

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

## THE REACTION BETWEEN MERCURIC CYANIDE AND CERTAIN METALS IN LIQUID AMMONIA

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The investigation described below was undertaken to further our knowledge of reactions taking place in liquid ammonia solution, especially of those leading to the formation of compounds unstable in an aqueous medium because of hydrolysis.

### Aluminum Cyanide

Normal aluminum cyanide has never been prepared in a pure state, for it is completely hydrolyzed even in relatively small volumes of water. Thus, aluminum reacts with an aqueous solution of mercuric cyanide to form aluminum hydroxide and hydrocyanic acid.<sup>2</sup> As liquid ammonia is a much poorer solvolyzing agent than water, one might expect to prepare stable solutions of a normal aluminum cyanide in the latter solvent by the action, for instance, of a solution of mercuric cyanide on aluminum.

The reaction between aluminum and a solution of mercuric cyanide in liquid ammonia takes place in two stages. The first stage, which is fairly rapid, results in the formation of an almost colorless liquid phase, slightly soluble in liquid ammonia at ordinary temperatures and for the most part settling underneath the solvent to the bottom of the reaction tube. In the experiments described in this paper, the initial stage of the action was practically complete at the end of half an hour, the heat developed causing a rather brisk evolution of bubbles of ammonia vapor from the aluminum wire used. This denser liquid phase, which was found to contain one or more double cyanides of aluminum and mercury, then disappeared within a few hours, yielding a colorless solution of aluminum tricyanide. The net reaction may be expressed by the equation,  $2Al + 3Hg(CN)_2 = 2Al(CN)_3 + 3Hg$ .

### Properties of Aluminum Cyanide

Aluminum cyanide in liquid ammonia shows a transition point similar to that exhibited by sodium sulfate in water. At the completion of the reaction between mercuric cyanide and aluminum and in the presence of a reasonable quantity of solvent, all of the salt formed is in solution, but as this solution stands at room temperature for a few hours, small, poorly defined crystals or crystalline crusts are deposited on the walls and bottom of the containing tube. When dried in a vacuum at ordinary temperatures, these have the composition represented by the

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<sup>2</sup> Varet, *Compt. rend.*, 114, 225 (1892).

formula  $\text{Al}(\text{CN})_3 \cdot 5\text{NH}_3$ . The solubility of this modification in liquid ammonia at  $25^\circ$  was found to lie between 7 and 8 g. per liter. The solubility increases greatly with cooling, reaching a maximum somewhere between  $0^\circ$  and  $-33^\circ$ . When a solution in a closed tube container is allowed to stand for several hours in an open liquid-ammonia bath (at  $-40^\circ$ , approximately) quantities of well-formed, colorless or white square columns of  $\text{Al}(\text{CN})_3 \cdot 13$  or  $14\text{NH}_3$  separate, forming a solid crystalline mass if the containing tube be left undisturbed. Even vigorous shaking seems generally to have little effect upon the formation of crystals unless some of the salt has already spontaneously crystallized. In one instance, no crystals were obtained after half a day's refrigeration at  $-40^\circ$  with occasional vigorous agitation, while again nearly complete crystallization occurred within ten minutes. When the reaction tube containing these crystals is removed from the liquid-ammonia bath, complete solution is seen to take place long before the temperature has risen to that of the surrounding air. After several hours at room temperature an abundant crop of ill defined crystals of the other modification result. This undoubtedly exists in solution as a higher ammonate than  $\text{Al}(\text{CN})_3 \cdot 5\text{NH}_3$ , for the latter is an effloresced white powder.

By successive deammonation of the crystals of the composition  $\text{Al}(\text{CN})_3 \cdot 13$  or  $14\text{NH}_3$  at  $-33^\circ$ , the nona- and hexammonates may be obtained as effloresced white solids. A substance of the composition  $\text{Al}(\text{CN})_3 \cdot 1\frac{1}{2}\text{NH}_3$  may be prepared by heating the penta-ammonate in a vacuum of a few millimeters at  $80^\circ$ . While apparently not sintered, this material dissolves in strong acid or alkali with great difficulty and only after long continued heating. For this reason it is possible that some internal change has taken place within the aluminum cyanide molecule.

