is seen in convergent light, indicating the uniaxial character. Optically negative as shown by quartz wedge, etc. Satisfactory measurements of the refractive indices were not obtained, but approximate determinations by the microscope method indicated that ε was about 1.7.

The cuprous-sodium-ammonium-thiosulphate appears to be isomorphous with the silver salt, but the small size of the crystals prevented exact measurement upon the reflecting goniometer, except by visual reflection. The few angles thus obtained (the prismatic zone) showed the tetragonal character. The habit of the crystals is identical with that of the silver salts, the third order pyramid terminating the combination of the unit and second order prisms. By using the microscope the plane angle between the prism edge and the pyramid-prism edge was measured for both salts and found to correspond within a degree.

The optical characters of the copper-sodium-ammonium salt are identical with those of the silver salt, except that the absorption is stronger in the case of the former. No section that would show the interference figure was obtained with this salt, but it is optically negative, as shown by quartz wedge.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY NO. 100.]

CHANGES IN THE COMPOSITION OF SOME FERROCYANIDES OF CADMIUM, AND ZINC AFTER PRECIPITATION.[1]

BY EDMUND H. MILLER AND M. J. FALK.

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IN 1897, in discussing[2] two papers read before the New York Section on the "Ferrocyanides of Zinc and of Manganese," the suggestion was made that these complicated precipitates could all be resolved into two ferrocyanides having simple ratios, *i. e.*, $RK_2Fe(CN)_6$ and $R_2Fe(CN)_6$, where R is a dyad metal. This idea was advanced as the alternative to supplying elaborate formulae to the precipitates formed, in order to satisfy the iron-manganese and iron-zinc ratios found by analysis.

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[1] Read at the Providence meeting of the American Chemical Society.

[2] Discussion by Miller: This Journal, 19, 556 (1897).

In 1900[1] it was shown that a particular potassium cadmium ferrocyanide, formed in an ammoniacal solution containing cadmium in excess, which agreed with the formula $K_2Cd_3(Fe(CN)_6)_2$, could be separated into $Cd_2Fe(CN)_6$ and $K_2CdFe(CN)_6$, and that the other potassium cadmium ferrocyanides, when treated with ammonia, yielded invariably $Cd_2Fe(CN)_6$ as the final insoluble product.

It was also shown that these ferrocyanides undergo changes in composition after precipitation, which proceed to definite points under given conditions of acidity and that these changes are hastened by heating.

In 1902[2] an attempt was made to obtain $K_2ZnFe(CN)_6$ and $Zn_2Fe(CN)_6$ from $K_2Zn_3(Fe(CN)_6)_2$, the potassium zinc ferrocyanide obtained in titration[3] by treatment with ammonia. The $Zn_2Fe(CN)_6$ was obtained, but not the other compound. Later the action of ammonia on $Cd_7K_6(Fe(CN)_6)_5$ was studied further by Mr. J. L. Danziger.[4] The ammoniacal solution yielded a white crystalline precipitate containing both ammonium and potassium, besides cadmium and ferrocyanogen in proportions represented approximately by the formula $Cd_8(NH_4)_3K(Fe(CN)_6)_5$; a white precipitate of $Cd_2Fe(CN)_6$ and, finally, crystals of $K_4Fe(CN)_6$. This work was not conclusive, but indicated the formation of an ammonium cadmium ferrocyanide and that the final products were $Cd_2Fe(CN)_6$ and $K_4Fe(CN)_6$.

In 1903 Waring[5] announced a new ammonium cadmium ferrocyanide which gave, on analysis, figures approximating the formula $(NH_4)_2CdFe(CN)_6$. This was obtained in titrating an acid cadmium solution by potassium ferrocyanide in the presence of ammonium chloride.

Waring also stated that the reaction between zinc chloride and potassium ferrocyanide proceeded in two steps: That the normal zinc ferrocyanide, $Zn_2Fe(CN)_6$, was first formed, which subsequently reacted with more potassium ferrocyanide, giving $K_2Zn_3Fe(CN)_6$, and that at 20° C. an end-point was obtained with uranium acetate at the completion of the first stage of the

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[1] Miller: This Journal, **24**, 239 (1902).

[2] Miller and Danziger: *Ibid.*, **24**, 827 (1902).

[3] See later.

[4] This work has not been published before.

