

due to the capillary structure alone by correcting, with the aid of the above formula, for the amount of gas dissolved in the water of the gel. Applying this formula,  $V = K \left( \frac{P_\sigma}{P_o} \right)^{1/N} + 0.048 K' \left( \frac{P_\sigma}{P_o} \right)^{1/N'}$ , to the measurements of ammonia made with the gel containing 4.8% water, the value of  $K$  becomes 0.1147. Doing the same with the measurements of sulfur dioxide, we find that the mean value for  $K$  does not differ much from 0.1038. The  $K$  for the anhydrous gel is 0.0955. From these experiments we see that the amount of different gases adsorbed due to capillarity is in good agreement.

### Summary.

1. The adsorption of ammonia by silica gel has been measured under various pressures at 0°, 30°, 40°, and 100°.
2. The influence of the water content of the gel on the adsorption has been studied.
3. It has been shown that the adsorption of ammonia may be satisfactorily explained on the basis of capillary condensation, provided corrections are made for the amount of the gas that dissolves in the water.

BALTIMORE, MARYLAND.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## A STUDY OF THE SYSTEM AMMONIA : MAGNESIUM : MERCURY. THE FORMATION OF MAGNESIUM HEXAMMONIATE.

By ALBERT G. LOOMIS.

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### Introduction.

The object of this investigation was to study the properties of the three-component system ammonia : magnesium : mercury, and to establish the constitution of the solid phase which separates when dilute magnesium amalgams are allowed to absorb ammonia. The separation of this solid phase was first observed by the late Dr. William Argo, and at his suggestion this work was undertaken. It was of interest to determine whether mercury is an essential constituent of the solid phase, and whether a compound of magnesium and ammonia, but containing no mercury, could be prepared corresponding to calcium hexammoniate  $\text{Ca}(\text{NH}_2)_6$ , calcium hexammoniate, discovered and studied by Kraus.<sup>1</sup> A study of the properties of this compound, together with such groups as methyl mercury, and solutions of the alkali metals in anhydrous ammonia has led Kraus to highly important conclusions regarding the theory of the metallic state and the mechanism of metallic conduction.

<sup>1</sup> Kraus, *THIS JOURNAL*, 29, 1557 (1907); 30, 653 (1908).

The metals which have been reported to be soluble in liquid ammonia are: sodium and potassium,<sup>2</sup> lithium,<sup>3</sup> rubidium and cesium,<sup>4</sup> calcium,<sup>5</sup> barium,<sup>6</sup> and strontium.<sup>7</sup> Magnesium goes into solution very slowly; if, however, it is first treated with a solution of an ammonium salt in liquid ammonia, allowing some hydrogen to be evolved, and then washed free of the ammonium salt, immediate solution takes place. Compounds of metals with ammonia of the following formulas have been reported:  $\text{NaNH}_3$ ,  $\text{KNH}_3$ ,<sup>8</sup>  $\text{LiNH}_3$ ,  $\text{Ca}(\text{NH}_3)_4$ ,<sup>5</sup>  $\text{Ba}(\text{NH}_3)_6$ ,<sup>9</sup> and  $\text{Sr}(\text{NH}_3)_6$ .<sup>10</sup> Kraus,<sup>1</sup> however, proved by phase rule criteria that sodium, potassium, and lithium do not form compounds with liquid ammonia, but true solutions. He found also that the compound with calcium was not calcium tetrammoniate as reported by Moissan, but calcium hexammoniate. This compound is prepared by allowing excess ammonia to dissolve calcium metal and pumping off ammonia to the dissociation pressure of the compound.

Several cases are known of compounds of two metals existing in liquid ammonia. Joannis<sup>11</sup> found that lead dissolves in ammonia solutions of sodium, two atoms of lead being present to one atom of sodium in solution. Other compounds reported by Joannis have the formulas  $\text{Na}_3\text{Sb}$ ,  $\text{NaPb}$ ,  $\text{NaPb}_4$ ,  $\text{Na}_3\text{Bi}$ ,  $\text{KPb}_2$ , etc. According to Peck,<sup>12</sup> Kraus has found that further reactions take place with an excess of the heavy metal, forming compounds richer in the heavy metal. Smyth<sup>13</sup> has studied the solutions of lead in sodium solutions in ammonia and reached the conclusion that there is an equilibrium between  $\text{Pb}_2^-$  and  $\text{Pb}_3^-$  in the presence of metallic lead.

