pressions are well represented by the Tait equation and the constant C in this equation is independent of temperature. Our results enable us to compute the $P-V-T$ relations and derived quantities with considerable precision over this range of pressure and temperature.

The temperature variation of the constant B in the Tait equation has been studied and B has been fitted empirically into an equation of state of the van der Waals type. Our results indicate that B is the difference between the a/v^2 and $RT/(v-b)$ attractive and repulsive forces in the liquid.

By matching the refractive indices of benzene under different conditions against those of optical glasses we have been able to estimate with considerable accuracy the change of the refractive index of benzene with pressure. Our results confirm the empirical worth of the Eykman specific refraction formula and show that with this formula the compressibility of benzene may be computed from refractive index–pressure measurements almost as accurately as it may be measured directly.

WASHINGTON, D. C. RECEIVED DECEMBER 30, 1937

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Action of Ammonium Hydroxide on Mercurous Chloride[1]

BY HERTHA R. FRECHE AND M. C. SNEED

Several equations have been formulated to express the reaction which takes place when mercurous chloride is treated with ammonium hydroxide. In 1825, Hennel[2] suggested that the chemical reaction between mercurous chloride and ammonium hydroxide produced mercurous oxide.

Kane and Ullgren[3] suggested the reaction

$$Hg_4Cl_4 + N_2H_6(-H_2Cl_2) \longrightarrow Hg_2Cl_2 + Hg_2N_2H_4$$

According to Rammelsberg[4] and Pesci[5] the reaction occurred according to the equation

$$2Hg_2Cl_2 + 4NH_3 \longrightarrow (Hg_2NCl{\cdot}NH_4Cl + 2Hg) + 2NH_4Cl$$

Barfoed[6] and Saha and Choudhuri[7] proposed the equation

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg + NH_2HgCl + NH_4Cl + 2H_2O$$

Druce[8] introduced the equation

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow NH_2Hg_2Cl + NH_4Cl + 2H_2O$$

Feigl and Sucharipa[9] separated this reaction into the following

$$2NH_3 + Hg_2Cl_2 \longrightarrow NH_2Hg_2Cl + NH_4Cl$$
$$NH_2Hg_2Cl \longrightarrow NH_2HgCl + Hg$$

According to Renz[10] the black substance obtained by the action of ammonium hydroxide on mercurous chloride is mercuric aminochloride and a mercurophotochloride (a stable adsorption product of mercury on mercurous chloride).

Shehigol[11] found that the results of qualitative tests indicated that the reaction between mercurous chloride and ammonium hydroxide is best expressed by the equation

$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow [Hg + Hg_2O + NH_2HgCl] + 3NH_4Cl + 3H_2O$$

Thus there is considerable lack of agreement regarding the chemical action of ammonium hydroxide on mercurous chloride. It was thought that this lack of agreement was due to the differences in concentration of the ammonium hydroxide used, as well as to the time of reaction. Therefore, in the present investigation the effects of dilute and concentrated ammonium hydroxide on mercurous chloride and the time of reaction were investigated. It was found that the end-products obtained, when concentrated ammonium hydroxide reacts with mercurous chloride, are a gray precipitate of the composition $Hg + NH_2{\cdot}HgCl$ and the water soluble fusible compound $HgCl_2{\cdot}2NH_3$. In case of dilute ammonium hydroxide, on the other hand, the speed of reaction is sufficiently slow to permit the identification of the intermediate products, namely, mercurous oxide and ammonium chloride, which in turn react to produce mercury and the infusible precipitate, NH_2HgCl.

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[1] Based upon a thesis submitted by Hertha R. Freche in partial fulfilment of the requirements for the Ph.D. degree at the University of Minnesota. Original manuscript received July 28, 1931.

[2] Hennel, *The Quarterly Journal of Science, Literature and the Arts*, **18**, 292 (1825).

[3] Kane and Ullgren, *Pogg. Ann.*, **42**, 380–381 (1837).

[4] Rammelsberg, *J. prakt. Chem.*, **138**, 563 (1888).

[5] Pesci, *Z. anorg. Chem.*, **21**, 361 (1899).

