5Mn(CN)_6$, can be prepared in an exactly analogous manner, but Manchot and Gall found it more expedient to start with the sodium salt, $Na_4Mn(CN)_6$. As before this compound was reduced with granular aluminum in a 2 per cent sodium hydroxide solution. It was filtered into a concentrated solution of potassium hydroxide and potassium cyanide, saturated with potassium chloride. The white precipitate from this solution was washed with cold water, and the still moist substance was analyzed for potassium and manganese. The potassium was weighed as the sulfate. The analyses gave potassium to manganese ratios of 5, 5.27, and 5.02 to 1. This product, which also possessed strong reducing properties gave 96.4 per cent of the theoretical iodine consumption for unipositive manganese. Thus, good evidence for the existence of $K_5Mn(CN)_6$ was presented.

b. Sodium and potassium tricyanomanganate(I). Manchot and Gall (11) reported that when the unipositive

manganese complex was precipitated from a solution which did not contain cyanide ion, a product was obtained which contained less alkali metal than corresponded to the formula for the hexacyano compound. The potassium to manganese ratio depended upon the method and extent of washing of the solid. The ratio decreased to as low as 1.88 and 1.84 to 1 on prolonged washing, but intermediate ratios, e.g., 4.29 and 2.85 to 1, were also obtained. Manchot and Gall concluded that the existence of salts having the empirical formulas $Na_2Mn(CN)_3$ and $K_2Mn(CN)_3$ is very probable.

c. Potassium tetracyanomanganate(I). Grube and Brause (12) reported the isolation of a white finely divided solid, potassium cyanomanganate(I), by the electrolytic reduction of potassium hexacyanomanganate(II) at 0°C. A potential of 0.225 volt was applied between polished platinum foil electrodes, with a 1.5N potassium cyanide anolyte in a diaphragm cell from which air was excluded.

Analysis of their preparation showed that the composition approached that of a compound $K_3Mn(CN)_4$, although the substance contained 1 to 1.5 per cent less manganese, and up to a 1 percent more potassium and cyanide than corresponded to the theoretical formula. Their results were as follows:

| | Potassium | Manganese | Cyanide |
|---|---|---|---|
| Found | 43.35% | 18.73% | 38.00% |
| | 43.27 | 18.87 | 38.22 |
| | 43.10 | 18.25 | 38.41 |
| Average | 43.24 | 18.62 | 38.21 |
| Theoretical | 42.47 | 19.88 | 37.66 |

Grube and Brause conducted a titration of the manganese complex with standard potassium ferricyanide solution, and reported that 90 per cent of the manganese in the complex was in the unipositive state. These investigators believed that the discrepancy in the analytical results could be attributed to superficial oxidation. On the other hand, Manchot and Gall (11) contended that the material obtained by these investigators was either a mixture of $K_2Mn(CN)_3$ and $K_5Mn(CN)_6$ or partially oxidized $K_5Mn(CN)_6$.

d. The double salt $K_2Mn(CN)_3 \cdot K_4Mn(CN)_6$. Treadwell, Gübeli, and Huber (13) repeated the work of Grube and Brause and proposed an entirely different formula for the product of electrolytic reduction. On the basis of previous solubility studies, Treadwell and co-workers claimed that the compound, $K_3Mn(CN)_4$, should be very soluble, whereas Grube and Brause had pointed out that the white compound they obtained was so slightly soluble

that they were unable to measure its solubility quantitatively. Treadwell, Gübeli, and Huber studied the electrolytic reduction product in potassium cyanide solution by a potentiometric titration with potassium ferricyanide. They reported that this white insoluble product required only half as much titrant to oxidize the manganese to the dipositive condition as was necessary to oxidize the resulting cyanide complex of dipositive manganese to the tripositive state. Analyses for potassium, manganese, and cyanide gave an approximate ratio of 6:2:9. From these data it was concluded that the reduction product was a double salt, $K_2Mn(CN)_3 \cdot K_4Mn(CN)_6$, rather than the complex $K_3Mn(CN)_4$.

Thus, conflicting data and contradicting statements have arisen among these groups of investigators. Each has proposed a different formulation for the electrolytic reduction product, but all have agreed that it contains at least some manganese in the unipositive state.

e. Potassium nitrosylpentacyanomanganate(I). Manchot and Schmid (14), and later Blanchard and Magnusson (15), reported the preparation of a potassium nitrosylcyanomanganate of the formula $K_3Mn(CN)_5NO$. The compound was prepared from an alkaline solution of manganese(II) chloride (or acetate), potassium cyanide, and potassium acetate in a nitric oxide atmosphere. Both the hydrated

and the anhydrous solids were moderately stable, particularly in closed containers in the absence of light. The dark violet-red water solution of the compound became turbid after standing for a day. Dilute mineral acids had no immediate effect, but after about two hours the color changed to a strong yellow. The color also changed slowly in both ammonium and sodium hydroxide solutions. The compound gave characteristic precipitates with manganese(II), zinc, ferrous, ferric, bismuth, and silver ions.

Although quantitative data were lacking, on the basis of qualitative observations Manchot and Schmid assumed that the NO group was a neutral addendum and concluded that the oxidation state of manganese in this compound was +2.

Later, Mellor and Craig (16), in magnetic studies of NO-containing complexes, found that $K_3Mn(CN)_5NO$ was diamagnetic and concluded that the NO group behaved as a positively charged addendum and that the complex contained unipositive manganese. Their reasoning was based upon a consideration of the following possibilities:

(a) If the NO group in the complex were positively charged ($:N\equiv O:^{+}$), the manganese central atom would have a single positive charge with no unpaired electrons.

(b) If the NO group were neutral (:N≡O:), the manganese atom would be dipositive with one unpaired electron, and the NO group would also have an unpaired electron. Such a molecule should have a magnetic moment corresponding to two unpaired electrons.

(c) If the NO group were negative (:N̈=Ö:⁻), the manganese atom would be tripositive and would have two unpaired electrons.

Thus, the magnetic measurements exclude all but the first case, in which manganese is unipositive. This problem provides a good example of the usefulness of magnetic measurements in inorganic chemistry. It also shows the ambiguity resulting from the assumption of a charge for the NO group without the aid of some supporting evidence. This group is known to exist positively and negatively charged, as well as neutral, in complex compounds.

B. Magnetic Studies on the Cyanomanganates.

In order to obtain the most accurate value for the magnetic moment of a paramagnetic substance, the magnetic susceptibility must be measured at two or more temperatures and the moment calculated according to the Curie-Weiss equation, $\mu = 2.84\sqrt{\chi_m (T-\vartheta)}$, where $\mu$ is the magnetic moment in Bohr magnetons, $\chi_m$ is the molar susceptibility, T is the absolute temperature, and $\vartheta$ is the molecular field constant or Weiss constant (17).

For many compounds the molecular field constant is approximately zero. For this reason in most cases magnetic measurements are made at only one temperature, and the moment is calculated according to the abbreviated Curie equation, $\mu = 2.84\sqrt{\chi_m T}$. Whereas the simple Curie law is adequate for most compounds, some compounds which contain elements close to iron in the periodic system deviate appreciably from this law.

Manganese(III) phosphate offers a good example of such deviation (18). If the Curie equation is used, the measured susceptibility gives a moment of only 4.49 Bohr magnetons, a value much lower than the theoretical 4.90 for manganese(III) ion. However, it has been shown that manganese(III) phosphate follows the Curie-Weiss law with a Weiss constant of -53. A recalculation of $\mu$ on this basis gives an effective moment of 4.89 Bohr magnetons, in excellent agreement with theory.

Several investigators have measured the susceptibilities of various cyanomanganates. In a recent article Goldenberg (9) reported a comprehensive study of the magnetic properties of both simple and complex manganese compounds. In it he summarized the results of his own careful measurements as well as those of others which are reported in the literature.

Table I presents a summary of the magnetic data for the cyanomanganates as taken from Goldenberg. The literature reference is noted, t is the centigrade temperature, $\chi$ is the measured susceptibility per gram, $\chi_m$ is the measured susceptibility per mole, $\delta$ is the correction for the diamagnetic contribution of the various constituents, $\mu_{obs}$ is the observed magnetic moment in Bohr magnetons, $\mu_{calc}$ is the theoretical magnetic moment as calculated from the expression $\mu = \sqrt{n(n+2)}$, and n is the number of unpaired electrons in the compound.

In commenting on the data, Goldenberg emphasized two facts. First, the compounds were investigated at only one temperature; therefore, the magnetic moment was calculated according to the approximate Curie equation. Second, but few of the observations have been accompanied by accurate analyses proving the identity of the compound, and this deficiency of analytical data may well account for many of the anomalies in susceptibilities reported in the literature.

Most of the observed data show considerable inconsistency, although they correspond roughly to the theoretical values. However, Goldenberg showed in some instances that if the measured susceptibilities were corrected by amounts equivalent to the impurities

TABLE I

MAGNETIC PROPERTIES OF THE CYANOMANGANATES

| Substance | Lit. Ref. | t | $\chi$ | $\chi_m$ | $\delta$ | $\mu_{obs}$ | $\mu_{calc}$ | n |
|---|---|---|---|---|---|---|---|---|
| $K_3Mn(CN)_6$ | 9 | 19.1 | 13.5 | 4423 | -100 | 3.25 | 2.83 | 2 |
| | 17 | 19.0 | 16.7 | 5478 | -100 | 3.61 | 2.83 | 2 |
| | 20 | 25.0 | 10.8 | 3543 | -100 | 2.95 | 2.83 | 2 |
| | 21 | 18.5 | 14.8 | 4980 | -100 | 3.40 | 2.83 | 2 |
| $K_3Mn_2(CN)_9 \cdot 4KOH$ | 9 | 18.5 | -0.7 | -49 | -167 | 0.62 | --- | -- |
| $K_4Mn(CN)_6 \cdot 3H_2O$ | 20 | 23 | 4.1 | 1727 | -149 | 2.11 | 1.73 | 1 |
| | 21 | | 4.5 | 1790 | -149 | 2.04 | 1.73 | 1 |
| | 22 | | | 3300 | -149 | 2.78 | 1.73 | 1 |
| | 9 | 17.6 | 4.53 | 1906 | -149 | 2.18 | 1.73 | 1 |
| $KMn(CN)_3$ | 9 | 18.7 | 44.1 | 7585 | -44 | 4.22 | 3.87 | 3 |
| $K_5Mn(CN)_6$ | 9 | 15.2 | 0.86 | 349 | -121 | 1.04 | 0.00 | 0 |
| | 23 | 20 | 3-5 | 1200 | -121 | 1.76 | 0.00 | 0 |

found by analysis, the moments would be in good agreement with the theoretical values. Since it is difficult to prepare dry samples of manganese complexes which do not contain small amounts of oxides as impurities, the poor agreement shown in the data is not surprising.