Lebeau<sup>14</sup> has reported that trilithium antimonide  $\text{Li}_3\text{Sb}$  is soluble in liquid ammonia. Kraus<sup>1</sup> has found that lead is soluble in ammonia solutions of potassium, giving a green color, and that tin is soluble in ammonia solutions of sodium, giving a red color. According to Peck,<sup>12</sup> Kraus has found also that tin, tellurium, selenium, and sulfur react and form compounds with solutions of the alkali metals in ammonia.

**Description of the Solid Phase.**—The crystals which are formed when magnesium amalgam absorbs ammonia have a bright metallic luster. The absorption of ammonia is exceedingly slow, probably on account of the slowness with which ammonia penetrates below the surface of the solid phase; the reaction is complete within 10 to 15 days. The adsorption of ammonia in all cases was allowed to take place at room temperature in a sealed tube in order that the high pressure of the ammonia (about 8 atmospheres at room temperature) might hasten the reaction. The crystals are slowly decomposed when exposed to air, or when the pressure of the ammonia vapor is reduced below about 2 atmospheres. The

<sup>2</sup> Weyl, *Ann. Phys.*, **121**, 601 (1864).

<sup>3</sup> Seely, *Chem. News*, **23**, 169 (1871).

<sup>4</sup> Moissan, *Compt. rend.*, **136**, 1177 (1903).

<sup>5</sup> Moissan, *ibid.*, **127**, 685 (1898).

<sup>6</sup> Guntz, *ibid.*, **133**, 874 (1901).

Mentrel, *ibid.*, **135**, 740 (1902).

<sup>7</sup> Guntz, *ibid.*, **133**, 1209 (1901).

<sup>8</sup> Joannis, *ibid.*, **109**, 900 (1889).

<sup>9</sup> Mentrel, *ibid.*, **135**, 790 (1902); *Bull. soc. chim.*, **29**, 493 (1903).

<sup>10</sup> Roederer, *Compt. rend.*, **140**, 1252 (1905).

<sup>11</sup> Joannis, *ibid.*, **113**, 795 (1891).

<sup>12</sup> Peck, *THIS JOURNAL*, **40**, 335 (1918).

<sup>13</sup> Smyth, *ibid.*, **39**, 1299 (1917).

<sup>14</sup> Lebeau, *Compt. rend.*, **134**, 284 (1902).

amalgam may be made to remain semi-liquid or completely solid, depending on the amounts of ammonia and magnesium added. Amalgams richer in magnesium than 0.15% become completely solid with excess of ammonia, while more concentrated amalgams become completely solid if more than 0.035 mol. of ammonia is added per 100 g. of amalgam. Even with the most dilute amalgams crystals of the compound separate, indicating their small solubility in the excess of amalgam. In practically all cases amalgams were used in which there was no solid phase of magnesium present.

*Solubility of Magnesium in Mercury.*—No data could be found on the solubility of magnesium in mercury, so this value was determined. Three determinations gave 0.323%, 0.322% and 0.324% of magnesium at room temperature (23°). These amalgams were made by warming pure mercury with excess magnesium *in vacuo* and, after cooling to room temperature, were allowed to stand for several days, with frequent shaking to avoid supersaturation. The saturated amalgam was filtered through a plug of glass wool by means of hydrogen pressure into an evacuated receiving bulb, which was sealed off *in vacuo* when a sufficient amount had filtered. The magnesium content was determined by the method of Gooch and Austin,<sup>15</sup> the mercury by difference.

#### Apparatus and Materials Used.

All ammonia used was obtained from large stock cylinders, dried with sodium, and kept in glass containers as a saturated solution in ammonium nitrate, known as Diver's solution. The ammonium nitrate had been previously dried with extreme care by heating with a boiling-water jacket for some hours *in vacuo*. Before using, the ammonia was always dried again with sodium, so that the final product was very pure after the several distillations and drying. All mercury used was purified by the Hulett method and stored in a glass container by distilling *in vacuo*. The magnesium was of very pure quality and carefully freed from all oxide. Vacuum stopcocks were used throughout the investigation, as were Trimount oil vacuum pumps capable of rapid exhaustion to 0.001 mm. of mercury. All glass containers and connecting tubes were thoroughly cleaned with strong caustic soda solution, chromic acid, and pure water. Before filling with the amalgams the containers were heated *in vacuo* with a free flame almost to the softening point of the glass. After evacuation for some time the containing vessel was filled with dry hydrogen and again evacuated. The hydrogen was made and dried with sodium-potassium alloy, as recommended by Hine.<sup>16</sup> This latter refinement was necessary on account of the extreme reactivity of magnesium amalgam with traces of moisture and air that remain on the surface of the glass. Using the precautions described above, amalgams were obtained free of all traces of oxide scum.