[6] Barfoed, *J. prakt. Chem.*, **39**, 211 (1889).

[7] Saha and Choudhuri, *Z. anorg. Chem.*, **67**, 357 (1910).

[8] Druce, *Chem. News*, **123**, 153 (1921).

[9] Feigl and Sucharipa, *Z. anal. Chem.*, **67**, 135 (1926).

[10] Renz, *Helv. Chim. Acta*, **15**, 1316 (1932).

[11] Shehigol, *Ann. chim. anal. chim. appl.*, **18**, 149 (1936).

Experimental Part

A. The Action of Concentrated Ammonium Hydroxide on Mercurous Chloride

1. **Preparation.**—For this purpose freshly redistilled ammonium hydroxide (sp. gr. 0.89) and mercurous chloride of high purity were stirred together by means of an electric stirrer. The gray precipitate was separated from the supernatant solution and again stirred with a fresh volume of ammonium hydroxide. The process was repeated until the final filtrate was free from mercuric salt. The filtrates obtained in this manner were evaporated *in vacuo*.

2. **Results and Discussion.**—The filtrate of the tenth extract contained only traces of the mercuric and chloride ions, and evaporation of this filtrate gave no crystals. The residual precipitate consisted of globules of metallic mercury and a white powder which corresponded to the composition of mercuric aminochloride, NH_2HgCl.

The salt in the successive filtrates crystallized in the form of rosets and rapidly decreased after the first three extracts. When heated, the greater portion of this salt melted, but there remained a residue which decomposed without melting. Continued washing with water and prolonged exposure to the air decomposed the crystalline salt, leaving an amorphous gray residue. The analyses of the crystalline salt which had been washed with water, alcohol and ether, and dried in a stream of purified and preheated nitrogen gave the following average results: Hg, 74.00%; Cl, 18.41%; N, 6.87%. These results lie intermediate between those of mercuric aminochloride, NH_2HgCl, and the fusible precipitate, $HgCl_2\cdot 2NH_3$.

These intermediate values, as well as the qualitative behavior of the crystalline salt, suggested that the crystalline salt was the fusible precipitate, $HgCl_2\cdot 2NH_3$, which had been decomposed partially during washing, forming mercuric aminochloride, NH_2HgCl, and ammonium chloride. Furthermore, the gradual disappearance of the fusible precipitate in the successive filtrates upon continued extracting suggested that the mercuric aminochloride formed during the reaction was converted into the soluble fusible precipitate, $HgCl_2\cdot 2NH_3$, by the ammonium chloride present, and that this reaction ceased after the ammonium chloride had been consumed. These assumptions were entirely in accord with the findings of Gaudechon,[12] according to whom mercuric aminochloride may be converted into the fusible precipitate by an ammoniacal solution of ammonium chloride, and according to whom this reaction is reversible. This observation was verified by Holmes[13] and by François.[14] The latter, however, demonstrated this behavior on the corresponding iodides.

Saha and Choudhuri[15] also obtained rosets of a mercuric salt upon evaporation of the filtrate when they added concentrated ammonium hydroxide to mercurous chloride. However, the result of their analysis of the crystals corresponded more closely to that of mercuric aminochloride than to that of the fusible precipitate, except that their value for mercury was approximately 0.9% lower and that of chlorine and nitrogen were, respectively, 0.9 and 0.1% higher than the corresponding values required by the formula NH_2HgCl. In view of Gaudechon's findings, namely, the reversibility of the reaction