Regarding the data for $K_5Mn(CN)_6$, Selwood (18) states: "The magnetic data suggest that not more than one electron is left unpaired in this cyanide, but it is not clear why the compound should not be diamagnetic. The slight paramagnetism may be due to partial oxidation, or perhaps to temperature independent paramagnetism."

Goldenberg prepared the unipositive manganese cyanide complex according to the method of Manchot and Gall (11). The white product, when exposed to air, immediately acquired a blue color on its surface. Because of the slowness of the filtration involved, and the consequent danger of oxidation, the product was washed considerably fewer times than had been advocated by Manchot and Gall. Hence the analyses did not check well with the calculated values. (Found: Mn, 10.57%; CN, 33.95%; calculated for $K_5Mn(CN)_6$: Mn, 13.55%; CN, 38.43%). The magnetic moment was calculated on the basis of the actual manganese content.

It should be pointed out that although the magnetic

moments for $K_5Mn(CN)_6$ reported by Goldenberg (9) and by Bhatnagar, Prakash, and Maheshwari (23) are quite large, only a small amount of impurity need be present to give such values. Simple calculations show that less than one per cent of manganese(II) hydroxide (which has five unpaired electrons), if present as an impurity, would be sufficient to give a moment of the magnitude reported by Goldenberg.

C. Reduction Reactions in Liquid Ammonia.

Liquid ammonia and some of the lower primary amines are unique in their ability to dissolve the alkali and alkaline earth metals. While water is a convenient medium in which to carry out reactions with strong oxidizing agents, it is not at all adapted to the carrying out of reactions with strong reducing agents. The effectiveness of strong reducing agents in water is limited by the fact that reducing agents stronger than hydrogen liberate hydrogen from water. Since the combination of an electron with an atom constitutes reduction, solutions of the alkali metals in liquid ammonia are the most powerful reducing agents available for carrying out reductions in a homogeneous system (24).

The reactions of such alkali metal solutions with simple salts have been rather thoroughly studied. Most salts of heavy metals, such as those of manganese, cad-

mium, lead, iron, silver, copper, zinc, and nickel, are reduced to the free metal in a finely divided state, which may or may not catalyze the reaction of the alkali metal with the solvent. Some salts react to form intermetallic compounds with the alkali metals. This is illustrated by the reaction of bismuth(III) iodide with sodium to give the compounds $Na_3Bi$, $Na_3Bi_3$, and $Na_3Bi_5$. Still other salts are not reduced, but are converted to compounds of the ammine type, such as $Zr(NK)_2 \cdot NH_3$ (25,26,27).

A number of complex compounds, including the cyanide complexes of silver, copper, zinc, and cadmium, also are reduced to the free metal. This is what would be expected for a complex ion which is markedly dissociated in solution. However, it has been shown that some coordination compounds which contain cyanide groups are reduced to new complexes in which the central atom has an unusually low oxidation state (27). This is not surprising, since solutions of the alkali metals in liquid ammonia are very strong reducing agents, and cyanide groups tend to stabilize lower oxidation states. The spectacular findings in this relatively unexplored area have commanded much attention in the last decade.

The first report of this type of reduction was reported in 1942 by Eastes and Burgess (28). They

prepared a dense bright red precipitate of potassium tricyanonickelate(I), $K_2Ni(CN)_3$, by treating an excess of potassium tetracyanonickelate(II), $K_2Ni(CN)_4$, with potassium metal in liquid ammonia. When the alkali metal was in excess, the dipositive complex was reduced to a bulky yellow to copper colored solid which possessed strong reducing properties. The compound was analyzed for potassium, nickel, and cyanide. The analyses showed the ratio K:Ni:CN to be approximately 4:1:4. Also, two moles of potassium per mole of the starting material were required for this reduction. The analytical data and the reacting ratio evidence indicated that a new compound, $K_4Ni(CN)_4$, had been prepared which contained nickel in an oxidation state of zero.

Potassium tricyanonickelate(I), which may also be prepared by the reducing action of amalgams in aqueous solution, was slowly oxidized in air, and reduced silver nitrate and iodine. It dissolved in water to give a red solution which slowly liberated hydrogen and finally turned yellow. It was converted to potassium tetracyanonickelate(0), $K_4Ni(CN)_4$, by an excess of potassium and potassium cyanide in liquid ammonia. The compound of zerovalent nickel was rapidly oxidized in air. It dissolved in water, liberating hydrogen to give a red solution of the unipositive nickel material.

The sodium and calcium complexes of both unipositive and zerovalent nickel also were prepared. They exhibited the same colors and chemical properties as the corresponding potassium salts.

With the exception of the metal carbonyls, potassium tetracyanonickelate(0) was the first compound to be reported which contained a metal in the zerovalent state. Actually, the cyanide ion and the carbon monoxide molecule are isoelectronic; therefore potassium tetracyanonickelate(0) and nickel tetracarbonyl, $Ni(CO)_4$, are analogous. The fundamental difference lies in the fact that the cyanide groups carry negative charges which must be balanced by corresponding charges on positive ions.

Burbage and Fernelius (29) reported that potassium tetracyanopalladate(II), $K_2Pd(CN)_4$, resembled the corresponding nickel complex in that reduction by a solution of potassium in liquid ammonia yielded a moderately soluble white precipitate with the composition $K_4Pd(CN)_4$. Here again was a compound of a metal in the zerovalent state. Potassium tetracyanopalladate(0) reduced silver and mercuric ions to the metals, and azobenzene to hydrazobenzene. Although it was stable enough to permit isolation, it slowly decomposed in a vacuum or in contact with liquid ammonia. No intermediate compound

analogous to $K_2Ni(CN)_3$ was found. However, by the action of potassium amalgam on $K_2Pd(CN)_4$ in aqueous solution Manchot and Schmid (30, 31) obtained a clear colorless solution which possessed strong reducing properties. The compound responsible for these characteristics was not isolated.

Potassium tetracyanoplatinate(II), $K_2Pt(CN)_4$, also reacted with a solution of potassium in liquid ammonia (29), but the complete characterization of the product was precluded by the relative insolubility of $K_2Pt(CN)_4$ and the marked evolution of hydrogen. When the reaction was carried out in the presence of potassium amide, very little hydrogen was evolved, and the reacting ratio was 2.06 gram-atoms of potassium per mole of platinum complex. Analysis of the white reduction product gave the following results. Found: K, 31.3%; Pt, 43.05%; calculated for $K_4Pt(CN)_4$: K, 34.32%; Pt, 42.84%. With no better analytical agreement than this the compound could not be positively identified as potassium tetracyanoplatinate(0), but the agreement is good enough to suggest that the compound probably contained platinum in the zerovalent condition.

A few attempts have been made by Fernelius and coworkers to reduce other cyanide complexes in a similar manner. However, the results were not conclusive, and

therefore were never published. Fernelius and Hood (32) reduced potassium hexacyanomanganate(III) by means of potassium in liquid ammonia and obtained a light orange product. Data from the analysis of the reduction product suggested $K_5Mn(CN)_6 \cdot NH_3$ as its probable formula, although the data did not correspond well with any simple formula. Fernelius and Bigelow (33) similarly investigated the reduction of potassium ferricyanide, $K_3Fe(CN)_6$, potassium hexacyanocobaltate(III), $K_3Co(CN)_6$, and potassium hexacyanochromate(III), $K_3Cr(CN)_6$. Apparently, the ferricyanide was reduced to the ferrocyanide and no further. Brown precipitates were obtained from both $K_3Cr(CN)_6$ and $K_3Co(CN)_6$. The investigators concluded that the cobalt and chromium in the complexes were both reduced to lower oxidation states, but neither the reacting ratios of complex to potassium nor the analytical compositions of the brown precipitates were consistent.

## III. PREVIOUS WORK IN THIS LABORATORY

The work of Robert N. Hammer on the reduction of manganese compounds by means of potassium in liquid ammonia was begun in 1947. He spent considerable time in designing an apparatus and in perfecting manipulative techniques for carrying out such reduction reactions. A yellow solid with strong reducing properties was prepared from potassium hexacyanomanganate(III). When it became evident that the definite characterization of this product would be very time-consuming, the problem was terminated with the qualitative information at hand. Some analyses and magnetic measurements were made, but these were regarded as having qualitative significance only.

Hammer tried three starting materials before a suitable one was found. First used was anhydrous manganese(II) chloride, prepared by heating $MnCl_2 \cdot 4H_2O$ almost to the fusion point in a stream of dry hydrogen chloride gas. It seemed probable that the manganese cyanide complex $K_4Mn(CN)_6$ could be prepared in liquid ammonia by treatment of the anhydrous manganese(II) chloride with excess potassium cyanide. This method, however, was not satisfactory, since the manganese(II) chloride swelled excessively in liquid ammonia, and also because it was difficult to wash out the chloride ion.

In all previous studies conducted in aqueous media, the dipositive manganese compound $K_4Mn(CN)_6 \cdot 3H_2O$ had been used as the starting material, but the three molecules of water associated with the compound made it unsuitable for liquid ammonia work. Hammer attempted to dehydrate the compound completely. The blue crystals were purified by recrystallization from aqueous potassium cyanide solution, washed with alcohol, and quickly transferred to a vacuum desiccator which contained fresh phosphoric anhydride. He found, as had Goldenberg(9), that the solid invariably became superficially brown on standing over night. This was true even when the residual air in the evacuated desiccator was immediately replaced by nitrogen which had been passed over hot copper turnings. The brown color was ascribed to the presence of a higher oxide of manganese; hence, this material was not regarded as a satisfactory starting material.