An important part of the containing tubes was an arrangement which we may call a "sealed stopcock," which was used by Lewis and Lacey<sup>17</sup> (see Fig. 1). It is impossible to keep liquid ammonia quantitatively at room temperature by means of an ordinary stopcock, and throughout the entire investigation this arrangement was used. The containing tube was attached at (C), while (E) was attached to the exhaustion pump.

<sup>15</sup> Gooch and Austin, *Zeit. anorg. Chem.*, **20**, 121 (1899).

<sup>16</sup> Hine, *THIS JOURNAL*, **39**, 882 (1917).

<sup>17</sup> Lewis and Lacey, *ibid.*, **37**, 1976 (1915).

After thorough evacuation stopcock (D) was closed. By heating the plug (B) of low-melting glass and pulling on the platinum wire (P) the small tube could be broken off at a file mark which had been made previous to making the ring seal at (R).

### Vapor-pressure Measurements.

Vapor-pressure measurements were made at  $0^\circ$  to study the form of the curve obtained by plotting vapor pressures of ammonia as ordinates against amounts of ammonia removed as abscissas. Our object was to obtain the solid compound just free of excess liquid ammonia in order to analyze it. Dilute amalgams were made, an excess of dry liquid ammonia was introduced, and the sealed tubes were allowed to stand for 10 days or longer. The containing tubes were made with several arms in order to have as much surface of compound exposed as possible, and were shaken at intervals in order to hasten the attainment of equilibrium. A large glass spiral made from tubing of small bore was used to gain flexibility and permit shaking without the use of rubber connections. The ammonia vapor was removed by allowing it to expand into an evacuated bulb of about 15cc. capacity. Vapor pressures were recorded as soon as the liquid ammonia phase had entirely disappeared. It was found in a separate experiment that the liquid ammonia phase was pure and contained no dissolved material. Consequently no vapor-pressure measurements were necessary while this phase was present, since the system was behaving practically as a one-component system.

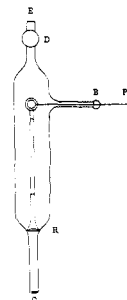


Fig. 1.

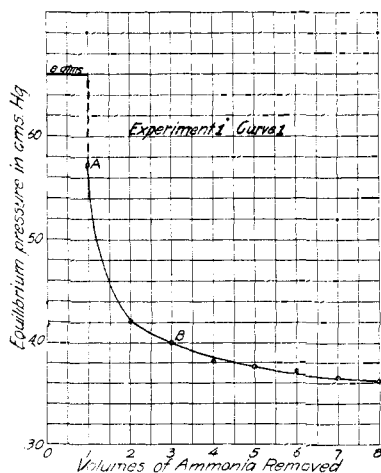


Fig. 2.

due to its decomposition. The pressures obtained were plotted against

<sup>18</sup> Kraus (Ref. 1) experienced the same difficulty in his work on the vapor pressure of  $\text{Ca}(\text{NH}_2)_6$ .

After the liquid ammonia phase had entirely disappeared, vapor pressures were recorded. Equilibrium was reached very slowly, the maximum pressure being reached in from 20 to 30 hours. Equilibrium could be approached only from the side of lower pressure, due to the extremely slow absorption of ammonia by the amalgam at that pressure.<sup>18</sup> The form of the curve was carefully examined in the region where the excess liquid ammonia had just disappeared and the solid was beginning to decompose, this point being indicated by the swelling of the solid

volumes of ammonia removed and Curve 1, Fig. 2 obtained. In this experiment about 5.0% of the crystals was decomposed by removing ammonia. This estimate was made from results which were obtained later in the investigation regarding the composition of the solid. In a second experiment, identical with the first one, more ammonia was removed, estimated to decompose about 15% of the solid. These results when plotted give a similar curve to that of Experiment 1, although the curves cannot be directly superimposed, since the concentrations of the amalgams in the two experiments were not identical. A summary of results is given in the following table.