$$NH_2HgCl + NH_4Cl \rightleftharpoons HgCl_2\cdot 2NH_3$$

these deviations may be regarded as positive indications that small amounts of the fusible precipitate were still present in the product, since the mercury content is lower, while the nitrogen and chlorine contents are higher in the fusible precipitate ($HgCl_2\cdot 2NH_3$) than in the infusible precipitate (NH_2HgCl). Saha and Choudhuri also observed that freshly prepared mercuric aminochloride is only sparingly soluble in concentrated ammonium hydroxide, while the product obtained by the addition of concentrated ammonium hydroxide to mercurous chloride is extremely soluble. They found that as much as 34.06% of the original amount of mercury in mercurous chloride had passed into the ammoniacal extracts. This observation eliminates completely the possibility that the crystalline salt, obtained upon evaporating the ammoniacal extracts from mercurous chloride and ammonium hydroxide, is mercuric aminochloride, NH_2HgCl, but confirms the suggestion that the salt is the fusible precipitate, $HgCl_2\cdot 2NH_3$, which decomposes upon washing with water yielding a mixture of the fusible and the infusible precipitates. The amount of $HgCl\cdot 2NH_3$ formed depends upon the concentration of the ammonium hydroxide. This is in agreement with Ephraim's statement that[16] concentrated ammonium hydroxide favors the formation of the amine $HgCl_2\cdot 2NH_3$, and that upon diluting the latter the ammonobasic salt NH_2HgCl is again produced.

Therefore, when mercurous chloride is triturated with concentrated ammonium hydroxide, a considerable quantity of ammonium chloride is produced which reacts with the mercuric amino-

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[12] Gaudechon, *Ann. chim. phys.*, [8] **22**, 181 (1911).

[13] Holmes, *J. Chem. Soc.*, **113**, 74 (1918).

[14] François, *Compt. rend.*, **130**, 332 (1900).

[15] Saha and Choudhuri, *Z. anorg. Chem.*, **67**, 357 (1910).

[16] Ephraim, "Inorg. Chem.," Second English Edition, 1934, pp. 558–563.

TABLE I

REACTION OF DILUTE AMMONIUM HYDROXIDE ON MERCUROUS CHLORIDE FOR INCREASING PERIODS OF TIME

Prepn.	Hg_2Cl_2, g.	Time of reacn.	% original Cl which passed into filtrate	Ppt. formed g.	Color of ppt.	Amalgamated gold[a]	% Hg	% Cl	% N	% H	Total %
1	3.290	10 min.	77.30	3.105	Black	No	93.40	3.60[b]	0.93	..	97.93
2	2.039	15 min.	73.60	1.825	Black	No	92.77	4.37[c]	1.50	..	98.64
3	3.843	30 min.	56.30	3.581	Dark gray	Yes	90.13	7.07[c] 7.10[b]	2.06	..	99.28
4	4.274	1.5 hrs.	46.90	4.064	Dark gray	Yes	88.50	8.25[c] 8.38[b]	2.83	..	99.64
5	2.432	2.5 hrs.	46.40	2.286	Dark gray	Yes	...	..	..	..	...
6	5.137	3.5 hrs.	45.70	4.862	Dark gray	Yes	...	..	..	..	...
7	9.778	6 hrs.	45.00	9.290	Dark gray	Yes	...	..	..	..	...
8	7.228	48[d] hrs.	45.10	6.789	Light gray	Yes	87.93	8.45[c] 8.76[b]	2.95	0.38	99.92
9	4.842	48[d] hrs.	...	4.941	Light gray	Yes	42.10	(metallic Hg)		..	...

[a] The moist precipitate was tested for the presence of mercury with a strip of gold sheet. [b] Calculated from per cent. of Cl in filtrate. [c] Determined by analysis of precipitate. [d] It is pointed out that the reaction does not cease here, but that further experiments showed that practically all the metallic mercury may react after twelve weeks, producing a white powder with only a slight gray tinge and an appreciable amount of the water-soluble $HgCl_2 \cdot 2NH_3$. After a reaction period of one week the filtrate contained 0.10% of the original mercury in mercurous chloride in the form of the amine, $HgCl_2 \cdot 2NH_3$.

chloride to produce the fusible precipitate $HgCl_2 \cdot 2NH_3$ according to the equation

$$NH_2HgCl + NH_4Cl \rightleftarrows HgCl_2 \cdot 2NH_3$$

B. The Action of Dilute Ammonium Hydroxide on Mercurous Chloride

1. **Preparation.**—For these preparations the redistilled ammonium hydroxide was diluted to 0.1 normal. A series of preliminary experiments had shown that the time of reaction and the concentration of the ammonium hydroxide affected the composition of the precipitate. To determine the effect of short periods of time, the mercurous chloride and dilute ammonium hydroxide were triturated. To determine the effects of longer periods of time, the mixtures were put in heavy-walled glass tubes, which were sealed off and shaken for predetermined lengths of time. To avoid decomposition of the resulting precipitates, all experiments were carried out in a dark, constant temperature room. After the absence of the mercuric ion in the filtrate had been confirmed, the chloride in the filtrate was determined.