Finally it was found that the tripositive manganese cyanide complex, $K_3Mn(CN)_6$, could be crystallized from aqueous solution without any water of hydration. This material was recrystallized several times from water, ground to a fine powder, and dried in a stream of dry air at reduced pressure. The product proved to be a satisfactory starting material for the reduction reaction.

In Figure I is shown the design of an apparatus similar to the one constructed by Hammer. The system, which was the result of continual modification during the course of his work, provided for a large variety of manipulations associated with reactions in liquid ammonia. Since only minor changes were necessary for the present investigation, the apparatus will be described in another section. Likewise, the general manipulative procedure and special techniques will be discussed later.

After the apparatus had been constructed and suitable techniques developed, Hammer conducted several reduction reactions. In most of these an excess of potassium was introduced and then the manganese complex was added. The yellow product always was obtained and samples were taken for study.

Hammer reported that when the potassium was added in small increments to the potassium cyanomanganate(III), intermediate colors of dull blue-gray, streaks of green, and sometimes a white precipitate could be detected. These colors probably correspond to $K_4Mn(CN)_6$, $KMn(CN)_3$, and $K_5Mn(CN)_6$, respectively.

The reduction product was analyzed for potassium, manganese, and cyanide. Samples were decomposed with sulfuric acid in a modified Kjeldahl apparatus (34), and the hydrocyanic acid liberated was distilled into

dilute sodium hydroxide solution. The cyanide in this solution was then determined by titration with standard silver nitrate solution, according to the Liebig-Dénigès procedure (35). The manganese and potassium in the residue from the distillation were separated by the precipitation of manganese either as sulfide (36) or dioxide (37). Manganese was then determined by the bismuthate method (38, 39), and the potassium was weighed as sulfate after treatment of the solution with sulfuric acid, evaporation, and ignition to constant weight (40).

These analytical methods were tried out on the starting material, $K_3Mn(CN)_6$. The results, as listed in Table II, were all lower than the theoretical percentages. The relatively large deviations from the theoretical values suggest that the analytical methods used were not suitable for the analysis of this compound. Hammer's principal analytical difficulties lay in the cyanide determination, which gave results several per cent too low, and in the separation of manganese from potassium. The formation of free sulfur made the filtration of manganese (II) sulfide so difficult that this method was abandoned. The separation of manganese as the dioxide, however, was far from ideal because of the difficulty of precipitating this compound quantitatively.

TABLE II

ANALYSIS OF $K_3Mn(CN)_6$ BY HAMMER

| | Potassium | Manganese | Cyanide |
|---|---|---|---|
| Found | 33.3% | 14.9% | 41.1% |
| | 34.2 | 16.0 | 42.0 |
| | 34.3 | 15.9 | 41.3 |
| | | | 42.4 |
| | | | 42.7 |
| Average | 33.9 | 15.6 | 41.9 |
| Theoretical | 35.7 | 16.7 | 47.6 |

Mn:K = 1:3.05

Mn:CN = 1:5.68

TABLE III

ANALYSIS OF THE REDUCTION PRODUCT BY HAMMER

| | Potassium | Manganese | Cyanide |
|---|---|---|---|
| Found | 45.7% | 12.6% | 32.5% |
| | 47.0 | 12.8 | 33.9 |
| | | 12.1 | 32.4 |
| Average | 46.4 | 12.5 | 32.9 |

Mn:K = 1:5.2

Mn:CN = 1:5.6

In Table III are listed Hammer's results for the analysis of the reduction product. The ratio found for K : Mn : CN, 5.2 : 1 : 5.6, does not agree well with any simple formula, but most nearly corresponds to $K_5Mn(CN)_6$.

Magnetic susceptibilities were measured on a Gouy balance, by the method described by Thompson (41). Measurements were carried out at 26°C. For the starting material, $K_3Mn(CN)_6$, a gram susceptibility value of $13.61 \times 10^{-6}$ was obtained. This gave an effective moment of 3.31 Bohr magnetons, as compared with a theoretical value of 2.85 Bohr magnetons.

Three samples of the reduction product yielded gram susceptibility values of 1.70, 1.86, and $3.04 \times 10^{-6}$ c.g.s. unit. To calculate an effective moment, it was necessary to assume a formula for the compound. The effective moment obtained (in Bohr magnetons) on the basis of the formulas which Hammer assumed follow:

| | $K_5Mn(CN)_6$ | $K_4Mn(CN)_4$ | $K_6Mn(CN)_6$ |
|---|---|---|---|
| Sample 1 | 1.29 | 1.14 | 1.35 |
| Sample 2 | 1.35 | 1.19 | 1.41 |
| Sample 3 | 1.72 | 1.52 | 1.80 |

All but one of the values are between those expected for a compound with one unpaired electron, as in

$K_6Mn(CN)_6$, and for one with no unpaired electrons, as in $K_5Mn(CN)_6$. Hammer pointed out that the sampling tubes were filled in the order 3,2,1. Since sample 3 had undergone the least oxidation, the magnetic data for it were regarded as being the most significant.

Hammer modestly stated that "The data obtained in this investigation should have little more than qualitative significance (1)". However, from the color and the strong reducing properties of the yellow product, he concluded that it was unlike anything previously prepared in aqueous media. From the analytical and magnetic data it was evident that manganese was present in either the unipositive or the zerovalent state. To reconcile the analytical data with the magnetic data, Hammer suggested the presence of $K_6Mn(CN)_6$ and $K_4Mn(CN)_6$ in approximately equimolar proportions. Each has one unpaired electron, and the composition of the mixture corresponds to the empirical formula $K_5Mn(CN)_6$.

# IV. EXPERIMENTAL

## A. The Reduction

By following Hammer's method for the reduction of potassium hexacyanomanganate(III) with potassium metal in liquid ammonia, it was possible to prepare consistently the yellow reduction product with which this investigation is concerned.

1. The Starting Material. The starting material, potassium hexacyanomanganate(III) was prepared by the reaction of manganese(III) phosphate with potassium cyanide (3,42). Manganese(III) phosphate was made by concentrating nearly to dryness an aqueous solution of manganese(II) chloride, phosphoric acid, and nitric acid. The gray-green precipitate of manganese (III) phosphate was washed with water and dried. It was slowly added, with continuous stirring, to an excess of a concentrated potassium cyanide solution at 80°C. (Overheating causes formation of manganese(III) oxide.) When all of the precipitate had dissolved the solution became deep red in color. This solution was allowed to cool and was then air-evaporated. The red crystalline needles of $K_3Mn(CN)_6$ were filtered off on a sintered-glass filter and sucked dry.

Several attempts were made to purify the salt by recrystallization from water, as suggested by Lower

and Fernelius (3). In the first recrystallization from water a brown oxide of manganese appeared on the liquid surface and on the sides of the crystallizing dish. In the second, third, and subsequent recrystallizations an increasingly larger amount of the brown oxide was quickly formed. The oxide was removed by filtration in some cases, but more appeared before crystals could be formed. Heating proved to be disastrous to the purity of the product. Evidently, the manganese(III) complex is readily hydrolyzed unless an excess of cyanide ion is present. Hammer had experienced the same difficulty. He used the product from the first recrystallization from a potassium cyanide solution, which probably contained a little oxide, and of course, some potassium cyanide.

It was decided that, for this investigation, it would be necessary to have as pure a starting material as possible, in order that the analytical data for the reduction product might have the desired significance. After several attempts to purify the salt by recrystallization from water had failed, it was decided to try precipitation from alcohol. The procedure which proved to be the most successful is as follows:

The impure crystals from the potassium cyanide solution were placed in a large fritted-glass filter

of medium porosity. This was attached to a filter flask containing absolute ethyl alcohol. Just sufficient water was added to the crystals to dissolve them. The troublesome brown oxide, which began to form as soon as the water was added, was removed when the solution was drawn through the filter by means of an aspirator. As fast as the solution came through the filter it dropped into the alcohol, where it was immediately precipitated. Sufficient alcohol was used so that at the end of the precipitation the supernatant liquid was at least two-thirds alcohol. Apparently no hydrolysis took place in the alcohol solution, because no brown oxide was observed.

Analysis for manganese was carried out on starting material which had been prepared and treated in the following ways: (a) the crude impure crystals from potassium cyanide solution, (b) the same, but rinsed with a small amount of water to remove adhering potassium cyanide, (c) after one precipitation from alcohol, and (d) after several reprecipitations from alcohol.

Since manganese(III) oxide is high in manganese content, high percentages indicate probable contamination with the oxide, and low percentages indicate possible contamination with potassium cyanide. Only in the case of the impure material (a) does the analysis

differ greatly from the theoretical value. The analyses indicate that in (b) and (c) the amount of impurity is probably very small, although in (b) there may be partially compensating impurities. Only in (d), however, does the manganese content agree closely with the theoretical percentage.

The results are shown below in Table IV.

TABLE IV

ANALYSIS OF THE STARTING MATERIAL FOR MANGANESE

| (a) | (b) | (c) | (d) |
|---|---|---|---|
| 12.90% | 16.59% | 16.85% | 16.71% |
| 13.37% | 16.58% | 16.91% | 16.69% |

Theoretical for $K_3Mn(CN)_6$ = 16.73%

In view of the results of these analyses, all of the starting material was purified by at least three precipitations from alcohol. It was then dried in the following manner. Open weighing bottles containing the starting material were placed in a large glass tube. One end was connected to a vacuum pump and the other end to a drying tube which contained anhydrous magnesium perchlorate. A stop-cock was attached to the drying tube. When the pump was running, the stop-cock was adjusted so that a small stream of dry air at reduced

pressure was slowly drawn through the tube. By this method, the material was obtained dry in a few days.