TABLE I  
VAPOR-PRESSURE MEASUREMENTS  
All Measurements at 0°

Vols. of Amm. Vapor Removed	1	2	3	4	5	6	7	8	18
Equilib. V.P. in Cm. of Hg.									
Expt. 1.....	57.3	42.2	40.0	38.1	37.7	37.3	36.7	36.1	....
Expt. 2.....	67.1	....	48.0	....	....	42.1	38.9	....	27.6

**Discussion of Curves Obtained.**—From the form of the curve obtained, showing gradually decreasing pressures as ammonia is removed, it is concluded that there are only two phases present besides the vapor phase, one at least of which is variable in composition. The variable phase is almost certainly the amalgam, the solid compound being the second phase. The pressures do not become constant as soon as the solid begins to decompose; for instance, at point B of Curve 1 (Fig. 2) the pressure rose from 9.2 cm. to 40.0 cm. of mercury after some hours. This behavior was repeated as more ammonia was removed. Since the pressures do not become constant as soon as the solid begins to decompose this method of analysis is eliminated. There is also no evidence from the study of the curves that the solid maintains constant composition, and this point was next investigated by direct analysis. Since from A to B on the curve the composition is changing too rapidly, we will choose for analysis the region in which the vapor pressure has assumed a more constant value.

#### Determination of Ratio of Magnesium to Ammonia in Crystals.

**Method of Making Amalgams.**—In order to determine the number of mols of ammonia combined with one gram atom of magnesium, amalgams of widely differing concentrations were made and excess of liquid ammonia added.

Magnesium, free of oxide, was weighed and introduced into Tube C (see Fig. 3). After the containing tube was sealed to the apparatus it was evacuated, heated with a free flame almost to the collapsing point of the glass, filled with dry hydrogen, and again evacuated and heated. Mercury which had been distilled in the reservoir (W) *in vacuo*

was allowed to fill the evacuated pipet (P) up to the zero mark on the capillary stem, the level of mercury being adjusted at will by means of hydrogen pressure through the stopcock above the stem. The pipet as well as the stem above the zero mark had previously been calibrated very carefully by introducing the mercury from W as described, and allowing it to run into a weighing bulb attached to the glass arm (N). By turning the 3-way stopcock (S) the pipet was allowed to empty into the containing tube (C). Any small droplets of mercury adhering to the glass were forced into C by means of hydrogen pressure. The containing tube was now shaken until all the magnesium had dissolved and excess liquid ammonia introduced from Tube T by immersing the bulb of C in a cooling mixture such as carbon dioxide snow and ether. The ammonia had previously been condensed into Tube T from the Diver's solution in order to dry it thoroughly with metallic sodium. Tube C was now sealed off at M and N under reduced pressure.

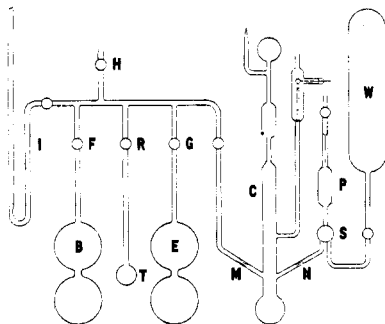


Fig. 3.

**Decomposition of Crystals.**—After the tubes had stood for several weeks at room temperature, and complete absorption of ammonia had taken place, they were sealed to the apparatus shown in Fig. 4. The sealed stopcock was thoroughly evacuated through Tube C, Stopcock B was closed, the containing tube cooled in a bath of liquid ammonia, and the small tube broken off at E. The excess liquid ammonia was allowed to escape through Tube A under a trap of mercury. After the excess liquid ammonia had all evaporated, the entire system was evacuated, which removed all ammonia vapor from above the crystals, shown by a low pressure on the gage G. Stopcock D was then closed and the crystals decomposed by heating and cooling Tube T in carbon dioxide snow and ether. After the decomposition was complete, Tube T was sealed off and the weight of ammonia determined. The volume of the containing and side tubes was next determined and the amount of ammonia vapor not condensed in T was calculated from the volume and the pressure as shown on the gage (G). This weight was added to the weight of the liquid ammonia condensed in T.