The following ammonates of aluminum chloride,<sup>3</sup> which have been described in the literature, are mentioned here for purposes of comparison:  $\text{AlCl}_3 \cdot 9\text{NH}_3$ ,  $\text{AlCl}_3 \cdot 6\text{NH}_3$  and  $\text{AlCl}_3 \cdot 2\text{NH}_3$ . Dr. Franklin has obtained an aluminum iodide with approximately 20 molecules of ammonia of crystallization.<sup>4</sup> It will be noted that all of the analyses are a trifle low in cyanide and most of them are a few tenths of a per cent. high in aluminum. This may denote a partial ammonolysis as a result of the washings of the crystallized salt or, more likely, further reaction with the excess of aluminum to form soluble ammonobasic cyanides. Amalgamated aluminum dissolves slowly in a liquid-ammonia solution of ammonium thiocyanate<sup>5</sup> presumably to form normal aluminum thiocyanate which, however, readily reacts with an excess of the metal to give very soluble

<sup>3</sup> Baud, *Compt. rend.*, **132**, 134 (1901). Stillman and Yoder, *Am. Chem. J.*, **17**, 748 (1895).

<sup>4</sup> Franklin, *THIS JOURNAL*, **37**, 849 (1915).

<sup>5</sup> Unpublished work of the author. Ammonium thiocyanate behaves as an acid in liquid-ammonia solution.

ammonobasic thiocyanates. Soluble ammonobasic aluminum iodides are known.<sup>4</sup> Aluminum cyanide penta-ammonate is decomposed by water, presumably with the formation of aluminum hydroxide, ammonia and ammonium cyanide. Solution is readily effected in dilute acids or alkalis.

### Experimental Work

In the preparation of all compounds described in this article, the familiar methods used by Franklin and his co-workers have been used.<sup>6</sup> In one leg of a two-legged reaction tube was placed a convenient quantity of purified and dried mercuric cyanide, together with an excess of pure aluminum wire. At the end of about 12 hours, when it was thought that the last traces of mercuric cyanide would have reacted with the metal, the clear solution containing the aluminum cyanide was decanted from the aluminum and mercury into the other leg of the reaction tube, concentrated and allowed to stand for a few hours. The crystals of ammonated aluminum cyanide separating were washed two or three times with successive small quantities of fresh solvent and dried in a vacuum at room temperature. In order to obtain the highest ammonate, it was necessary to keep the crystals at  $-40^{\circ}$  during the operations connected with the preparation of the specimen tube for drying under reduced pressure. The method of procedure followed, which has been outlined by Franklin,<sup>7</sup> was found necessary because the penta-ammonate absorbed ammonia only very slowly when covered with a few cubic centimeters of the solvent at  $-40^{\circ}$ .

After drying under reduced pressure the analyses were carried out in the following manner:

The salt, while still in the specimen tube, was dissolved completely in dil. nitric acid, and an excess of silver nitrate then allowed to enter the tube to precipitate the hydrocyanic acid.<sup>8</sup> The specimen tube then contained a white curdy precipitate of silver cyanide, together with a solution of aluminum and ammonium nitrates. This solution, together with the precipitate, was removed from the tube, the silver cyanide filtered off and ignited to silver, and aluminum and ammonia nitrogen determined in aliquot parts of the filtrate. In certain instances it was found convenient or necessary because of the relative sizes of the specimen and container to remove clear acid or alkaline solutions. In these cases, loss of hydrogen cyanide or ammonia was prevented by interposing a wash bottle with suitable absorbent between the suction and the flask designed to receive the solution of the preparation. In all cases it was necessary to remove hydrocyanic acid as silver cyanide and filter this off before determining ammonia.

<sup>4</sup> Franklin and co-workers, (a) *THIS JOURNAL*, 27, 821 (1905); (b) 29, 1694 (1907); (c) 35, 1460 (1913); (d) *J. Phys. Chem.*, 15, 510 (1911); (e) 16, 694 (1912).