2. The Apparatus. In Figure I is shown the design of the apparatus which was used in this investigation to carry out the reduction reactions. In general, it is the same as that used by Hammer. Some parts of the apparatus were eliminated, and a few other modifications were made. A device for sampling the product, which had proved to be unsatisfactory, was eliminated. Also, a chamber for drying the ammonia was not required, because the ammonia from the cylinder (Spencer's refrigeration grade) was sufficiently pure and dry.

The apparatus was constructed entirely of Pyrex-glass with standard taper joints. Individual sections of the apparatus were connected with flexible Tygon tubing. The use of Tygon practically eliminated the fractures due to stress and strain on the apparatus which had plagued Hammer throughout his work.

The reaction chamber was about 3.5 centimeters in diameter and approximately 25 centimeters long. Duplicate sampling bulbs A and B served to hold the starting materials, potassium and potassium hexacyanomanganate(III). The bulbs containing the solids were inserted in the apparatus through ground glass joints. When the reaction was started, the reagents were introduced by rotat-

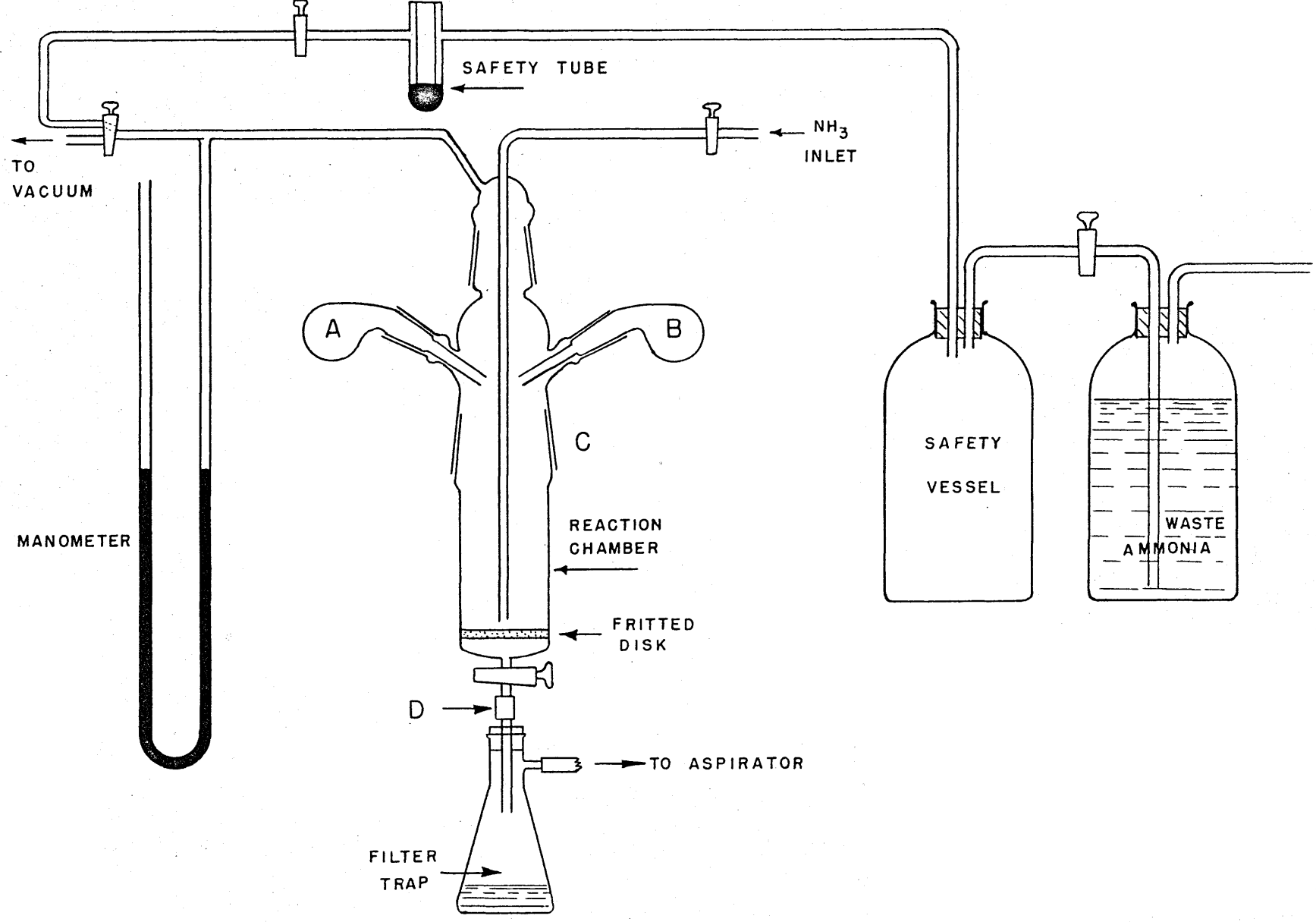


Figure 1 — Apparatus for Reactions in Liquid Ammonia

ing the bulbs in their joints until, in the inverted position, the solids slid into the reaction chamber. The ammonia delivery tube extended to the bottom of the reaction chamber so that the ammonia which bubbled through would have a stirring effect on the suspension.

The fritted-glass disk in the reaction chamber served to hold the insoluble solid which was formed in the reaction. A filter trap could be attached at D so that the solvent could be withdrawn by means of an aspirator. At C, a large standard-taper joint permitted the removal of the lower part of the reaction chamber for sampling purposes.

A manometer was attached to indicate the internal pressure. A two-way stop-cock in the system supplied an outlet through which the system could be evacuated. The waste ammonia was absorbed in a carboy which was filled almost completely with water. The delivery tube, which extended almost to the bottom of the absorption vessel, caused a positive pressure head in the system approximately equal to this head of water.

Two safety devices were employed in the apparatus. The first was a safety tube filled with mercury. It permitted air to be drawn into the system if the pressure became too low, and it acted as a release valve for ammonia if the pressure became too great. The other

safety device was a large carboy through which the exit ammonia passed before being absorbed in a similar carboy. The large volume of the vessel served to damp sudden fluctuations in pressure. Its prime purpose, however, was to contain any water from the absorption vessel which might back up if the ammonia pressure became too low. It is not difficult to imagine what might have happened if the water had been permitted to back through the apparatus to the compartment containing potassium.

A large dry box was acquired for use in sampling the reduction product. The box was of the two-compartment type, with a large window, three glove holes, and a large working space. To keep the box dry anhydrous calcium chloride was placed on the floor of the box and covered with a heavy wire screen. In order to have an oxygen-free atmosphere in the dry box it was flushed with ammonia gas. Nitrogen was not used because of the difficulty in removing the last traces of oxygen.

3. Manipulative Techniques. The general features of manipulative procedure for carrying out reactions in liquid ammonia systems have been well described in the literature (26, 28, 43). However, because of special difficulties which arose, Hammer found that some special techniques became necessary.

To prepare the apparatus for a reaction, the several pieces of the reaction chamber assembly were cleaned and dried in an oven at 110°C. The apparatus was then completely assembled except for the side bulbs. The openings for the bulbs were stoppered with standard-taper plugs. Ammonia was passed through the system for at least an hour to sweep out the air and to dry the apparatus completely.

The side bulbs were charged with starting materials and flushed with ammonia. Then the bulbs were quickly inserted in their proper places in the apparatus. A positive internal pressure prevented air from entering while this was being done.

Hammer had devised a novel method for introducing oxide-free potassium to the reaction chamber. A specially designed side tube was filled with pieces of potassium. Before the ammonia had been condensed in the reaction chamber, the amount of potassium required for the reduction was introduced by melting the metal, and, by means of a vacuum pump, drawing it through a capillary into the reaction chamber.

However, that method was not suitable in this investigation. In order to study the ratios of the reactants it was necessary to devise means for weighing both of them. It was possible to suspend a bulb from the beam

of an analytical balance by means of a wire. Thus, by weighing the bulb before and after filling, it was not at all difficult to weigh out the desired quantity of the starting material, $K_3Mn(CN)_6$. It was somewhat more difficult to weigh the potassium and to introduce it to the system without its becoming oxidized. This could conceivably be done by weighing the potassium under an inert liquid.

Ether was the first liquid which was tried. The bulb containing some very dry ether, was weighed. A few pieces of potassium were cut under dry ether and quickly transferred to the bulb, which with its contents, was again weighed. The bulb was flushed out with ammonia to displace the air and then inserted in the apparatus. The ether soon evaporated and the reactants were ready to be added.

Several milliliters of ammonia were condensed by means of a cooling bath which surrounded the reaction chamber. The cooling bath consisted of a Dry Ice - isopropyl alcohol mixture in an unsilvered Dewar flask. By rotating the bulb, the potassium was added to the liquefied ammonia in the chamber. Then the starting material was added in the same way. Apparently the final product was the same whether the reactants were added

a little at a time or all at once, and it was also immaterial which reagent was added first.

The yellow product prepared in this manner was so unstable that representative samples could not be taken for analysis. The product turned perceptibly gray, even on standing for a very short time in weighing bottles which contained the ammonia atmosphere of the dry box, and its weight changed so rapidly that it was futile to try to weigh samples accurately.

The principal reason that ether was not a satisfactory liquid for use in weighing potassium was that by the time the weighing was completed some of the ether had evaporated. Thus the weight of potassium was not sufficiently accurate for reacting ratio studies. Benzene and the common aliphatic hydrocarbons were also too volatile. Toluene was tried because it seemed to possess suitable volatility and it also was available in a fairly dry condition.

The potassium was cut and weighed under dry toluene and inserted in the apparatus as before. Since the toluene did not evaporate off in any convenient length of time, it was poured into the reaction vessel along with the potassium. Surprisingly, the reduction product prepared with potassium weighed under toluene was considerably more stable than any which had been previously

prepared. Its color and composition did not change rapidly in the weighing bottles. Apparently a protective coating was formed on the particles of reduction product by the toluene. Thus it was possible to get fairly accurate weights of samples. The success of the investigation was probably due in no small degree to this chance discovery.

The potassium was handled in this manner throughout the course of the study, except for a few runs in which it was cut under ether and weighed under toluene. This was done to improve the accuracy of the weighing in some of the reacting ratio studies, because otherwise a small amount of toluene adhered to the pieces of potassium during transfer for weighing.