[5] This Journal, **26**, 13 (1904).

reaction. This work seemed to shed new light on these ferrocyanides and, with the consent of Mr. Waring, the authors of the present paper took up the work again in January, 1904.

CADMIUM AMMONIUM FERROCYANIDES.

In order to confirm the work of Waring the following precipitates were made:

A. Ten grams of cadmium chloride were dissolved in water. 79.8 cc. of hydrochloric acid (sp. gr. 1.20) and 70 grams of ammonium chloride (free from iron) were added and the whole diluted to 2800 cc., then heated to 50° C. and potassium ferrocyanide solution, 44 grams per liter, run in until a very slight excess of ferrocyanide was present. The precipitate was allowed to settle and washed with water till free from chlorides; it was dried over sulphuric acid *in vacuo*, as drying at 100 C. in an airbath caused a change in color to dark blue-green, due to partial decomposition.

The precipitate was white, slightly crystalline, soluble in hot hydrochloric acid (either concentrated or dilute), and was decomposed by caustic alkali with the liberation of ammonia.

B was made in the same way except that a considerable excess of potassium ferrocyanide was added. Its properties were the same as those of A.

C was made like A, except that the temperature was 100° C. Color, light green.

D was made under the same conditions as B, except that the temperature was 100°C. Color, dark blue.

These precipitates were analyzed by the following method: Half a gram of the precipitate was digested with concentrated nitric and sulphuric acids until decomposed, and evaporated first with nitric and then with sulphuric acids till the solution on dilution showed no blue color. The solution was neutralized with sodium hydroxide, acidified with 4 cc. of concentrated hydrochloric acid and the cadmium precipitated as sulphide. The cadmium sulphide was filtered, dissolved and weighed as cadmium ammonium phosphate, $CdNH_4PO_4H_2O$, and this checked by ignition to pyrophosphate. In the filtrate the iron was oxidized, precipitated by ammonia, dissolved, reduced and titrated by potassium permanganate. The filtrate from the ferric hydroxide was examined for potassium.

Ammonia was determined in a separate portion by distillation with very weak barium hydroxide, 1 to 1.5 grams in 500 cc., so as to prevent any decomposition of the $Fe(CN)_6$ group.

The results were as follows:

	Cd.	NH_4.	$Fe(CN)_6$.
A	1.015	1.95	1
B	1.05	1.92	1
	1.06	1.92	1
C	1.01	1.92	1
D	1.00	1.94	1

A and C, made under the conditions given by Waring, except for temperature, confirm his formula, $Cd(NH_4)_2Fe(CN)_6$. The blue color he reports is due to a partial decomposition, as the precipitates formed at 50° C. and dried *in vacuo* are perfectly white. As the iron-cadmium ratio is 1 : 1.07 in the ordinary titration of cadmium by potassium ferrocyanide,[1] and is 1 : 1 in the presence of ammonium chloride due to the formation of $Cd(NH_4)_2Fe(CN)_6$, it is evident why the addition of ammonium chloride makes a difference in the results obtained in titrating cadmium.

Next, precipitates were made as before, at 50° C. (E) and at 100° C (F), but by pouring the cadmium chloride solution into an excess of potassium ferrocyanide. They were light to dark blue in color and were still further decomposed by drying at 105° C. The ratios obtained, by analysis, were as follows:

	Cd.	NH_4.	K.	$Fe(CN)_6$.
E	0.99	1.4	0.61	1
	0.992	1.4	0.603	1
F	0.995	1.42	0.605	1
	0.996	1.42	0.603	1

These results, which are almost identical, correspond either to $Cd_5(NH_4)_7K_3(Fe(CN)_6)_5$, or to a mixture of $3CdK_2Fe(CN)_6$ and $7Cd(NH_4)_2Fe(CN)_6$.

The formation of such a precipitate is not strange under these conditions. There are present NH_4, K, Cd and $Fe(CN)_6$ ions. Cadmium chloride is added and forms precipitates with either alkali metal and the $Fe(CN)_6$ group, depending on their relative concentration, as the two precipitates are quite insoluble. On the other hand, when the ferrocyanide is added gradually, as in titra-

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[1] Miller: This Journal, **24**, 231; also Miller and Fisher: *Ibid.*, **22**, 542.

tion, to a solution containing a high concentration of NH_4 ions the ammonium cadmium ferrocyanide results. The influence of the potassium chloride formed is not to be disregarded, as will be shown later, but if the operation is stopped as soon as an excess of potassium ferrocyanide is present or if the potassium is removed by decantation, as in making the preceding precipitates, its influence is extremely small.