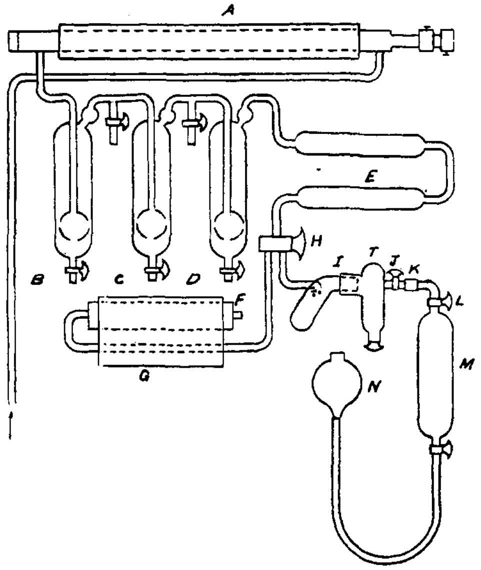

Fig. 1.—Apparatus used for drying and decomposition of the black precipitate.

The precipitates, obtained in the manner described above, were washed, dried in an atmosphere of purified nitrogen, weighed, and analyzed. The apparatus used for purifying the nitrogen[17] and drying the precipitates is illustrated by Fig. 1. No rubber tubing connections were used. The nitrogen was purified and dried in A, B, C, D and E. Tube A, which was electrically heated, contained high purity copper filings for the removal of oxygen from the nitrogen. The automatic bubbling gas analysis pipets B, C and D contained an acidified potassium permanganate solution, a potassium hydroxide solution and concentrated sulfuric acid, respectively. The two small glass tubes E contained redistilled crystalline phosphorus pentoxide. The precipitates were dried in the glass tube F supported in the electrically heated oven G with temperature control (Fig. 1). While most of the samples of the precipitate were dried in purified and dry nitrogen, a few were dried in purified and dry ammonia, followed by several hours of drying in nitrogen, to remove any adsorbed ammonia. The precipitates were kept in a dark desiccator for several days before they were analyzed.

The constituent elements were determined by the following methods: chlorine, gravimetrically as silver chloride; nitrogen, according to the modified Dumas method; mercury, gravimetrically as mercuric sulfide; and hydrogen, gravimetrically as water.

2. **Results.**—The gradual change in composition of the precipitates and the decrease of the

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(17) Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Gases, Third Edition, Pub. by Carnegie Steel Company, Pittsburgh, Pennsylvania.

ammonium chloride in the successive filtrates for the increasing periods of time of reaction are given in full in Table I.

3. **Discussion of Results.**—From Table I it is apparent that metallic mercury does not appear in the precipitate at first when dilute ammonium hydroxide reacts with mercurous chloride. This observation was also made by Feigl and Sucharipa[18] and Druce.[19]

The total mercury content which was in the combined form in the precipitate, after a time of reaction of ten minutes, corresponded to 93.40%. This decreased 5.47% within forty-eight hours, while the chlorine and nitrogen contents in the precipitate increased 5.16 and 2.02%, respectively, during the same period of time. The percentage of chlorine which passed into the filtrate decreased rapidly during the first thirty minutes and approached an approximately constant value after the first six hours. Figure 2 illustrates this decrease of the chlorine content in the filtrate within forty-eight hours.