The product was removed for sampling under a layer of liquid ammonia in a manner similar to that described by Hammer. Hammer had used a special cap which fit over the lower part of the reaction vessel, but this was found to be very awkward. A one-hole rubber stopper worked admirably to keep the air out and to allow a stream of ammonia to escape. The ammonia was permitted to evaporate in the dry box, which had been flushed with ammonia gas over night. The weighing bottles or sampling tubes were individually flushed with ammonia, and the dry or still damp yellow product was transferred to

them by means of a spatula. The stoppered samples were then ready to be taken from the dry box for whatever measurement was to be made.

It was necessary to prepare a fresh sample each time a measurement was to be made because the product could not be preserved for more than a few hours at the most. Four to eight hours were usually required to prepare a sample for study. In the course of this investigation some ninety reductions were made.

4. The Reduction Product. The reduction product, which has been described as possessing strong reducing properties, was changed to a buff color immediately upon contact with air. Its color, after prolonged exposure to air, finally became dark brown. When a little water was present (as when atmospheric water condensed on the precipitate still cold from the liquid ammonia solvent), first a dirty white, then a blue, and finally an orange colored oxidation product was observed. These colors correspond to the previously reported uni-, bi-, and tripositive hexacyanomanganates, respectively.

Qualitative observations were made on the behavior of the yellow product in aqueous medium. When it was thrown into distilled water, a very finely divided light yellow precipitate was formed which was distinctly different in appearance from the original material. The

precipitate, which was almost a paste, was very difficult to filter. Both the light yellow solid and its yellow supernatant liquid reduced silver nitrate. When the yellow solid was washed several times with water it became white. Upon exposure to air it turned bluish and finally became brown. The color changes, however, were not clearly defined.

Several attempts were made to analyze the white solid, but the results were inconsistent. Since the samples taken for analysis were not pure substances, this was not surprising. Also, because of the paste-like nature of the precipitate, the surface was oxidized while the interior was shielded from oxidation. The best analytical results gave K : Mn ratios between 4.5 and 5.5. On the basis of these results, and because of its white color and strong reducing properties, the white compound was conjectured to consist primarily of the unipositive manganese complex, $K_5Mn(CN)_6$, which was first reported by Manchot and Gall (11). The white precipitate was formed directly when the reduction product was thrown into sodium hydroxide solution.

The yellow product behaved somewhat differently when it was thrown into a buffered ammonium hydroxide solution. A yellow precipitate was first formed, which turned to a bluish color when air was bubbled through

the solution. Continued oxidation by air changed it to a colorless solution. Finally, a brown precipitate was formed.

B. Reacting Ratio Experiments.

In order to arrive at some idea of what takes place in the reduction reaction, it was decided to conduct a series of reacting ratio experiments. In these experiments, a variety of ratios of the reactants, potassium and potassium hexacyanomanganate(III), were used. If the combining ratio of the reactants were known, it should then be possible to write an equation for the reaction, and perhaps to determine the formula of the reduction product.

Since solutions of potassium in liquid ammonia have an intense blue color, it is very easy to detect an excess of potassium in the solution. It was reasoned that if more than the theoretical amount of potassium required to complete the reaction were present, a blue color should persist; if less than the theoretical were present, the color should disappear, provided the reaction goes to completion. By a series of runs varying from an excess of one reactant to an excess of the other, one should be able to determine the critical ratio at which all of the potassium just disappears.

In Table V are listed the results of such a series of runs, in order of decreasing number of moles of potassium per mole of $K_3Mn(CN)_6$. It is seen that when the number of moles of potassium per mole of $K_3Mn(CN)_6$ was greater than three, the intense blue color due to excess potassium persisted for a long time. Sometimes this blue color disappeared after several hours, but this was probably due to slow amide formation. The reaction with $K_3Mn(CN)_6$ is much more rapid.

When the mole ratio was between 2.5 and 2.8, apparently most of the potassium was used up, but enough remained at the end of the reaction to impart a blue color to the solution. Although only a very small amount of potassium is required to give a dark blue solution, the solution may appear much lighter in color when it contains small yellow suspended particles.

In the cases in which the mole ratio was slightly less than 2.5, the blue color completely disappeared, usually in less than an hour. The apparent anomalies in the lengths of time required for the disappearance of the blue color are due, as explained previously, to the fact that a more accurate method of weighing the potassium was used in some cases. The ratios preceded by an asterisk represent runs in which the potassium was cut under ether and weighed under toluene. The results

TABLE V

RESULTS OF REACTING RATIOS EXPERIMENTS

| Mole Ratio Used ($K : K_3Mn(CN)_6$) | Blue Color of Excess Potassium |
|---|---|
| 14.94 | persisted, no noticeable change |
| 3.79 | " " " " |
| *3.61 | " " " " |
| 3.33 | " " " " |
| *3.19 | " " " " |
| 3.00 | " " " " |
| 2.79 | after 15 min. solution became light blue. |
| 2.74 | same as immediately above. |
| 2.69 | after 15 min. solution became very light blue, but color disappeared after 2 hrs. |
| 2.55 | same as immediately above. |
| 2.48 | disappeared after 15 min. |
| *2.47 | disappeared after about 1½ hours |
| 2.47 | disappeared after 15 min. |
| *2.45 | practically disappeared after 30 min. |
| *2.36 | " " " " " |
| 2.00 | disappeared after 15 min. |
| 1.54 | disappeared after 10-15 min. |

* Potassium was cut under ether and weighed under toluene. In other runs, potassium was cut and weighed under toluene.

of these runs are more reliable than those of the runs in which the potassium was cut and weighed under toluene.

For ratios below 2.0, the blue color disappeared within ten or fifteen minutes. Undoubtedly the manganese complex was in excess in these cases. This probably represents a lower limit for the time required for the reaction.

One would expect the stoichiometric ratio of potassium to $K_3Mn(CN)_6$ to be one of small whole numbers. From the information in Table V, however, it is apparent that the ratio lies between 2.7 and 2.3.

At the 2.7 ratio the light blue color persisted for about two hours before it disappeared. Its final disappearance may be attributed to slow amide formation. At the 2.3 ratio it disappeared in about half an hour. This slowness was ascribed to two factors:

The reaction probably required at least fifteen minutes under the most favorable circumstances. When nearly stoichiometric ratios were used, the concentrations of both reactants were greatly reduced near the end of the reaction. Consequently, a long time was required to complete the reaction. The second factor resulted from the design of the apparatus. The fritted-glass disk in the reaction chamber served much too effectively to separate the solutions above and below it.

Even when the potassium had disappeared in the bulk of the solution, the portion below the disk was sometimes still distinctly blue. The entire solution could be mixed by the tedious process of successive expansion and contraction of the lower solution by warming with the hands and then cooling. This was so time consuming, however, that it was often difficult to estimate when the solution should have cleared up.

When an excess of potassium was used, the reaction time apparently was less than an hour. In the standardized procedure which was adopted, the mixture was allowed to react for at least an hour to insure complete conversion.

It is recognized that a line of demarcation between an excess of potassium and an excess of the manganese complex could not be clearly defined. However, from these semi-quantitative observations it appears likely that 2.5 moles of potassium per mole of $K_3Mn(CN)_6$ react to form the reduction product. A stoichiometric ratio of 2.5 suggests that the reduction product contains potassium, manganese, and cyanide in the ratio 5.5 : 1 : 6. A compound of this formula would contain manganese with a mean oxidation state of one-half.

C. Analysis of the Product.

1. Procedure. A good set of analytical data is considered to be the most convincing evidence which can be

obtained in the identification of a new compound. Consequently, when this problem was started, it was decided that it would be necessary to perfect an analytical scheme which would be applicable to the analysis of the reduction product. This decision stemmed from two considerations. First, Hammer had experienced considerable difficulty in his analytical work. Second, the formulas of several possible reduction products were so close together that good analytical data would be needed to distinguish between them.

The objective of perfecting a suitable analytical scheme was approached in the following manner: First, a thorough search of the literature was made for all types of analytical methods for potassium, manganese, and cyanide. Also the descriptive chemistry of these ions, both simple and complex, was studied. Then several of the more promising methods were tried on known mixtures containing potassium, manganese, and cyanide.

In developing the analytical procedure it would have been desirable to work with a pure complex of potassium, manganese, and cyanide if such a standard compound had been available. Since no such standard was available, it was decided to use a mixture of simple salts whose purity and composition could easily be checked by analysis.

Potassium cyanide and manganese(III) sulfate were used for this purpose because they were the most nearly pure salts available. The manufacturer claimed 97 per cent purity for the potassium cyanide. The manganese(II) sulfate, in the form of the monohydrate, was C. p. grade. The percentage purity of these compounds was determined by analysis.

Potassium cyanide was used in the commercial form because it could not be purified beyond 97 per cent by recrystallization from water. Its purity was established by the modified Liebig method, e.g., titration with standard silver nitrate, with an iodide indicator. This method, which is recommended by Thompson (44) of the Bureau of Standards, is considered to be standard for the analysis of simple cyanides.

The potassium cyanide was dried at 125°C in the presence of sodium hydroxide pellets (to absorb the $CO_2$ present). The silver nitrate titration yielded results of 97.73, 98.00, 97.44, and 97.61 per cent potassium cyanide in the sample. The average, 97.7 per cent, was taken to represent the true purity of the reagent. This figure corresponds to a cyanide content of 38.9 per cent. All subsequent analyses were compared with this value.

The potassium cyanide was analyzed also for potassium. The sample was treated with sulfuric acid, the

solution evaporated, and the residue ignited to the sulfate. The results of the analyses showed 59.53, 59.54, 59.81, and 59.83 per cent potassium present in the potassium cyanide. The average of these results, 59.7 per cent, is only slightly less than theoretical 60.2 per cent for pure potassium cyanide.

Since the potassium cyanide was impure, the analytical method utilized for potassium was checked by applying it to the analysis of analytical grade potassium chloride, which was regarded as being 100 per cent pure. These analyses gave the results 99.45, 99.50, 99.74, and 99.76 per cent of theoretical. The average, 99.6 per cent, represents the probable accuracy of this method, which was considered to be satisfactory.