<sup>7</sup> Ref. 6 d, p. 513.

<sup>8</sup> Bohart, *J. Phys. Chem.*, 19, 547 (1915).

*Preparation 1.* Subs., ( $-40^\circ$ , 1 cm.) 1.2035, ( $19^\circ$ , 2 mm.) 1.0825: ( $\frac{1}{4}$ ) 0.0740  $\text{Al}_2\text{O}_3$ ; ( $\frac{1}{4}$ ) 0.5667  $\text{AgCN}$ .<sup>a</sup>

*Preparation 2.* Subs., ( $20^\circ$ ) 0.7074 ( $\frac{1}{4}$ ) 0.0472  $\text{Al}_2\text{O}_3$ , ( $\frac{1}{4}$ ) 0.2952 Ag and 0.06702 of  $\text{N}_2$ , ( $\frac{1}{10}$ ) 0.00562 g. of N in absorption bottle.

*Preparation 3.* Subs., ( $20^\circ$ ) 0.5097, ( $83^\circ$ , 2 mm.) 0.3591: ( $\frac{1}{4}$ ) 0.0697  $\text{Al}_2\text{O}_3$ .

*Preparation 4.* Subs., ( $-40^\circ$ , 14 mm.) 1.6263, ( $25^\circ$ ) 1.2047: ( $\frac{1}{10}$ ) 1.9825 Ag; ( $\frac{1}{10}$ ) 0.04537 g. of N, ( $\frac{3}{10}$ ) 0.0996  $\text{Al}_2\text{O}_3$ .

*Preparation 5.* Subs., ( $20^\circ$ ) 0.5260: ( $\frac{2}{3}$ ) 0.0576  $\text{Al}_2\text{O}_3$ ; ( $\frac{2}{3}$ ) 0.07612 N.

*Preparation 6.* This experiment was performed primarily to determine ammonia of crystallization at  $-40^\circ$ . Ammonia was removed from the crystals until they had just begun to effloresce, this occurring at a decomposition pressure of about 13 cm.

Subs., ( $-40^\circ$ , 13 cm.) 0.6184, ( $-40^\circ$ , 16 mm.) 0.4847, ( $20^\circ$ , 2 mm.) 0.3548: ( $\frac{1}{4}$ ) 0.5949 Ag; ( $\frac{2}{3}$ ) 0.05217 N, ( $\frac{2}{3}$ ) 0.0392  $\text{Al}_2\text{O}_3$ .

## SUMMARY OF ANALYTICAL RESULTS

|              | Calc. for<br>$\text{Al}(\text{CN})_3 \cdot 13\text{NH}_3$<br>% | Found, No. 6<br>( $-40^\circ$ , 13 cm.)<br>% | Calc. for<br>$\text{Al}(\text{CN})_3 \cdot 9\text{NH}_3$<br>% | No. 6<br>% | Found ( $-40^\circ$ ,<br>13-16 mm.)<br>No. 4<br>% |
|--------------|--|--|---|------------|---|
| Al           | 8.3  | 8.4  | 10.45   | 10.7       | 10.8  |
| CN           | 23.0   | 23.2   | 30.2  | 29.6       | 29.4  |
| $\text{N}^a$ | 55.8   | 56.2   | 48.8  | 49.0       | 49.3  |

<sup>a</sup> That is, ammonia nitrogen.

## Dried under reduced pressure at room temperature

| Calc. for<br>$\text{Al}(\text{CN})_3 \cdot 5\text{NH}_3$<br>% | Found      |            |            |            |            |            |
|---|------------|------------|------------|------------|------------|------------|
|   | No. 1<br>% | No. 2<br>% | No. 3<br>% | No. 4<br>% | No. 5<br>% | No. 6<br>% |
| Al  | 14.2       | 14.5       | 14.1       | 14.5       | 14.6       | 14.6       |
| CN  | 41.1       | 40.7       | 40.2       | ..         | 39.7       | ..         |
| N   | 36.9       | ..         | 38.7       | ..         | 37.7       | 36.2       |

Calcd. for  $\text{Al}(\text{CN})_3 \cdot 6\text{NH}_3$ : Al, 13.0; CN, 37.7. Found: No. 1 ( $-40^\circ$ ,  $<1$  cm.): Al, 13.0; CN, 36.6.