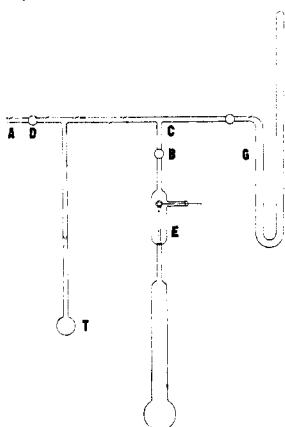


Fig. 4.

The results are summarized in Table II.

It is seen from the table that the ratio of the number of gram atoms of magnesium to mols of ammonia is approximately 1 to 6 for amalgams of widely differing concentrations. Probably some ammonia vapor is enclosed mechanically in the crystals which would cause uniformly high results. Therefore we may safely conclude that the formula of the compound is  $Mg(NH_3)_6Hg_x$ . The problem of determining whether mercury is combined in the crystal now presents itself.

TABLE II  
RATIO OF AMMONIUM TO MAGNESIUM IN CRYSTALS

Expt.	Wt. of Mg. per 100 g. of Hg. G.	Gram atoms of Mg.	Mols of ammonia combined	Mols of ammonia combined with 1 g. atom of Mg.
1	0.0508	0.00209	0.0128	6.12
2	0.0536	0.00201	0.0140	6.33
3	0.0813	0.00335	0.0205	6.12
4	0.0976	0.00401	0.0253	6.32
5	0.3122	0.01284	0.0764	5.95
6	0.3768	0.01550	0.0972	6.27
7	0.4262	0.01752	0.1056	6.02
8	0.4604	0.01892	0.1166	6.16
9	0.5118	0.02200	0.1330	6.04

### Determination of Combined Mercury in the Crystals.

**General Methods.**—The chief difficulty to overcome in the determination of the constitution of solid phases which separate from amalgams is due to the fact that it is impossible to completely free the solid phase of adhering mother amalgam.

Kerp<sup>19</sup> and Kerp, Böttger, Winter and Iggena<sup>20</sup> determined the composition of crystals from amalgams by removing the mother amalgam on a Gooch crucible. This method was later shown to give erroneous results due to incomplete removal of amalgam. Centrifugal machines also give imperfect removal of the mother liquor (C. van Eyk<sup>21</sup>). A. van Bijlert<sup>22</sup> and Bancroft<sup>23</sup> have discussed the method of adding a reference substance to the mother liquid which does not form part of the crystal. From an analysis of the crystals for the reference substance the amount of adhering mother liquor may be calculated. Bijlert<sup>22</sup> used silver as the reference metal in his study of the tin antimony alloys. Van Heteren<sup>24</sup> made use of cadmium as reference metal in the study of tin amalgams. Bancroft<sup>23</sup> has discussed the method of analyzing the filtrate to determine by indirect means the constitution of the solid phase which separates. Some experiments were made with gold amalgams in order to test the possibility of using this metal for reference. The solubility of gold in mercury at 20° was found from 3 determinations to be 0.00154, 0.00156, and 0.00156 g. of gold per g. of amalgam. From these results it was concluded that gold would make a good reference metal, since we desired a very dilute amalgam in order to change the chemical character of the mercury as little as possible. It was found, however, that gold was practically insoluble in magnesium amalgam, and this method was abandoned in favor of the method of directly analyzing the filtrate.

**Theory of the Method of Analyzing the Filtrate.**—Starting with an amalgam of known concentration, a known amount of liquid ammonia is introduced into the containing tube. Since we have established the fact that 6 mols of ammonia combine with 1 gram atom of magnesium we

<sup>19</sup> Kerp, *Z. anorg. Chem.*, **17**, 284 (1898).

<sup>20</sup> Kerp, Böttger, Winter and Iggena, *ibid.*, **25**, 1 (1900).

<sup>21</sup> C. van Eyk, *Proc. Acad. Sci.*, Amsterdam, **10**, 859 (1902).

<sup>22</sup> A. van Bijlert, *Z. physik. Chem.*, **8**, 343 (1891).

<sup>23</sup> Bancroft, *J. Phys. Chem.*, **6**, 178 (1902).