CHANGES IN THE CADMIUM FERROCYANIDES AFTER PRECIPITATION.

It was thought, in 1902, that the action of ammonia on cadmium potassium ferrocyanides might give an ammonium cadmium ferrocyanide with liberation of potassium hydroxide, but this could not be found. Now, assuming the production of $Cd(NH_4)_2Fe(CN)_6$, the action of ammonia may be as follows:

$$2CdK_2Fe(CN)_6 + 4NH_4OH = 2Cd(NH_4)_2Fe(CN)_6 + 4KOH,$$

while the potassium hydroxide, when it reaches a certain concentration, reacts as follows:

$$2Cd(NH_4)_2Fe(CN)_6 + 4KOH = Cd_2Fe(CN)_6 + K_4Fe(CN)_6 + 4NH_4OH.$$

To test this theory some $CdK_2Fe(CN)_6$ was made and analyzed. Two grams were placed in a beaker with 500 cc. of strong ammonia water and stirred mechanically for a week at a temperature of 50° C. The precipitate was then washed with a solution of magnesium sulphate, dried and analyzed. The results corresponded to a formula of $Cd_{16}(NH_4)_6K_2(Fe(CN)_6)_{10}$, or to a mixture of $6Cd_2Fe(CN)_6.3Cd(NH_4)_2Fe(CN)_6$ and $1CdK_2Fe(CN)_6$. (G.)

To test the second half of the reaction alone some dry $Cd(NH_4)_2Fe(CN)_6$ was placed in a beaker with 500 cc. of water and heated; to this was added 1 gram of potassium hydroxide dissolved in water. After being stirred mechanically for one week it was washed, dried and analyzed, and gave values corresponding to $Cd_5(NH_4)_7K_3(Fe(CN)_6)_5$, that is, to the precipitates formed when cadmium chloride was run into potassium ferrocyanide in the presence of ammonium chloride and hydrochloric acid. (E and F.)

These experiments bear out the theory of the action of ammonia, but show that the reaction is incomplete under the conditions used and point certainly to a definite compound which is, at least, a stopping point in the progress of the reaction.

The next experiment was to test the influence of ammonium chloride on $CdK_2Fe(CN)_6$. The precipitate was agitated, as already described, with 50 grams of ammonium chloride and a drop of hydrochloric acid. The results of the analysis corresponded to $Cd_{13}(NH_4)_{12}K_2(Fe(CN)_6)_{10}$, or to a mixture of $3Cd_2Fe(CN)_6$, $6Cd(NH_4)_2Fe(CN)_6$ and $1CdK_2Fe(CN)_6$. (H.) Comparing these results with those obtained by the treatment with ammonia (G), we see that the action is similar, but that it progressed farther with the ammonia, giving a greater proportion of the normal cadmium ferrocyanide, $Cd_2Fe(CN)_6$.

It remained to test the action of potassium chloride on $Cd(NH_4)_2Fe(CN)_6$; this was done in the same way, 70 grams of potassium chloride being used. The precipitate was found to be $Cd_{13}(NH_4)_{12}K_2(Fe(CN)_6)_{10}$, or identical with that obtained by the action of ammonium chloride on the $CdK_2Fe(CN)_6$.

If this reaction were strictly reversible, the resulting compound would be $Cd_{13}K_{12}(NH_4)_2(Fe(CN)_6)_{10}$, but as the substitution of the potassium proceeded only to such a limited extent and the same compound was obtained as before, the conclusion seems to be that there is such a definite compound and that it is the most insoluble of these double ferrocyanides under the conditions.

ZINC FERROCYANIDES.

The precipitate obtained when the zinc titration is made, as is usual in the presence of ammonium chloride, was prepared as follows: Zinc oxide was dissolved in hydrochloric acid, neutralized with ammonia and then hydrochloric acid added so that there were 2 cc. present for every 200 cc. of solution. Seven grams of ammonium chloride were added for every 300 mg. of zinc present, and the solution was titrated at 60° C. till the potassium ferrocyanide was just in excess. The precipitate was washed, dried at 95° C and analyzed. A slight change in color on drying suggested the presence of ammonia, as the double potassium ferrocyanides were not decomposed on drying at 105° C.