Calcd. for  $\text{Al}(\text{CN})_3 \cdot 1\frac{1}{2}\text{NH}_3$ : Al, 20.7. Found: No. 3 ( $83^\circ$ , 2 mm.): Al, 20.6.

## Pressure-Composition Diagram

The pressure-composition diagram was determined at  $-33^\circ$  approximately the temperature of the bath of liquid ammonia used, by pumping successive small quantities of ammonia from the crystals stable at that temperature, observing the equilibrium pressure, attained frequently only after hours of standing, and titrating the ammonia removed. The apparatus consisted of a Töpler pump with a device for collecting the gases expelled through the delivery tube, and connected by means of a stopcock with the system comprising the manometer and specimen tube. This stopcock was open only during removal of ammonia from the specimen. In view of the fact that equilibrium was very hard to attain, some of the results are rather erratic. As it was found impossible to continue these preliminary measurements due to lack of time, it was thought worth while to publish the data obtained.

<sup>9</sup> For the method of reporting analytical data see THIS JOURNAL, 46, 1547 (1924).

The four horizontal lines of Fig. 1 indicate the constant pressures corresponding to the following equilibria: the top line: saturated solution,  $\text{Al}(\text{CN})_3 \cdot 14(?)\text{NH}_3$ , vapor.  $P = 78$  cm.; the next lower line:  $\text{Al}(\text{CN})_3 \cdot 14\text{NH}_3$ ,  $\text{Al}(\text{CN})_3 \cdot 9\text{NH}_3$ , vapor.  $P = 46$  cm.; the next lower line:  $\text{Al}(\text{CN})_3 \cdot 9\text{NH}_3$ ,  $\text{Al}(\text{CN})_3 \cdot 6\text{NH}_3$ , vapor.  $P = 10$  cm.; the lowest line:  $\text{Al}(\text{CN})_3 \cdot 6\text{NH}_3$ ,  $\text{Al}(\text{CN})_3 \cdot (?)\text{NH}_3$ , vapor.  $P < 1$  cm. The pressures are all approximate.

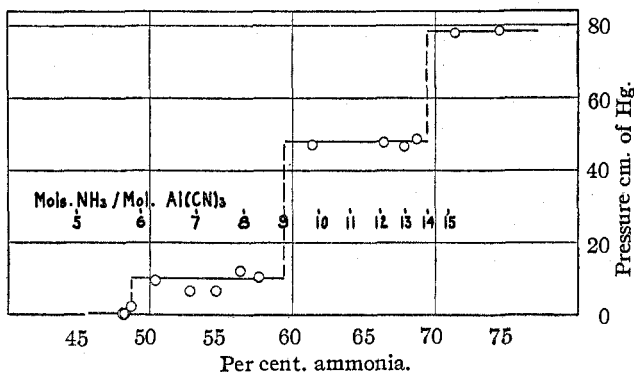


Fig. 1.—Pressure-composition diagram at  $-33^\circ$ .

The points are not distributed well enough to indicate with certainty the formula for the higher ammonate. From the diagram, both the 13 and 16 ammonates appear improbable.

An attempt made to determine the pressure-composition diagram at  $0^\circ$  by a similar method to that followed above resulted in an explosion, and the work was abandoned for lack of time. A previous preliminary determination at the same temperature showed the possible existence of a salt containing more ammonia than the penta-ammonate.