<sup>24</sup> Van Heteren, *Z. anorg. Chem.*, **42**, 129 (1904).

can calculate from the total amount of ammonia introduced the weight of magnesium that is removed from solution. This value must be corrected, however, for the solubility of the crystals in the residual amalgam and for the vapor pressure of the crystals which corresponds to the amount of ammonia not reacting. Using this corrected value for the amount of magnesium removed from the liquid phase we may indicate the number of gram atoms of mercury that are also removed from the liquid phase by letting  $x$  represent the number of gram atoms of mercury present in the crystal with 1 gram atom of magnesium and 6 mols of ammonia. The ratio of the remaining amount of mercury to magnesium in the liquid phase may now be equated to the ratio of magnesium found by direct analysis in the filtrate. The equation is written as follows,

$$\frac{W_1 - \left\{ \left[ \frac{1}{6} (N - P) - S.A \right] 200.6 x \right\}}{W'_1 - W''_1} = \frac{W_2}{W'_2}$$

where  $W_1$  is the weight of mercury in the original amalgam,  $N$  the number of mols of ammonia introduced,  $P$  the number of mols of ammonia that remain in the vapor phase,  $S$  the solubility of the crystals expressed as gram atoms of magnesium per gram of mercury,  $A$  the number of grams of mercury in the filtrate (liquid phase),  $W'$  the weight of magnesium in the original amalgam,  $W''_1$  the weight of magnesium removed in the crystals,  $W_2$  the weight of mercury in the filtrate,  $W'_2$  the weight of magnesium in the filtrate,  $\frac{1}{6}$  the ratio of gram atoms of magnesium to mols of ammonia and 200.6 is the atomic weight of mercury. The quantity in brackets  $\left\{ \left[ \frac{1}{6} (N - P) - S.A \right] 200.6 x \right\}$  represents the number of grams of mercury removed from the liquid phase as part of the crystals.

$W''_1$  is equal to  $\left\{ \frac{1}{6} (N - P) - S.A \right\} 24.32$  g. of magnesium, where 24.32 is the atomic weight of magnesium. In multiplying  $S$  by  $A$ , the number of grams of mercury in the filtrate, we are neglecting the weight of mercury present in the amalgam adhering to the crystals. However, since  $S$  is very small and the amount of amalgam adhering to the crystals is small, we are making only a small error and gaining simplicity in the equation.

**Method of Introducing a Known Weight of Ammonia.**—The amalgams were made by weighing out the magnesium and introducing the mercury from the Reservoir  $W$  (see Fig. 3) *in vacuo* by means of a calibrated pipet ( $P$ ) and a 3-way stopcock ( $S$ ), as described above. The volume of the containing tube ( $C$ ) up to Stopcock  $S$ , plus the connecting tubes to Stopcocks  $F$ ,  $R$ ,  $G$  and  $H$ , was determined by filling with dry ammonia gas, reading the pressure recorded on the gage ( $I$ ), and allowing the ammonia gas to expand into one of the expansion bulbs ( $B$  or  $E$ ), whose volumes were accurately known. From the new pressure recorded on the gage ( $I$ ) and the temperature, the volume was calculated. The volume of the containing tube was determined in the same manner.

Since we wished to filter these amalgams after the crystals had been formed it was necessary to condense into  $C$  only a limited amount of ammonia, excess of magnesium being used in all cases. The maximum amount of ammonia that could be used and still allow filtering was about 0.065 mol. for 200 g. of amalgam. Ammonia was condensed



into T through H where it was freed of traces of moisture with metallic sodium. Stopcock R was opened to the vacuum pump several times in order that any small amounts of hydrogen evolved in the drying process might be removed. The dry liquid ammonia in T was now allowed to expand into the containing tube, the connecting tubes, and one or both of the Bulbs B and E, depending on the amount that was desired. After reading the pressure on the gage (I) the ammonia gas was condensed into C by cooling in carbon dioxide and ether mixture until the desired pressure was shown on the gage. The containing tube was then sealed off at M and N under reduced pressure. From the initial and final pressures on the gage, the volumes of the connecting tubes, the Bulbs B and E, and the containing tube, with the temperature, the number of mols of ammonia introduced into C could be calculated. Since ammonia vapor deviates appreciably from a perfect gas under these conditions, all calculations were made using the Berthelot equation of state, which holds closely enough for ammonia vapor at these temperatures and pressures for our purposes. Corrections were made for the different heights of the mercury columns on the gage and for the lengths of tubing sealed off above M and N to the stopcocks.