Since the composition of the precipitate changed only slightly during the period of one and one-half to forty-eight hours, it was assumed that, for practical purposes, the reaction was complete after forty-eight hours. Therefore, the atomic ratios of the components of the final product were calculated from the analysis of the sample corresponding to a time of reaction of forty-eight hours (see Table I, preparation 8). These atomic ratios were found to be

Mercury	2.08	Nitrogen	1.00
Chlorine	1.15	Hydrogen	1.81

which approximately correspond to the empirical formula $Hg + NH_2HgCl$. The percentage of metallic mercury in this mixture was determined from preparation 9 (Table I) by extracting the precipitate with dilute hydrochloric acid and weighing the residual washed and dried mercury. The metallic mercury in this mixture corresponded to 42.10%. According to the equation, which at the present time is used to describe the reaction between mercurous chloride and ammonium hydroxide

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg + NH_2HgCl + NH_4Cl + 2H_2O$$

the percentage of metallic mercury in the precipitate should be 44.31. The somewhat lower experimental value of the metallic mercury was due to the volatilization of the finely divided mercury which adhered to the sides of the crucible. Barfoed[20] previously had found 41.6% metallic mercury by volatilizing the mercury and weighing the residue. He attributed his low value of mercury to the "fixation" of the metallic mercury by the precipitate, forming again mercurous chloride. It may be assumed, however, just as readily that the mercurous chloride which Barfoed observed in the precipitate was due to incomplete reaction of the original mercurous chloride with the ammonium hydroxide, because it was found that the precipitate tends to form a protective sheath over the particles of mercurous chloride, thus preventing further reaction with the ammonium hydroxide. This sheath was only removed by continued trituration or prolonged vigorous shaking.

From the preceding it is apparent that only the forty-eight hour sample, produced by the action of dilute ammonium hydroxide on mercurous chloride, satisfies the conditions of the equation

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg + NH_2HgCl + 2H_2O + NH_4Cl$$

which is used at the present time to describe the reaction of both dilute and concentrated ammonium hydroxide on mercurous chloride. Ephraim has pointed out that in case of dilute ammonium hydroxide the reaction stops with the formation of the ammonobasic salt NH_2HgCl but, he also adds, that in presence of concentrated ammonium hydroxide the amine, $HgCl_2 \cdot 2NH_3$, is formed which has been confirmed experimentally, and described in the previous section. Thus the above equation does not completely define the reactions which occur when concentrated ammonium hydroxide reacts with mercurous chloride or when dilute ammonium hydroxide reacts with mercurous chloride for a long period of time (see footnote, Table I).

In addition, the above equation does not define the reaction which occurs at first when ammonium hydroxide reacts with mercurous chloride. As is apparent from Table I, after a time of reaction of ten minutes, no positive test for metallic mercury in the precipitate was obtained, but there were found in the precipitate 93.40% combined mercury, 3.60% chlorine, and 0.93% nitrogen; while the filtrate contained no mercuric ion but 77.30% of the chlorine, in the form of ammonium chloride, from the original mercurous chloride. It is also apparent from Table I that the chlorine and nitro-

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(18) Feigl and Sucharipa, *Z. anal. Chem.*, **67**, 135 (1926).

(19) Druce, *Chem. News*, **123**, 153 (1921).

(20) Barfoed, *J. prakt. Chem.*, **39**, 211 (1889).

gen contents in the precipitate gradually increase while the mercury content decreases until they reach almost constant values after one and one-half hours. This immediately suggests a progressive reaction. Finally, it is also apparent from Table I that there exists a striking difference between the sums of the percentages of the components for the successive determinations. Thus the sum of the percentages of the components of preparation 1 (Table I) corresponds to 97.93, while that of preparation 8 corresponds to 99.92. This definitely points to the fact that mercury, chlorine, nitrogen and hydrogen are not the only components of the precipitate formed first when ammonium hydroxide reacts with mercurous chloride.

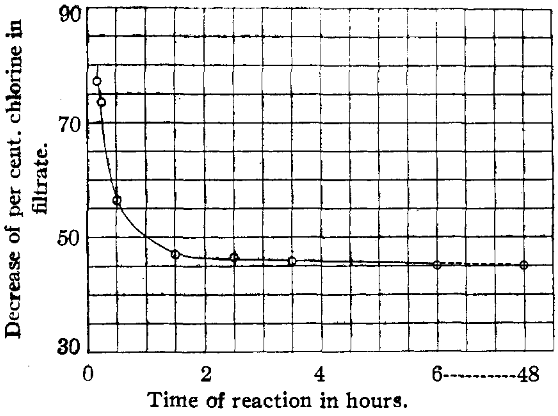

Fig. 2.—Decrease in chlorine content in filtrate.