#### Composition of the Denser Liquid Phase Formed Initially by the Action of Mercuric Cyanide on Aluminum

The reaction between aluminum and mercuric cyanide has been briefly described at the beginning of this article. Several minutes elapse after bringing a solution of mercuric cyanide in contact with aluminum before the formation of the almost colorless denser phase begins, subsequent increase in its volume proceeding rapidly until a practical maximum is reached in about half an hour. Thereafter a slower diminution in volume to zero takes place due to interaction of this phase with an excess of aluminum to form normal aluminum cyanide. The denser phase could be concentrated to an almost unpourable sirup without appearance of solid. If ammonia was distilled upon the concentrated solution so formed, the two liquid phases would reappear when a definite volume had been reached. The relative volumes of the two phases changed with temperature due to

the alteration of their mutual solubilities. The system exhibited a lower critical end-point at some temperature between  $-12^{\circ}$  and  $-40^{\circ}$ , resembling in this particular the corresponding manganese derivative to be described further on.

It was not found possible to isolate a compound of definite composition from the denser liquid phase, for no separation of the constituents could be made by crystallization. Analysis showed that the white powder obtained by removal of solvent from this phase consisted of one or more double cyanides of aluminum and mercury, containing approximately three molecules of mercuric cyanide to two of aluminum cyanide. Water slowly reacted with this material with the development of heat. Solution was readily effected by treatment with dil. nitric acid or sodium hydroxide. Varet<sup>2</sup> by the action of aluminum upon mercuric cyanide dissolved in ammoniacal alcohol obtained a double mercuric aluminum cyanide which he was unable to analyze with accuracy.

The equation for the reaction resulting in the formation of the double aluminum mercuric cyanide may be written,  $2Al + 6Hg(CN)_2 = 3Hg(CN)_2 \cdot 2Al(CN)_3 + 3Hg$ , assuming that the formula for the compound is correct as represented, and disregarding ammonia of crystallization.

### Experimental Work

The experimental method was the same as employed in the case of aluminum cyanide, the reaction being arrested shortly after the denser phase had begun to decrease from its maximum volume by pouring both liquid layers into the other leg of the reaction tube. In view of the impossibility of obtaining crystals by concentration of the solution some purification was effected by washing the denser phase a few times with successive portions of the fresh solvent. It was thereby hoped to remove aluminum cyanide.

The cyanide corresponding to the aluminum present could be precipitated upon addition of silver nitrate, the remainder, equivalent to the mercury, could be obtained only after removal of the latter metal as sulfide.<sup>10</sup> Mercury was weighed as sulfide. The other analyses were made as described for aluminum cyanide.

*Preparation 1.* Subs., ( $25^{\circ}$ ) 1.8894: ( $\frac{1}{4}$ ) 0.0499  $Al_2O_3$ ; ( $\frac{1}{4}$ ) 0.3032 Ag, HCN pptd. directly from original solution; ( $\frac{1}{4}$ ) 0.0529 N; ( $\frac{1}{4}$ ) 0.2764 HgS.

*Preparation 2.* Subs., ( $25^{\circ}$ ) 1.3738: ( $\frac{1}{4}$ ) 0.0319  $Al_2O_3$ , and 0.2174 HgS; ( $\frac{1}{4}$ ) 0.3780 Ag (total —CN); ( $\frac{1}{4}$ ) 0.0905 Ag from HCN retained in the wash bottle; ( $\frac{1}{4}$ ) 0.03832 N.

*Preparation 3.* Subs., ( $20^{\circ}$ ) 1.4138: ( $\frac{1}{4}$ ) 0.8104 Ag, HCN pptd. directly from original solution; ( $\frac{1}{4}$ ) 0.1619 Ag, un-ionized HCN corresponding to  $Hg(CN)_2$ ; ( $\frac{1}{4}$ ) 0.1730 HgS; ( $\frac{3}{4}$ ) 0.0267  $Al_2O_3$ ; ( $\frac{1}{4}$ ) 0.03357 N.