The manganese(II) sulfate monohydrate was heated at 400°C for 24 hours on a sand bath to remove the water of hydration. Both the hydrate and the anhydrous salt were analyzed for manganese.

Most methods for manganese analysis are designed for the determination of low percentages and traces as found in steel. Several of these methods were tried, but the results were not consistent.

It was found that the bismuthate method was satisfactory, even for large percentages of manganese, when certain optimium conditions are followed. Cunningham

(45), of the Bureau of Standards, recommends these conditions:

(1) The concentration of manganese should not be over 0.1 gram per 100 milliliters of solution, preferably less than 0.05 gram.

(2) The temperature should be kept below 15°C by use of an ice bath. This retards the decomposition of the permanganate ion.

(3) The concentration of nitric acid should be 11 to 22 per cent by weight.

The manganese (II) sulfate sample was put into solution at the proper concentration and then cooled. The manganese was oxidized to permanganate by means of sodium bismuthate, which was added in the amount of about 26 grams per gram of manganese. This mixture was shaken for at least a minute, diluted with an equal volume of cold water, and filtered through a fritted-glass filter. The unused bismuthate remained on the filter plate, and the solution of permanganate passed through the filter. To the filtrate was added an excess of Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. The excess ferrous ion was determined by titration with standard potassium permanganate solution. A check of the equivalent weight of Mohr's salt was made by titrating it against standard permanganate. An average of 389.3 for its equivalent

weight was used in the calculations, whereas for the pure substance, the formula weight is 392.1.

When manganese(II) sulfate was analyzed according to the above procedure, the following results were obtained. Found, for the hydrate, 32.44% manganese; theoretical, 32.50%. Found, for the anhydrous salt, 36.38%; theoretical, 36.38%. Thus it was concluded that the manganese sulfate reagent was virtually 100 per cent pure. The anhydrous salt was the one used in subsequent study.

Since this method had worked so well on the simple salt, it was tried on a mixture of six moles of potassium cyanide per mole of manganese(II) sulfate. The mixture was treated just as if it were a complex compound. In fact, as soon as water was added some complexing took place, as was evidenced by the green and blue colors which appeared.

The complex was decomposed by heating with dilute sulfuric acid. This liberated the cyanide as hydrogen cyanide gas and left a solution containing manganese(II) and potassium ions. This solution was then analyzed for manganese in the presence of potassium by the special bismuthate method.

The results of several of the manganese analyses are listed in Table VI. They are reported as per cent of man-

TABLE VI

ANALYSIS OF THE MIXTURE, $MnSO_4$-6KCN

| Manganese* | Cyanide** | Potassium*** |
|---|---|---|
| 36.13% | 38.55% | 59.84% |
| 36.21 | 38.60 | 60.18 |
| 36.23 | 38.68 | 60.18 |
| 36.23 | 38.73 | 60.26 |
| 36.24 | 38.78 | 60.31 |
| 36.32 | | 60.40 |
| 36.34 | | |
| 36.40 | | |
| 36.50 | | |
| Average 36.3 | 38.7 | 60.2 |
| In simple salt 36.4 | 38.9 | 59.7 |
| Difference 0.1 | 0.2 | 0.5 |
| Theoretical 36.4 | | |

* Reported as per cent Mn in $MnSO_4$ (in presence of 6 KCN)

** Reported as per cent CN in KCN (in presence of 1/6 $MnSO_4$)

*** Reported as per cent K in KCN (in presence of 1/6 $MnSO_4$)

ganese in the manganese(II) sulfate in order that they may be compared with the results previously reported for the pure salt. The results which were questionable, due to experimental errors, are not included. It is seen that none of these values differs greatly from the theoretical. Also, their average of 36.3 per cent is in good agreement with the 36.4 per cent found for the simple salt and with 36.4, the theoretical per cent for pure manganous sulfate. It was concluded that this method was suitable for the analysis of manganese in cyanide complexes.

After a study of the various methods for analysis of potassium, the previously tried method of determination as sulfate seemed to be the most promising, provided the manganese could first be quantitatively removed. As has already been explained, Hammer had experienced difficulty in separating the manganese. However, no difficulty was experienced when it was done in the following manner.

The complex mixture was treated with dilute sulfuric acid to expel the cyanide. The solution was then made alkaline with ammonium hydroxide, buffered with an ammonium salt, and saturated with hydrogen sulfide. This mixture was allowed to stand for at least a day to permit coagulation of the manganese(II) sulfide precipitate.

It was then filtered through a fritted-glass filter of medium porosity. The filtrate contained the potassium, while the manganese remained on the filter plate. The filtrate was treated with sulfuric acid, evaporated to dryness, and ignited to the sulfate at 1000° C. The large amount of ammonium salts present, which caused the residue to creep on some of the dishes, constituted a nuisance in several cases.

The results of the analyses of the mixture for potassium also are listed in Table VI. The results which were known to contain experimental errors were not tabulated. Three values, 61.37, 61.70, and 62.17 per cent, which were much higher than the others, are not included in the list; they were discarded because they show no consistency, either with one another or with the other results. These three high results were probably due to incomplete separation of manganese. The results of the potassium analyses which appear in Table VI are not only self-consistent, but also in fairly good agreement with the analyses of the simple salt. Most of the discrepancy is undoubtedly due to the small amount of manganese which could not be separated. It was concluded that this method was satisfactory for the analysis of potassium in a complex compound of potassium, manganese, and cyanide.

The cyanide determination, in the analysis of a complex compound, is usually the one which involves the greatest error. The accurate Liebig titration and similar methods are not applicable to the direct analysis for cyanide in a complex. The complex must first be decomposed, usually with an acid. In doing this it is easy to lose some of the hydrogen cyanide gas which is liberated.

The modified Kjeldahl method, as described by Bigelow (34), is the method generally used for determining cyanide in a complex. In this procedure, a suitable sample is distilled with dilute sulfuric acid. A quantity of the distillate is caught in a dilute sodium hydroxide solution. This solution, after acidification, is titrated with standard silver nitrate, with an iodide indicator.

This method was tried on the standard mixture. Ground glass equipment was used throughout, and all joints were greased to eliminate leaks. Dilute sulfuric acid was added to the dry material by means of a graduated dropping funnel. The distillate was bubbled through two sodium hydroxide solutions in series. In spite of these precautions the results of the cyanide analyses were all low by 5 to 20 per cent. It was noticed that the sodium hydroxide solution became hot

from the condensing steam which came over with the distillate, Since hydrogen cyanide is a very weak acid and boils at 26° C, it was suspected that some might be lost by vaporization even though the solution was alkaline.

After repeated failures with the above method, it was decided to try immersing the sodium hydroxide solution in an ice bath. The encouraging results of several analyses in which this modification was used are listed in Table VI. The average of these results is within one per cent of the average obtained by the reliable Liebig method for the simple salt. It was concluded that this modification of the Kjeldahl method was suitable for the analysis of cyanide in a manganese complex, even though the results were always somewhat low.

In a later stage of this research, another method was found to be equally satisfactory for the analysis of cyanide in the yellow reduction product, provided that the approximate amount of cyanide present was known. The sample in solution was made ammoniacal, and about 95 per cent of the required amount of standard silver nitrate was added. The ammonia prevented the precipitation of silver. The combination of silver with the cyanide caused the manganese complex to dis-

sociate, and the hydroxide brought about the precipitation of an oxide of manganese, which darkened the entire solution. The manganese precipitate was removed by filtration, and the clear filtrate containing the cyanide was titrated to an end-point with potassium iodide serving as indicator. Thus cyanide was determined in a complex without conversion to hydrogen cyanide. The results were about the same as, or even a little higher than, those obtained by the other method.

In recapitulation of results reported in Table VI, the good agreement between the average percentages found for the simple salts and for the mixtures should be pointed out. On an absolute percentage basis the differences are only 0.1, 0.2, and 0.5 per cent for the analysis of manganese, potassium, and cyanide, respectively. On a relative basis the differences are 0.3, 0.5, and 0.8 per cent. Although errors of this magnitude might be considered large in some determinations, it is believed that, in view of the difficulty of the analyses, they are acceptable here.

The methods which had been shown to be satisfactory for the analysis of a manganese cyanide complex were applied to the analysis of the reduction product. The problem of sampling the product has already been

discussed. The samples in the weighing bottles were weighed as soon as the latter had been filled. Once the sample bottles were weighed, there was no urgency about the rest of the analysis. The sample was emptied into a container, and the empty weighing bottle was weighed for the tare. From this point on, the analyses were carried out according to the tested procedure.

At the time that the preliminary analytical work was being done, it was not known that the reduction product contained bound ammonia. However, after this had been discovered, it was no problem to determine the amount of ammonia present by the simple Kjeldahl method. The product was placed in a closed flask and treated with sodium hydroxide solution. The ammonia was distilled into a measured quantity of standard acid, which was then back-titrated with standard base.

The results of the analyses of the yellow reduction product by the previously described methods are listed in Table VII. The results of analyses which were known to contain an experimental error are not reported. In general, the results are consistent among themselves. The average percentages for the constituents, potassium, manganese, and cyanide, total 100.2 per cent.

TABLE VII

ANALYSIS OF THE REDUCTION PRODUCT

| | %K | %Mn | %CN | %$NH_3$ |
|---|---|---|---|---|
| | 47.92 | 12.33 | 34.64 | 3.71 |
| | 48.00 | 12.38 | 34.86 | 4.48 |
| | 48.13 | 12.46 | 35.09 | 4.69 |
| | 48.33 | 12.49 | 35.12 | |
| | 48.64 | 12.52 | 35.46 | |
| | 48.71 | 12.69 | 35.48 | |
| | | 12.72 | | |
| Average: | 48.3 | 12.5 | 35.1 | 4.3 |

Total: 100.2%

Empirical formula: $K_{10.9}Mn_2(CN)_{11.9}\cdot 2.1NH_3$

These results may be used to calculate an empirical formula for the product of the reduction. The empirical formula which was obtained in this manner is $K_{10.9}Mn_2(CN)_{11.9} \cdot 2.1NH_3$. Obviously these figures should be rounded off to give the empirical formula $K_{11}Mn_2(CN)_{12} \cdot 2NH_3$. Since manganese complexes are usually six-coordinated, it is preferable to formulate the compound as the double salt $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6 \cdot 2NH_3$. A compound of this formula contains manganese in both the unipositive and zerovalent states in equimolar proportions. It might also be said that manganese exists in this compound with a mean oxidation state of one-half. This formula, found by analysis, is in agreement with the findings of the reacting ratio experiments.