The results of the analysis showed a ratio of

$$Zn : NH_4 : K : Fe = 1.5 : 0.8 : 0.2 : 1,$$

corresponding to the formula $Zn_{15}(NH_4)_8K_2(Fe(CN)_6)_{10}$. So this familiar precipitate is also complex and the change in appearance noted[1] near the end of the titration in the presence of ammonium or other salts, is probably due to the change from the ferrocyanide first formed to this or some similar compound.

In order to find whether the zinc precipitates, like those of cadmium, would undergo changes after precipitation, some of the precipitate just described was placed in a beaker with 500 cc. of water, 5 cc. of concentrated hydrochloric acid and 70 grams of potassium chloride, heated to 70° C. and stirred constantly for a week. On analysis it was found that the compound had been converted completely into $Zn_3K_2(Fe(CN)_6)_2$, the ferrocyanide obtained when no ammonium chloride is present in the titration.

To test the reverse reaction $Zn_3K_2(Fe(CN)_6)_2$ was treated, as just described, with 50 grams of ammonium chloride. After a week the precipitate was washed, dried and analyzed. It was found to be $Zn_{15}(NH_4)_8K_2(Fe(CN)_6)_{10}$, identical with that obtained in titration in the presence of ammonium chloride.

This work on zinc confirms the results with cadmium and, though the extent of the conversion is not the same with the two metals, it affords further evidence that these precipitates are, in some cases at least, definite compounds, not mixtures.

We believe that Waring's statement that the reaction between zinc and ferrocyanide proceeds in two steps is correct; for, on titrating a zinc solution at 0° C., a yellow color was obtained with uranium nitrate when about half the quantity of ferrocyanide was used. This color faded out in the spot tests on standing, while the usual pinkish brown end-point grows darker on standing. This fact, which has often caused trouble to those not experienced with the method, is explained by the excess of potassium ferrocyanide, which causes the reaction with uranium gradually combining with the $Zn_2Fe(CN)_6$ to form either $K_2Zn_3(Fe(CN)_6)_2$ or the ammonium potassium compound, either of which is less soluble than the uranium ferrocyanides.

The same experiments were tried with cadmium, but the results were not conclusive, as the cadmium ferrocyanide always reacts slightly with the indicator. Tests were also made using other indicators: Cobalt nitrate, green color; ammonium molybdate, yellow; ammonium tungstate, green; ammonium vanadate, red; but nothing was found preferable to uranium nitrate for an acid solution.

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[1] Miller and Hall: *School of Mines Quarterly*, 21, 269.

When the titration of zinc is carried on in an ammoniacal solution, a strong citric acid solution of ferric chloride, when used as a spot-test, gives a very satisfactory end-point and is preferable to copper sulphate. As the normal zinc ferrocyanide is always formed in an ammoniacal solution, whether zinc or ferrocyanide be in excess, this method has the advantage that it is possible to run over with a standard ferrocyanide solution and then titrate back with zinc solution, which is not possible when the titration is done in an acid solution on account of the variation in the composition of the precipitate.

QUANTITATIVE LABORATORY,
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ON THE REACTION BETWEEN CARBON DIOXIDE AND SOLUBLE NITRITES.

BY RICHARD B. MOORE.

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SEVERAL years ago, while working on the preparation of the nitrosulphides and nitroprussides, C. Marie[1] and R. Marquis found that carbon dioxide would liberate nitrous acid from a solution of sodium nitrite. More recently Meunier[2] denied that such a reaction takes place, whereupon Marie[3] and Marquis repeated the following experiments in proof of their contention: (1) Pure carbon dioxide was passed into a solution of sodium nitrite containing potassium iodide and starch paste. A blue color indicated the fact that iodine had been liberated by nitrous acid. (2) A solution of sodium nitrite containing potassium iodide, when shaken with chloroform, gave no coloration, but a similar solution saturated with carbon dioxide turned the chloroform violet. (3) Carbon dioxide was passed through a solution of sodium nitrite and then into a solution of potassium iodide and starch paste, which was turned perceptibly blue.

Meunier claims that the results obtained in the first two experiments were due to the presence of potassium iodide. In order to show this he saturated a solution of sodium nitrite with carbon

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[1] *Compt. Rend.*, **122**, 137 and 473.

[2] *Ibid.*, **137**, 1264; **138**, 502.

[3] *Ibid.*, **138**, 367.