<sup>10</sup> Method of Rose. See Treadwell-Hall "Analytical Chemistry," Wiley and Sons, 2, 338 (1915).

| SUMMARY OF ANALYSES |  |       |        |       |
|---------------------|--|-------|--------|-------|
|                     | Calcd. for<br>$3\text{Hg}(\text{CN})_2 \cdot 2\text{Al}(\text{CN})_3 \cdot 9\text{NH}_3$ | No. 1 | No. 2  | No. 3 |
|                     | %  | %     | %      | %     |
| Al                  | 4.8  | 5.6   | 4.9    | 5.0   |
| N                   | 11.2   | 11.2  | 11.2   | 11.9  |
| Ion. CN             | 13.9   | 15.5  | } 28.1 | 13.8  |
| Un-ion. CN          | 13.9   |       |        | 13.8  |
| Hg                  | 53.7   | 50.4  | 54.6   | 52.8  |

Specimen 1 contains more aluminum cyanide than corresponds to that calculated from the formula. This may signify the presence of aluminum cyanide as an impurity or possibly the existence of other double aluminum mercuric cyanides. In view of the impossibility of effecting a purification by crystallization, the individuality of a compound of the formula given above is not entirely certain.

Franklin and Kraus<sup>11</sup> observed the similar formation of a two-liquid-phase system while working with mercuric chloride. In liquid ammonia this salt separated as a relatively dense liquid phase whose composition was found to be  $\text{HgCl}_2 + 12\text{NH}_3$ . Ten molecules of ammonia were given off at atmospheric pressure and solid  $\text{HgCl}_2 \cdot 2\text{NH}_3$  remained. The composition of this liquid phase was found not to vary greatly with the temperature, indicating an almost pure compound.<sup>12</sup>

### Ammonated Double Cyanides of Mercury and Manganese

Manganous cyanide is not known in the pure state. It was thought that its preparation might be effected in a manner analogous to that followed in the preparation of aluminum cyanide.

Like aluminum, manganese reacts with a solution of mercuric cyanide to form two liquid phases, the denser of which contains a double cyanide of mercury and manganese. The reaction, however, practically stops at this point. On standing, the denser liquid very slowly diminishes in volume without greatly altering in composition. As no manganous cyanide was obtained from the upper liquid, it is probable that insoluble compounds, such as manganous manganocyanide, were slowly formed by further interaction between the denser phase and the excess of manganese.

The two phases exhibit a lower critical end-point between  $+4^\circ$  and  $+5^\circ$ . The relative volumes of the two phases were found to vary very markedly with the temperature. Fortunately it was found possible to crystallize a double cyanide of manganese and mercury with comparative ease from the yellowish lower phase. Most of the color was removed with the mother liquor, for the crystals were nearly colorless and on re-solution in a sufficiently large volume of ammonia formed two almost colorless liquid phases. Analysis of the products so obtained indicated a

<sup>11</sup> Franklin and Kraus, *Am. Chem. J.*, **23**, 300 (1900).

<sup>12</sup> Franklin and Kraus, unpublished observations.

formula  $\text{Hg}(\text{CN})_2 \cdot \text{Mn}(\text{CN})_2 \cdot 2-3\text{NH}_3$ . Expt. 4 shows that the composition of the solid obtained from the lower phase simply by evaporating the solvent corresponds closely with this formula, and Expt. 5 proves that its composition did not alter appreciably after the liquid had stood for several months in contact with an excess of manganese. The reaction may be written,  $2\text{Hg}(\text{CN})_2 + \text{Mn} = \text{Hg}(\text{CN})_2 \cdot \text{Mn}(\text{CN})_2 + \text{Hg}$ , disregarding ammonia of crystallization.

### Experimental Work

The experimental method for the preparation of manganous mercuric cyanide is identical with that described for the preparation of aluminum mercuric cyanide, with the substitution of an excess of lump manganese in place of the aluminum wire. Initially a strongly colored, homogeneous, yellow solution is rapidly formed, disappearing within one or two hours when the formation of the lower phase begins. Within a few hours the volume of the latter has practically reached a maximum, thereafter decreasing very slowly with lapse of time. The initial, strongly colored yellow solution, when separated from the mercury and manganese by decanting into the clean leg of the reaction tube, decomposed on standing with the precipitation of a small quantity of light yellow material, but with the appearance of no new liquid phase. Manganese is readily acted upon by ammonium cyanide dissolved in liquid ammonia to give a solution behaving in a very similar manner.<sup>13</sup>

After one or more days in contact with the excess of manganese, both phases were separated from solid matter by decantation into the other leg of the reaction tube. Most of the lighter, ammonia-rich phase was then decanted back into the leg containing the manganese and mercury and the remaining liquid was then concentrated until crystals had been obtained in sufficient quantity. The mother liquor was poured into the residue leg and the crystallization repeated as many times as deemed advisable. The procedure from this point, including analysis, is the same as described for aluminum mercuric cyanide. Manganese was determined as pyrophosphate.