The number of ammonia molecules which are attached is not constant. It is believed that one molecule is tightly held, because an analysis showed that a sample which had been standing for a week contained one molecule of ammonia. Samples which were analyzed immediately lack consistency, but, on the average, a fresh sample contained two molecules of ammonia.

In Table VIII are listed the starting complex material and what were thought to be the most likely possibilities for the reduction product. The percent-

TABLE VIII

THEORETICAL COMPOSITIONS OF SOME POSSIBLE REDUCTION PRODUCTS

| | %K | %Mn | %CN | %$NH_3$ |
|---|---|---|---|---|
| $K_3Mn(CN)_6$ | 35.72 | 16.73 | 47.55 | |
| $K_4Mn(CN)_6$ | 42.56 | 14.95 | 42.49 | |
| $K_5Mn(CN)_6$ | 48.09 | 13.51 | 38.40 | |
| $K_6Mn(CN)_6$ | 52.64 | 12.32 | 35.03 | |
| $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6$ | 50.47 | 12.89 | 36.64 | |
| $K_5Mn(CN)_6 \cdot NH_3$ | 46.15 | 12.97 | 36.86 | 4.02 |
| $K_6Mn(CN)_6 \cdot NH_3$ | 50.70 | 11.87 | 33.74 | 3.68 |
| $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6 \cdot NH_3$ | 49.48 | 12.64 | 35.92 | 1.96 |
| $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6 \cdot 2NH_3$ | 48.53 | 12.40 | 35.23 | 3.84 |
| Experimental | 48.3 | 12.5 | 35.1 | 4.3 |

age compositions of the constituents are given for each compound. The table was made to show what possible formulas the data of Table VII might fit, and to ascertain whether or not other possibilities were eliminated. The table also shows why careful analytical data was essential for the successful conclusion of this problem.

The percentages which could correspond to the experimental values are enclosed in rectangles. Only one formula corresponds with experimental values for more than two of the four constituents. It is seen that $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6 \cdot 2NH_3$ corresponds with all four experimental values. If the data were not reliable it would be difficult to prove, from analytical data alone, that the reduction product was not the simple complex $K_5Mn(CN)_6 \cdot NH_3$ or $K_6Mn(CN)_6 \cdot NH_3$. In fact, with inconclusive data, Hood (32) had surmised that the reduction product probably was $K_5Mn(CN)_6 \cdot NH_3$.

D. Reducing Power Experiments.

In order to establish the oxidation state of a metal atom in a complex, it is desirable to conduct experiments for the measurement of its oxidizing or reducing power. In the case of a coordinated metal in a low oxidation state, a reagent is selected which will oxidize it to some known oxidation state. The

other constituents of the complex must not be oxidized or reduced, and the reagent must lend itself to quantitative measurements.

The first oxidizing agents which were tried on the reduction product were aqueous silver nitrate and aqueous iodine solutions. The weighed samples in tightly stoppered weighing bottles were submerged in the oxidizing solutions and then broken. The iodine solution proved to be unsatisfactory because extremely large amounts of iodine were required. It was demonstrated that the iodine had reacted not only with the manganese, but also with the cyanide. The silver nitrate solution also was unsatisfactory. Immediately upon breaking the bottle a black precipitate of free silver appeared, which showed that reduction had taken place. The free silver was separated and weighed as silver chloride. The results of these experiments were inconsistent, however, and the calculated reducing power was much less than was to be expected on the basis of the analytical data. Evidently some of the reducing power was lost when the product was placed in water.

It was reasoned that since silver nitrate was soluble in liquid ammonia, the reducing power of the yellow product might be accurately measured in its

"natural habitat." A known amount of starting material was used, and it was assumed that it reacted quantitatively with the potassium to give the yellow product. It was proved that practically none of the manganese complex was lost in the washings, since an analysis of the washings showed that only one per cent of the manganese passed through the filter plate.

When an excess of silver nitrate was added to the yellow product in the ammonia suspension, the vessel immediately became filled with a black precipitate of free silver. The silver was separated and weighed as the chloride. The results of the first few runs were meaningless, but after the technique had been perfected they became more consistent.

The standardized procedure for the reducing power measurements was as follows. The reduction product was prepared in the usual manner. The starting material was weighed accurately and added to the potassium in the reaction chamber. The remaining complex was washed out of the bulb by condensing some ammonia in the bulb. In order to keep solids out of the tapered joint, the liquid level was kept low in the reaction vessel. The yellow product was washed at least twice with liquid ammonia to remove the excess potassium. Silver nitrate, in excess of four and one-half moles

per mole of starting complex (this was to allow one and one-half moles for the reduction, and at least three moles for combination with the six cyanide groups). was placed in a clean dry side bulb. It was flushed with ammonia gas and allowed to cool. The reaction of silver nitrate with ammonia is highly exothermic. The bulb was inserted into the system, and the silver nitrate was washed into the reaction chamber by condensing ammonia in the bulb.

After the mixture had had sufficient time to react, the solvent was withdrawn. The residue was washed several times with liquid ammonia to remove the excess silver nitrate and any silver cyanide, simple or complex, which might have been present. It was then washed at least twice with distilled water, which apparently hydrolyzed a manganese compound which was present in the residue. Next the residue was treated with dilute hydrochloric acid, which washed out all manganese, as well as uncombined chloride and cyanide. The free silver which remained was dissolved with hot dilute nitric acid. This solution, with its washings, was treated with dilute hydrochloric acid to precipitate the silver as the chloride. It was then filtered, and the precipitate was weighed.

Experience showed that in order to get a quanti-

tative reduction it was necessary occasionally to detach the lower part of the reaction chamber and to stir the liquid ammonia suspension well, especially in the cracks around the fritted plate. Spatulas of iron or aluminum were not suitable for this purpose, because they reduced silver nitrate. A sharp pointed glass stirring rod was used instead. The error of incomplete mixing was the last to be corrected in a series of refinements that finally led to accurate reducing power measurements.

Only the results obtained by use of the above procedure are considered pertinent. These values for the reducing power of the reduction product are 1.52, 1.50, 1.53, and 1.55 gram-atoms of silver per gram-atom of manganese. These results demonstrated that the manganese underwent a mean valence change of one and one-half in its oxidation by silver nitrate. Since it was oxidized to the dipositive condition, it must have existed originally in a mean oxidation state of one-half. This result is in complete agreement with the results of the reacting ratio experiments and with the analytical data. Whereas the analytical data are the strongest evidence in support of the proposed formula, the reducing power measurements give the best clue of the oxidation state of the manganese atom.

E. Magnetic Susceptibility Measurements.

Whenever a new transitional metal compound is to be identified, it is desirable to make magnetic studies. If the results from magnetic measurements agree with other conclusions regarding the compound, then they are said to lend support to these conclusions. On the other hand, if they do not quite agree, some reasonable explanation must be sought.

A Gouy type magnetic balance was used for these measurements. Directions for the use of the balance and methods for calculating magnetic moments were found in standard reference works by Selwood (18) and by Weissberger (17), as well as in Thompson's thesis (41).

Compounds whose susceptibilities are known were measured in order that the writer might become familiar with the technique of using the magnetic balance. The weighing tube was filled with air, with water, and then with the test material whose susceptibility was to be measured. In each case it was weighed with the magnetizing current on and off.

The calculation of the volume susceptibility was made by means of the following relationship.

$$\frac{(W_3-W_1)(K_w-K_a)}{W_2-W_1} = K_x-K_a, \text{ where}$$

$W_1$ = weight with current on minus weight with current off when the tube is filled with air.

$W_2$ = this same difference for water.

$W_3$ = this same difference for the test material.

$K_a$ = known volume susceptibility of air.

$K_w$ = known volume susceptibility of water.

$K_x$ = volume susceptibility of test material.

Division of the volume susceptibility by the apparent density gave the gram susceptibility. The gram susceptibility was then multiplied by the molecular weight to give the molar susceptibility. The diamagnetic contribution calculated by means of Pascal's constants (46) for each constituent of the complex compound except the metal atom was subtracted from the molar susceptibility. Then, on the assumption that the abbreviated Curie law holds, the effective moment in Bohr magnetons was calculated according to the Curie equation,

$$\mu_{eff} = 2.84\sqrt{\chi_m T}\text{ , where}$$

$\mu_{eff}$ is the magnetic moment in Bohr magnetons, $\chi_m$ is the molar susceptibility, and T is the absolute temperature. All measurements were made at 25°C.

The susceptibility of Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, was determined at three different field strengths. Effective moments of 5.34, 5.34, and 5.32 Bohr magnetons were obtained. These values are in excellent agreement with values of 5.25 and 5.46 reported in the literature

(47), and with Thompson's value of 5.40 (41). The theoretical value for the four unpaired electrons in this compound is 4.90 Bohr magnetons. The susceptibility of the starting material, $K_3Mn(CN)_6$, was measured also. An effective moment of 2.94 Bohr magnetons was obtained. This compares favorably with the literature values of 3.25 (9), 3.61 (19), 2.95 (20), and 3.40 (21), as well as with the theoretical value of 2.83 Bohr magnetons.

From these results it was concluded that the techniques employed in using the magnetic balance were suitable for the accurate measurement of the susceptibility of the yellow reduction product. The weighing tube was cleaned, dried, and flushed with ammonia in the dry box. By means of a spatula and a glass rod, the yellow product was quickly transferred and tightly packed into the weighing tube. Then the sample was weighed in the same manner as were the preliminary trial samples.