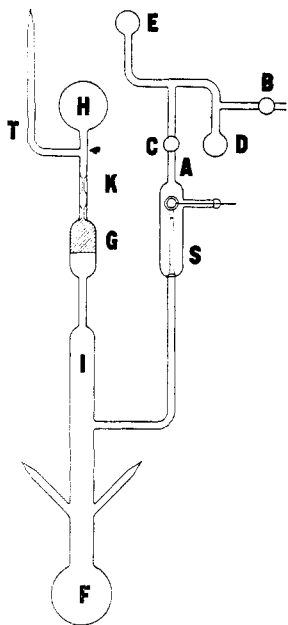


Fig. 5.

slowly force itself through the sealed stopcock and back of the crystals and amalgam. As the ammonia pressure in I gradually became greater the liquid amalgam was forced smoothly, drop by drop, into the receiving bulb (H). When the filtering was complete the highly compressed ammonia gas in I forced itself through the crystals and began to escape under the surface of the mercury. The receiving bulb was now sealed off at T and at K.

The filtrates were analyzed for magnesium by the method of Gooch and Austin;<sup>15</sup> the mercury was obtained by difference. A summary of results is given in Table III below.

**Solubility Determinations.**—The solubility term enters into the ratio equation given above, and this value was next determined. Excess of liquid ammonia was used in all cases and small amounts of magnesium. Not over 0.2700 g. of magnesium for 200.00 g. of mercury could be used,

for otherwise the material became too viscous to filter. Using excess of liquid ammonia, all of the magnesium was removed from the amalgam except that due to the solubility of the crystals. The total concentration of the magnesium in the filtrate represents the solubility.

After absorption, the excess of liquid ammonia was allowed to escape and the amalgam filtered as described above. Three determinations gave 0.0061 g., 0.0057 g., and 0.0060 g. of magnesium for 100.000 g. of mercury. The mean of these values, 0.00593 g. of magnesium for 100.000 g. of mercury is chosen as representing the solubility of the crystals in the amalgam at room temperature (22.4°).

**Vapor-pressure Measurements.**—In order to calculate the number of mols of ammonia that reacted with the magnesium to form the crystals it was necessary to obtain the vapor pressures of the crystals at the temperature at which the amalgams were filtered. Knowing the vapor pressures and the volumes of the containing tubes, the number of mols of ammonia not reacting could be calculated. The number of mols of ammonia that entered the crystals was obtained by subtracting this value from the total number of mols of ammonia introduced into the tube. It was impossible to make vapor-pressure measurements of the crystals which we wished to analyze, for a certain amount of decomposition takes place as the pressures came to equilibrium. Consequently, amalgams were made of the same concentrations as those which were filtered and approximately the same amounts of ammonia introduced. After standing for 4 weeks the vapor pressures were determined, keeping the bulbs at 22.4° in a water thermostat, constant within 0.05°. The average temperature at which the amalgams were filtered was 22.4°, hence this temperature was chosen as the one at which the vapor pressures were measured. The equilibrium pressure was reached in about 12 hours. A table of results is given below.

TABLE III  
VAPOR-PRESSURE MEASUREMENTS  
(See Fig. 6, Curve C)  
All Measurements in Thermostat at 22.4°

Expt.	Magnesium G.	Mercury G.	Ammonia introduced Mols.	Vapor pressures cm. of Hg
1	0.4293	206.490	0.0606	175.2
2	0.4617	206.564	0.0627	171.7
3	0.5545	206.878	0.0544	166.2
4	0.5696	206.582	0.0518	165.9
5	0.5965	206.832	0.0633	164.8

The curve is plotted with concentrations of magnesium as abscissas and vapor pressures as ordinates. Using the vapor pressures and the volumes of the containing tubes in which the amalgams were filtered, the number of mols of ammonia remaining in the vapor phase is calculated

and substituted in the equation given on p. 15. A table summarizing all results is given below.