In Preparation 4 the denser phase was simply evaporated to dryness and the resulting solid submitted to analysis. In Preparation 5, the lower liquid phase had been left in contact with the excess of manganese used in the experiment for six months in order to see whether or not manganous cyanide would eventually be formed. All specimens were dried in a vacuum at room temperatures and at a pressure of approximately 2 mm.

*Preparation 1.* Subs., 0.5100: ( $\frac{1}{2}$ ) The HCN absorbed in the wash bottle gave 0.0067 g. of Ag; ( $\frac{1}{2}$ ) 0.0376 HgS; ( $\frac{1}{2}$ ) 0.0754 HgS and 0.0475  $\text{Mn}_2\text{P}_2\text{O}_7$ ; ( $\frac{1}{2}$ ) 0.00669 N; ( $\frac{1}{2}$ ) 0.0639 Ag, ionized HCN; ( $\frac{1}{2}$ ) 0.1327 Ag, total CN.

<sup>13</sup> Unpublished observations of the author.



*Preparation 2.* Subs., 0.5053: ( $\frac{1}{3}$ ) 0.2976 Ag, ionized CN; ( $\frac{1}{3}$ ) 0.0514 Ag, un-ionized CN; ( $\frac{2}{3}$ ) 0.1138 HgS and 0.0818  $Mn_2P_2O_7$ ; ( $\frac{1}{3}$ ) 0.00889 N.

*Preparation 3.* Subs., 0.7994: ( $\frac{1}{3}$ ) 0.4800 Ag, pptd. CN; ( $\frac{1}{3}$ ) 0.01341 N; ( $\frac{2}{3}$ ) 0.1284  $Mn_2P_2O_7$ ; ( $\frac{2}{3}$ ) 0.0900 HgS.

*Preparation 4.* Subs., 1.0787: ( $\frac{1}{3}$ ) 0.6344 Ag, ionized CN; ( $\frac{1}{3}$ ) 0.1187 Ag, un-ionized CN; ( $\frac{2}{3}$ ) 0.2449 HgS and 0.1697  $Mn_2P_2O_7$ ; ( $\frac{1}{3}$ ) 0.01708 N.

*Preparation 5.* Subs., 0.2791: ( $\frac{2}{3}$ ) 0.1006 HgS and 0.0643  $Mn_2P_2O_7$ ; ( $\frac{2}{3}$ ) 0.01022 N; ( $\frac{1}{3}$ ) 0.1600 Ag, ionized CN.

## SUMMARY OF ANALYSES

|                | Calcd. for<br>$Hg(CN)_2 \cdot Mn(CN)_2 \cdot 2.5NH_3$ | No. 1             | No. 2 | No. 3 | No. 4 | No. 5 |
|----------------|---|-------------------|-------|-------|-------|-------|
| Mn             | 13.7  | 14.4              | 15.6  | 15.5  | 15.2  | 14.9  |
| Hg             | 49.8  | 50.9              | 48.5  | 48.5  | 48.9  | 51.8  |
| Ion. CN        | 13.0 <sup>a</sup>                                     | 12.4              | 14.2  | 14.5  | 14.2  | 13.8  |
| Un-ion. CN     | 13.0 <sup>b</sup>                                     | 13.0              | 12.3  | 12.1  | 13.3  | ..    |
| N <sub>2</sub> | 8.7   | 10.5 <sup>c</sup> | 8.8   | 8.4   | 7.9   | 9.2   |

<sup>a</sup> Pptd. from acid solution of specimen by  $AgNO_3$ .