In order that the observed moment might be compared with the theoretical value, the calculation was made on the basis of the double molecule. The formula $K_{11}Mn_2(CN)_{12}\cdot 2NH_3$ was used in calculating the molecular weight, because all of the evidence points to this formulation. The unipositive manganese atom in this compound should have no unpaired electrons, and the zerovalent atom should

TABLE IX

SAMPLE DATA AND CALCULATIONS FOR MAGNETIC STUDIES

$W_1 = -0.00211$ g $\qquad K_w = -0.72 \times 10^{-6}$

$W_2 = -0.00427$ g $\qquad K_a = +0.029 \times 10^{-6}$

$W_3 = -0.00142$ g

Current = 4.57 amperes

Field Strength = 2400 gauss

Temperature = 25°C

$$\frac{(W_3 - W_1)(K_w - K_a)}{(W_2 - W_1)} = K_x - K_a$$

$$\frac{(-0.00142 + 0.00211)(-0.72 \times 10^{-6} - 0.029 \times 10^{-6})}{(-0.00427 + 0.00211)} = K_x - 0.029 \times 10^{-6}$$

$K_x = 0.268 \times 10^{-6}$

volume of sample = 1.242 $cm^3$

weight of sample = 0.8937 grams

$$0.268 \times 10^{-6} \times \frac{1.242}{0.8937} = 0.372 \times 10^{-6} = \chi_g \text{ (gram susceptibility)}$$

molecular weight = 887

$0.372 \times 10^{-6} \times 887 = .333 \times 10^{-6} = \chi_m$ (molar susceptibility)

TABLE IX (Cont.)

Corrections for diamagnetic contribution.

$$K = -18.5 \times 10^{-6}$$

$$CN = -10.77 \times 10^{-6}$$

$$NH_3 = -14.4 \times 10^{-6}$$

$$11K + 12CN + 2NH_3 = -362 \times 10^{-6}$$

$$333 \times 10^{-6} - (-362 \times 10^{-6}) = 695 \times 10^{-6} = \chi_m \text{ (corrected)}$$

$$\mu_{eff} = 2.84 \sqrt{695 \times 10^{-6} \times 298}$$

$$\mu_{eff} = \underline{1.29 \text{ Bohr magnetons}}$$

have one unpaired electron. Thus, the entire molecule would be expected to have a moment of 1.73 Bohr magnetons. The experimental values obtained are 1.29, 1.22, 1.20, 1.37, and 1.17 Bohr magnetons.

These values are somewhat lower than the theoretical value for the proposed formula. However, it can be shown that the discrepancy might readily be accounted for in terms of a partial oxidation of the product. A mixture of forty per cent of the zerovalent and sixty per cent of the unipositive manganese complex would have a theoretical value of the same magnitude as the experimental values.

In view of these facts, the values for the effective moment of the reduction product may be regarded as being in agreement with the other findings of this investigation and as lending support to them.

An attempt was made to follow the oxidation of the yellow product by means of susceptibility measurements, but these were inconclusive. This is probably due to the fact that the zerovalent part of the compound became less paramagnetic and the unipositive part more paramagnetic upon oxidation. Both of these processes probably occurred at the same time.

F. Miscellaneous Qualitative Experiments.

A few qualitative experiments were performed to explore the possibilitities of reducing some of the complex

cyanides of other first row transition elements. Those tried were cyano complexes of chromium, iron, and cobalt.

In one exploratory run on the reduction of $K_3Cr(CN)_6$, a ratio of 3.5 moles of potassium per mole of complex was used. After about an hour the blue solution became lighter in color, but the last of the blue color did not disappear. This was an indication that most of the potassium--possibly three moles--had been used in the reaction. The reduction product, which was definitely brown in color, was very sensitive to air oxidation. Upon exposure to air the brown solid immediately turned deep yellow, then greenish, and finally the same light yellow color as the starting material. The first color change was practically instantaneous; the second occurred after about one minute, and the third after about twenty minutes.

The product showed strong reducing properties, converting silver nitrate to free silver. This indicated that the chromium in the product was in a low oxidation state. Some of the product which had been air-oxidized to a green color was thrown into water, and was found to give a red solution. The compound $K_4Cr(CN)_6$ is green in the solid state and red in solution.

Since the light yellow color corresponds to the tripositive and the green to the dipositive chromium complex, it is possible that the deep yellow compound might

contain unipositive and the brown product zerovalent chromium. In the compound $K_6Cr(CN)_6$, chromium would have an effective atomic number of 36, which is the configuration of krypton. Since the rare gas configurations are known to be especially stable, it seems quite possible that a chromium complex could be reduced to the zerovalent state. This problem appears to be a promising one for future work.

In the first few experiments with the cobalt complex, $K_3Co(CN)_6$, no reduction by potassium in liquid ammonia was observed. When the complex was added to the potassium, amounts as small as one-half mole of potassium per mole of complex were used, and the blue color did not disappear. Even when a large excess of potassium was used, the starting material showed no evidence of change after several hours. The precipitate which remained after treatment with potassium did not reduce silver nitrate.

It was found, however, that when the potassium was added to a suspension of $K_3Co(CN)_6$, a reaction did take place. Since the starting complex is difficultly soluble, the sample was agitated in liquid ammonia for a half hour. Potassium without a coating of toluene was then added to the solution. When it was added in small in-

crements, the solution was observed to turn definitely yellow as soon as the first piece of potassium was added. As more potassium was added, the solution became deeper yellow and then brownish. Finally, when an excess of potassium had been added, the solution turned blue. Approximately three gram-atoms of potassium per mole of $K_3Co(CN)_6$ were required before potassium appeared to be in excess. It is not known whether all of this potassium was used for the reduction of the complex, or whether some of it was converted to the amide.

The definitely brown reduction product was very unstable with respect to air and water. The product turned red immediately upon contact with air, and the final air oxidation product was yellow. The brown product also showed strong reducing power in that it reduced silver nitrate in liquid ammonia. From the properties of the product and from the ratio of the reactants it is evident that a compound has been prepared which contains cobalt in a low oxidation state, possibly +1 or zero.

When potassium ferrocyanide was treated with potassium in liquid ammonia no reduction was observed. Small amounts of potassium did not disappear after several hours. The precipitate which remained was of the same color as the starting material, and it did not reduce silver nitrate.

The findings with the chromium, cobalt, and iron complexes are in qualitative agreement with those of Fernelius and Bigelow (33) which were previously mentioned.

It might be expected that $K_3Co(CN)_6$ and $K_4Fe(CN)_6$ would be difficult to reduce because in each case the metal atom has a stable krypton configuration. This reasoning seems to be valid in the case of the ferrous complex, but it is not clear why the cobalt complex should be reduced.

# V. SUMMARY

Potassium was found to react with potassium hexacyanomanganate(III) in liquid ammonia to produce a yellow compound which possesses strong reducing properties. The problem of characterizing this yellow reduction product was approached in four ways:

1. A study was made of the ratio in which the reactants combined. The study indicated that 2.5 moles of potassium per mole of potassium hexacyanomanganate (III), $K_3Mn(CN)_6$, reacted to give the reduction product. This evidence suggested the following equation for the reaction:

$$K_3Mn(CN)_6 + 2.5K = K_{5.5}Mn(CN)_6$$

2. A complete analysis of the reduction product was made. First, a scheme of analysis applicable to manganese complexes was devised, and was verified on known mixtures of potassium, manganese, and cyanide. The reduction product was then analyzed by means of this scheme.

The analytical data gave the following empirical formula for the compound: $K_{10.9}Mn_2(CN)_{11.9}\cdot 2.1NH_3$, or $K_{11}Mn(CN)_{12}\cdot 2NH_3$. The formula is preferably written as an ammoniated double salt $K_5Mn(CN)_6\cdot K_6Mn(CN)_6\cdot 2NH_3$. This formula is in agreement with the one which was suggested by the evidence from the reacting ratio experiments.

3. The reducing power of the yellow product was measured with silver nitrate in liquid ammonia. About 1.5 moles of silver nitrate were reduced to free silver per gram-atom of manganese. Since the manganese was oxidized to the dipositive condition, the yellow reduction product must have contained manganese with a mean oxidation state of one-half. The product probably consisted of equimolar proportions of unipositive and zerovalent manganese complexes. This conclusion is in complete agreement with the evidence from the reacting ratio experiments and with the analytical data.

4. The magnetic susceptibility of the compound was also measured. An average magnetic moment of 1.25 Bohr magnetons was obtained for the double molecule. This is somewhat lower than the theoretical value of 1.73 Bohr magnetons which would be expected for a compound of the proposed formula. However, this discrepancy is not very significant. A mixture of forty per cent of the zerovalent and sixty per cent of the unipositive manganese complexes would have a theoretical moment of about 1.25 Bohr magnetons. Thus the magnetic evidence supports the other findings of this investigation.

All of the evidence from these four independent measurements leads to the conclusion that the reduction product contains manganese in both the unipositive

and zerovalent states in equimolar proportions. Undoubtedly, the formula of the compound should be written $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6 \cdot 2NH_3$.

# VI. SUGGESTIONS FOR FUTURE WORK

Now that the yellow reduction product of potassium and potassium hexacyanomanganate(III) in liquid ammonia has been characterized, suggestions for further work may be classified under two headings.

A. Properties of $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6 \cdot 2NH_3$.

Only qualitative information exists as to the chemical properties of the yellow product. Its behavior in acidic, basic and neutral aqueous media, its reactions with inorganic salts, and most of its physical properties are unknown. An investigation of these properties should be made if the importance of the product warrants it.

B. Similar Reductions of Other Complexes.

From the qualitative experiments it appears that a study of the reduction of potassium hexacyanochromate(III) and potassium hexacyanocobaltate(III) would be very promising. Undoubtedly the metals in both of these complexes are reducible to lower oxidation states. The problem of identifying the brown reduction products should be undertaken. It seems probable that this could be done by methods similar to those used in this investigation. Also, attempts should be made to reduce complexes of the other members of the chromium and cobalt families.

It appears unlikely that the hexacyano complexes of iron can be reduced lower than to the divalent state as long as they are six-coordinated. However, if their pentacyano complexes could be prepared, it would be worth while to investigate their reducibility.

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