TABLE IV

GRAM ATOMS OF MERCURY PRESENT					
Determination	$W_1$	$W'_1$	$N$	$P$	$S. A.$
1	206.490	0.4293	0.0610	0.00725	0.00026
2	206.564	0.4617	0.0624	0.00783	0.00020
3	206.582	0.5696	0.0519	0.00793	0.00020
4	206.832	0.5965	0.0636	0.00813	0.00016
5	206.686	0.6108	0.0586	0.00743	0.00020
	$\left\{ \frac{1}{6}(N-P) - S.A. \right\} 24.32$	$W'_1 - W''_1$	$W_2$	$W'_2$	$\alpha$
1	0.2116	0.2177	106.1872	0.1322	18.1
2	0.2163	0.2454	82.8769	0.1163	17.8
3	0.1734	0.3962	91.8776	0.2002	17.5
4	0.2209	0.3756	64.5023	0.1394	18.0
5	0.2025	0.4083	86.9291	0.2017	18.4

**Discussion of Results.**—The average value of  $\alpha$ , as given in the foregoing table, is 17.96, which represents the number of gram atoms of mercury for each atom of magnesium in the solid phase. It appears, in consideration of this rather large value

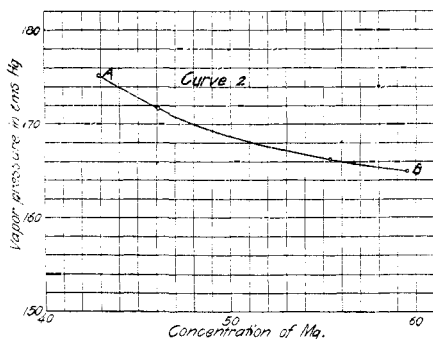


Fig. 6.

for the amount of mercury in the solid phase and the small range of concentration covered in the analyses, that the compound magnesium hexammoniate forms a solid solution with the excess mercury of the amalgam. It is impossible to extend the measurements over wider ranges of concentrations than those given in Table IV, *i. e.*, between points A and B of Curve 2, for with larger amounts of magnesium than represented by B of Curve 2, and for larger amounts of ammonia than those given in Table IV, the entire amalgam becomes solid and cannot then be filtered. Thermal measurements are impracticable in this case on account of the very slow reaction in the system. The lack of a sharp melting point of the crystals is further evidence of the formation of solid solutions. It is to be expected that the formation of solid solutions would favor the formation of this molecular compound since its dissociation pressure is lowered thereby.

It is interesting to compare the values of  $W'_1 - W''_1$  with corresponding values of  $W'_2$  in the table. In each case  $W'_1 - W''_1$  is considerably larger, which indicates the amount of mother amalgam that wets the crystals,

even though they were subjected to a pressure of 6 to 7 atmospheres in the process of filtration by the pure liquid ammonia at room temperature.

### Summary.

A description is given of the general properties of a solid phase which separates from dilute magnesium amalgams when liquid ammonia is allowed to react with these amalgams.

Vapor-pressure measurements were made at  $0^\circ$  as ammonia vapor was removed from the system, thus decomposing the solid phase. From phase rule relationships it was concluded that two solid phases were present besides the vapor phase, one at least of which was variable in composition.

Experiments were undertaken to determine if the solid phase was variable in composition. A method is described for making pure amalgams and determining the ratio of magnesium to ammonia combined in the solid phase. It is shown that this ratio is 1 gram atom of magnesium to 6 mols of ammonia for amalgams of widely differing concentrations.

The solubility of magnesium in mercury at room temperature ( $22.4^\circ$ ) was determined, also the solubility of gold in pure mercury and in magnesium amalgams at  $22.4^\circ$ .

Various methods are discussed for analyzing the crystals for mercury of constitution, and a ratio equation developed to determine their constitution by analysis of the filtrate.

A method is described for making pure magnesium amalgams of known concentrations and introducing a known weight of pure liquid ammonia. The method of filtering the crystals from these mixtures is described in detail.

The solubility of the crystals in pure mercury was determined at  $22.4^\circ$ .

Vapor-pressure measurements were made of mixtures of exactly the same compositions as those which were filtered, and the results plotted.

Using a ratio equation containing terms that take into account the weight of magnesium and mercury in the original amalgam, the number of mols of ammonia added, the solubility and vapor pressure of the crystals, and the analysis of the filtrate, calculations are made for the amount of mercury combined in the crystal. This value is found to be 18 gram atoms of mercury to 1 gram atom of magnesium and 6 mols of ammonia.

From the large value thus obtained for the amount of mercury combined it is concluded that solid solutions are formed by the molecular compound magnesium hexammoniate with the excess mercury present.

In conclusion it is a pleasure to acknowledge my thanks to the late Dr. William Argo, who suggested the problem and gave valuable assistance; also to Professor W. C. Bray for his helpful suggestions in interpreting many of the results.

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