While Feigl and Sucharipa's scheme accounts for the absence of mercury in the precipitate, it does not explain the high concentration of ammonium chloride in the filtrate. The absence of metallic mercury, the high percentage of combined mercury in the precipitate and the excess ammonium chloride in the filtrate rather indicate that Hennel's suggestion that mercurous oxide and ammonium chloride are first formed was not entirely unfounded. It appears that when ammonium hydroxide reacts with mercurous chloride a series of consecutive reactions occur and that the end-products are entirely dependent upon the time of reaction and the concentration of the ammonium hydroxide. Thus mercurous oxide and ammonium chloride are first formed which react immediately to produce the ammonobasic salt NH_2HgCl which under ordinary conditions is the end product in case of a dilute solution of ammonium hydroxide, while in a concentrated solution of ammonium hydroxide a portion of the NH_2HgCl is converted into the amine $HgCl_2 \cdot 2NH_3$. This scheme is in agreement with the findings of Shehigol, according to whom the precipitate, produced by the action of ammonium hydroxide on mercurous chloride, is a mixture of mercury, mercurous oxide and mercuric aminochloride as was pointed out previously. That mercurous oxide reacts with an ammoniacal solution of ammonium chloride to form mercuric aminochloride will be shown subsequently.

A known quantity of freshly prepared and dried mercurous oxide was triturated with an ammoniacal solution of ammonium chloride. The resulting filtrate contained a large quantity of the amine $HgCl_2 \cdot 2NH_3$, while the precipitate was found to contain metallic mercury, traces of mercurous chloride and a component soluble in dilute hydrochloric acid. The precipitate was extracted with hydrochloric acid and the mercury content in the acid-soluble salt was determined. This corresponded to 78.90% of mercury. Mercuric aminochloride is also soluble in dilute hydrochloric acid and contains 79.52% of mercury. The close agreement between the determined mercury content in the hydrochloric acid extract and the theoretical percentage of mercury in mercuric aminochloride NH_2HgCl, as well as the qualitative tests, showed that one of the products formed when mercurous oxide reacts with ammonium chloride is mercuric aminochloride.

4. The Determination of Oxygen in the Precipitate Obtained by the Action of Dilute Ammonium Hydroxide on Mercurous Chloride.—For this purpose a sample of black precipitate was prepared by shaking together known quantities of mercurous chloride and dilute ammonium hydroxide for forty-five minutes. In accordance with the curve, illustrated by Fig. 2, the decomposition of the mercurous oxide formed at first had progressed appreciably and the samples of precipitate contained metallic mercury. However, it had been found that the black precipitate first formed, coated the mercurous chloride and prevented further reaction and that only prolonged shaking effected complete reaction. Since the sample was large, it could not very well be triturated, which accounts for the long time of reaction. The precipitate was washed free from ammonium chloride, dried and decomposed in purified nitrogen. The apparatus (Fig. 1) and the method of purification of the nitrogen have been described previously.

The apparatus used for the decomposition of the black precipitate and for collecting the gaseous decomposition products is also shown in Fig. 1. The sample of the black precipitate was placed in the sublimation tube I (Fig. 1) which had a capacity of about 20 cc. The gas sample tube M (Fig. 1) was attached to the sublimation tube at K, a ground glass joint. The tube from J to L (Fig. 1) was a capillary tube and corresponded to 0.1 cc. The sample tube M, which had a three-way stopcock L, was filled completely with mercury, and the apparatus was then flushed with purified nitrogen which escaped through the opening in the stopcock L, until a gas analysis of the 150-cc. blank showed no detectable amount of oxygen. The apparatus used for gas analysis was modeled according to the one recommended by the United States Steel Corporation and is illustrated in Fig. 3.