<sup>b</sup> Pptd. only after removal of mercury as sulfide. Ionized HCN removed before determination. This corresponds to the mercury present.

<sup>c</sup> Probably high.

In all of the specimens analyzed there is an excess of manganese above that calculated for the formula  $Hg(CN)_2 \cdot Mn(CN)_2 \cdot 2\frac{1}{2}NH_3$ . This may be due either to small quantities of manganous cyanide, whose concentration in the solution cannot become great because of a slow decomposition into insoluble products, or to admixture with a small quantity of a double manganese mercuric cyanide containing a relatively greater proportion of manganese. According to the experiments performed, crystallization does not effect a separation of the chemical individuals contained in the mixture. It seems probable that this latter consists chiefly of the compound  $Hg(CN)_2 \cdot Mn(CN)_2 \cdot 2-3NH_3$ .

### The Action of Mercuric Cyanide on Iron, Magnesium, Zinc and Tin

Mercuric cyanide reacts more slowly with iron than with either aluminum or manganese. The products obtained were insoluble or very slightly soluble in liquid ammonia and consisted chiefly of a yellowish-green questionably crystalline substance together with some finely divided yellow material and a few large, brown needles. The separation of a definite compound was not accomplished. Analysis of one specimen showed it to be a very impure ferrous cyanide, mixed probably with ferric cyanide (?), mercury, and with a double iron mercury cyanide. This mixture was unaffected by water, while dil. nitric acid at once produced dull green iron cyanogen compounds.

Mercuric cyanide solution reacts rapidly with magnesium with the initial formation of two liquid phases just as in the case of aluminum. These two phases exhibited a critical end-point at some temperature

between  $0^{\circ}$  and  $-40^{\circ}$ . After standing for a few hours in contact with an excess of magnesium, the denser phase, which undoubtedly contained a magnesium mercuric cyanide, disappeared, leaving a gray apparently amorphous precipitate consisting of ammoniated magnesium cyanide mixed with finely divided mercury. Magnesium cyanide was found to be but very slightly soluble in liquid ammonia.

Zinc reacts readily with a solution of mercuric cyanide to form a solution of zinc cyanide and mercury without, however, the appearance of two phases. It is possible that these may appear at higher temperatures.

Tin reacts readily with a solution of mercuric cyanide to form a solution containing chiefly stannous cyanide together with some white precipitate. Stannous cyanide is extremely soluble in liquid ammonia. One experiment having failed to give a definite compound, the reaction was not further investigated.

In conclusion the author wishes to express his thanks to Dr. E. C. Franklin for his kind and helpful interest in this work.

### Summary

1. Aluminum reacts with a solution of mercuric cyanide in liquid ammonia initially with the formation of two liquid phases, the denser of which contains a double cyanide of aluminum and mercury. Further reaction with an excess of aluminum leads to the formation of a solution of aluminum cyanide. The 1.5(?), 5, 6, 9 and 14(?) ammoniates have been prepared. Solutions of aluminum cyanide in liquid ammonia exhibit a transition temperature between  $0^{\circ}$  and  $-33^{\circ}$  similar to that shown by sodium sulfate in water. Separation of crystals either of the modification stable above  $0^{\circ}$  or of that stable at  $-33^{\circ}$  was found to be very slow.

2. Mercuric cyanide reacts with manganese more slowly than with aluminum, but the reaction practically stops with the formation of the two liquid phases. Although manganous cyanide was not obtained by this method, a double manganous mercuric cyanide of the probable formula  $\text{Hg}(\text{CN})_2 \cdot \text{Mn}(\text{CN})_2 \cdot 2-3\text{NH}_3$  was isolated in not altogether pure condition from the denser liquid phase. The two phases have a lower critical end-point between  $+4^{\circ}$  and  $+5^{\circ}$ .

3. Mercuric cyanide and iron react to form products insoluble in ammonia and of indefinite composition. Magnesium and mercuric cyanide react initially to form two liquid phases, and with the disappearance of these to form sparingly soluble magnesium cyanide, which was not obtained in a pure condition. Zinc and tin react readily with a solution of mercuric cyanide.