During the thermal decomposition the sample of precipitate turned at first yellow and then decomposed into metallic mercury and long white acicular crystals which sublimed on the sides of the tube I. The temperature of decomposition was gradually raised to 400° and fluctuated between 400 and 450°. After decomposition was complete, the sublimation tube was flushed with a volume of purified nitrogen equivalent to about twice the volume of the gas collected in the sample tube. The gases were allowed to cool and analyzed in the apparatus illustrated by Fig. 3. The ammonia was absorbed in a sulfuric acid solution (specific gravity 1.7), any hydrogen chloride, which was thought might be formed, in a 33% potassium hydroxide solution and the oxygen in a potassium pyrogallate solution. It was found that no hydrogen chloride was liberated during the thermal decomposition. The total volumes of oxygen and ammonia were noted, reduced to standard conditions of temperature and pressure and the per cent. of oxygen and ammonia in the precipitate was calculated. The analytical data are summarized in Table II.

TABLE II

GAS ANALYSIS OF THERMAL DECOMPOSITION PRODUCTS FROM BLACK PRECIPITATE

Weight of sample of precipitate, g.	4.671
Total volume of gas, cc.	158.3
Total volume of ammonia in precipitate, cc.	50.4
Total volume of oxygen in precipitate, cc.	5.8
Oxygen in precipitate, %	0.17
Ammonia in precipitate, %	.82

The gas analysis identified directly the presence of oxygen in the black precipitate, and, therefore, confirmed the presence of mercurous oxide in the precipitate first formed when dilute ammonium hydroxide reacts with mercurous chloride. This mercurous oxide then reacts with the ammonium chloride to produce the insoluble ammonobasic salt, NH_2HgCl. The reaction ceases here under ordinary circumstances because of the dilution as Ephraim has pointed out, but continues to form the amine $HgCl_2 \cdot 2NH_3$ when concentrated ammonium hydroxide is used. It is very likely that mercurous oxide is also formed when concentrated ammonium hydroxide is added to mercurous chloride, but the rate of reaction is so rapid that it cannot be identified. Therefore, if ammonium hydroxide reacts with mercurous chloride, the reactions which occur are

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow Hg_2O + 2NH_4Cl + H_2O$$

$$Hg_2O + NH_4Cl \text{ (ammoniacal)} \longrightarrow NH_2HgCl + Hg + H_2O$$

In view of the fact that the decomposition of the mercurous oxide occurs almost immediately, the reaction is best represented by the equation suggested by Shehigol, namely

$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow [Hg + Hg_2O + HgNH_2Cl] + 3H_2O + 3NH_4Cl$$

The presence of concentrated ammonia, in addition, favors the formation of the amine, $HgCl_2 \cdot 2NH_3$ from the ammonobasic salt NH_2HgCl according to the reaction

$$NH_2HgCl + NH_4Cl \text{ (ammoniacal)} \rightleftarrows HgCl_2 \cdot 2NH_3$$

This latter fact already has been established by Gaudechon, Holmes and François, as was pointed out previously. Therefore, the composition of the final product from the reaction between mercurous chloride and ammonium hydroxide depends entirely upon the time of the reaction and the concentration of the ammonium hydroxide.

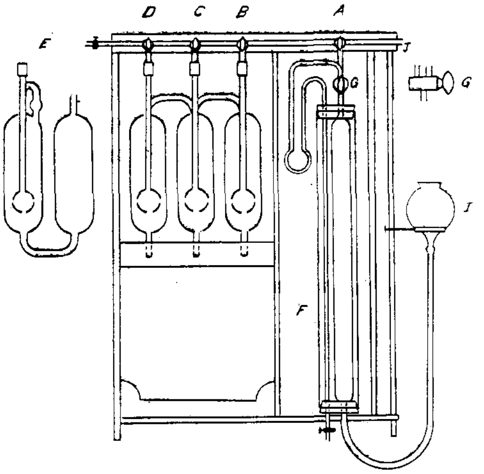

Fig. 3.—Gas analysis apparatus.

A comparison of the amount of nitrogen corresponding to the ammonia obtained by the thermal decomposition of the black precipitate to the percentage of nitrogen obtained by means of the Dumas method indicated that all of the nitrogen in the precipitate was not liberated upon heating. Therefore, the white acicular needles were removed from the sublimation tube. In view of the fact that the crystals were slightly contaminated with metallic mercury, they had to be picked out under a microscope so that the sample was too small to permit a quantitative nitrogen determination. However, the qualitative test, using Nessler's reagent, gave a very pronounced test for nitrogen. Two mercury determinations were made, and the average of these two determinations was found to be 83.75%. The mercury in mercurous chloride is 84.92%.

The crystals did not absorb moisture when exposed to the air at ordinary temperature, potassium and ammonium hydroxide turned them black and pyridine, glycerol and hydrogen peroxide decomposed them, forming metallic mercury.

5. The Action of Dry Hydrogen Chloride on the Precipitate Produced by the Action of Dilute Ammonium Hydroxide on Mercurous Chloride.—Ullgren[21] observed that the black precipitate readily adsorbed hydrogen chloride to form mercurous chloride and ammonium chloride. His experiment was repeated on a precipitate for which the time of reaction did not exceed fifteen minutes. The precipitate was dried in nitrogen according to the procedure described. The dry hydrogen chloride was passed over a sample of this dry precipitate for several hours and over two samples which had been moistened.

Result.—It was found that the dry precipitate did not react, but merely adsorbed hydrogen chloride which it again liberated on standing in a vacuum desiccator. The moist precipitate, however, reacted immediately and formed mercurous chloride.

Summary

1. When ammonium hydroxide reacts with mercurous chloride, the product formed is a mixture the composition of which depends upon the time of reaction and the concentration of the ammonium hydroxide. When dilute ammonium hydroxide is used, the mercurous oxide which is first formed can be identified, and the reaction ceases, under ordinary conditions, with the formation of $HgNH_2Cl$ and Hg. However, if concentrated ammonium hydroxide is used, the water-soluble amine $HgCl_2 \cdot 2NH_3$ is formed in addition.

In view of the fact that the product is a mixture the reaction occurring under ordinary conditions between mercurous chloride and ammonium hydroxide is best represented by means of the equation

$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow [Hg + Hg_2O + NH_2HgCl] + 3NH_4Cl + 3H_2O$$

2. Dry hydrogen chloride does not react with the dry black precipitate, but yields mercurous chloride with the moist precipitate.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 28, 1937

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[21] Ullgren, *Pogg. Ann.*, **42**, 381 (1837).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 622]

The Structures of the Hydrides of Boron. IV. B_2NH_7 and $B_3N_3H_6$. The Structure of Dimethylamine

BY S. H. BAUER*

An interesting derivative of diborane, B_2NH_7, recently has been discovered by D. M. Ritter working under the direction of Professor Schlesinger. Details of the preparation have not yet appeared in the literature. The existence of the compound was called to my attention by Dr. Anton B. Burg, who very kindly furnished the samples of this substance and of triborine triamine used in the electron diffraction experiments. These investigators were particularly interested in the structure determination since their studies, soon to be published, on the diammonate of diborane, $B_2H_6 \cdot 2NH_3$, led to the conclusion that in the latter compound the boron atoms are not linked to each other but are both linked to a nitrogen atom, thus forming the boron–nitrogen chain B–N–B. The diammonate is not itself suitable for an electron diffraction experiment due to its involatility; the compound B_2NH_7, in which a similar link was suspected, is a volatile liquid at room temperature. In turn, the configuration of the diammonate is significant in that important conclusions regarding the structure of diborane and of similarly constituted boron hydrides may be deduced from it. The experimental results herein reported show that the order of arrangement in B_2NH_7 is B–N–B thus being in accord with the conclusions reached by Burg and Schlesinger concerning the diammonate of diborane.

As an aid in the structure determination, I considered it advisable to reinvestigate the interatomic distances in $B_3N_3H_6$[1] so that a value for the single covalent separation of boron and nitrogen could be deduced, and to obtain electron diffraction photographs of dimethyamine for comparison with those of B_2NH_7.

Triborine Triamine.—The purity of the material used in the electron diffraction experiment was

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(1) A. Stock and R. Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931), found the B–N separation to be 1.47 ± 0.07 Å. The single-bond B–N distance in borine trimethylammine is also known with a relatively large uncertainty—1.62 ± 0.15 Å., S. H. Bauer, THIS JOURNAL, **59**, 1804 (1937).