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SOLUTION OF METALS IN NON-METALLIC SOLVENTS; II.[1] ON THE FORMATION OF COMPOUNDS BETWEEN METALS AND AMMONIA.

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Solutions of metals in liquid ammonia were first obtained by Weyl,[2] who brought together sodium and potassium with gaseous ammonia under pressure. However, he mistook the solutions which are formed under these conditions for simple compounds and assigned to them the formulae $NaNH_3$ and KNH_3, respectively. These compounds he supposed to be structurally analogous to the hypothetical free ammonium group, being derived therefrom by substitution of an atom of hydrogen by one of the metal in question. Taking account of this relationship in his nomenclature, he introduced the terms sodammonium and potassammonium, respectively, which nomenclature has been largely adopted by subsequent investigators and commentators.

The study of solutions of metals in ammonia was materially advanced by Seely,[3] who showed conclusively that solutions result in the action of ammonia on the alkali metals. From a consideration of the optical properties of these solutions, he concluded that a compound was not formed between the two components. Neither Weyl nor Seely, however, was able to adduce quantitative data in support of his contention.

These investigations on the action of ammonia on the alkali metals

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[1] For the first paper of this series, "I. General Properties of Solutions of Metals in Liquid Ammonia," see THIS JOURNAL, 29, 1557–1571 (1907).

[2] *Ann. Physik*, 121, 601 (1864).

[3] *Chem. News*, 23, 169 (1871).

seem to have excited little active interest for, excepting an isolated observation by Gore,[1] we find no further investigations recorded until 1889, when Joannis[2] undertook an extended series of investigations in this field. To him belongs the credit of bringing quantitative data to bear on the problem of the compounds formed by sodium and potassium with ammonia. He devised a means of isolating and analyzing these compounds, to which he assigned the composition $NaNH_3$ and KNH_3 respectively, and to which, like Weyl, he ascribed an ammonium structure. Employing the method devised by Joannis, Moissan obtained the compounds $LiNH_3$, $Ca(NH_3)_4$[3] and $LiCH_3NH_2$,[4] while Mentrel obtained the compound $Ba(NH_3)_6$[5] and Roederer the compound $Sr(NH_3)_6$.[6]

In the preceding paper[7] attention was called to the fact that the concentrated solutions of metals in ammonia exhibit metallic reflection and are consequently opaque. It is plain, therefore, that the formation of a compound cannot be ascertained by visual observations nor can separation of the different phases in these concentrated solutions be carried out by the simple means usually employed in the preparation of a pure substance. The method adopted by Joannis in preparing and identifying the compounds in question is therefore an indirect one, as will be seen from the description given below. Objections have been raised from time to time to the results obtained by Joannis as well as to those obtained by other chemists employing the same method.

It is the purpose of the present paper to determine, if possible, whether or not compounds are formed. To this end I shall first examine such evidence as is already at hand. The solutions of sodium and potassium in ammonia have been studied extensively and, as will be seen below, the available data are sufficient to enable us to draw the conclusion that solid compounds are not formed. In the case of other metals it has been found necessary to adduce new experimental evidence. It will thus be shown that lithium, like sodium and potassium, does not form a solid compound, while calcium forms the compound $Ca(NH_3)_6$ with ammonia. Finally the questions of constitution and nomenclature will be considered and the physical properties of the compound $Ca(NH_3)_6$ will be discussed briefly.

Criterion for the Appearance of New Phases.

In determining whether compounds are formed between a solvent and a dissolved substance, it is of primary importance to possess a clear

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[1] *Phil. Mag.*, **44**, 315 (1873).

[2] *Compt. rend.*, **109**, 900 (1889).

[3] *Ibid.*, **127**, 685 (1898).

[4] *Ibid.*, **128**, 26 (1899).

[5] *Ibid.*, **135**, 790 (1902); *Bull. soc. chim.*, **29**, 493 (1903).

[6] *Compt. rend.*, **140**, 1252 (1905).

[7] THIS JOURNAL, **29**, 1570.

knowledge of the phase relations before attempting to identify any of these phases as compounds by means of chemical analysis. Since the solutions of metals in ammonia constitute two component systems, it follows that if ammonia is withdrawn from the system, the pressure must become constant as soon as a third phase appears. If, on continuing the withdrawal of ammonia, one phase disappears the pressure will again vary when ammonia is withdrawn. If, however, one of the three phases is substituted by a new third phase, the pressure changes abruptly to a new constant value. One of the phases present is always gaseous ammonia; the other two phases may either be both solid or liquid, or one may be liqiud and the other solid. It is an easy matter to determine how many new phases make their appearance in withdrawing ammonia from a dilute solution of a metal until the free metal and gaseous ammonia are left behind. The study of the vapor pressure of a system of metal and ammonia is therefore a necessary preliminary in determining whether compounds are formed. The nature of the phases present at any time may, in general, at once be determined by visual-examination, and by proper means it is always possible to transform the entire system into any desired phase, when its composition may be determined by analysis.

Non-existence of the Compounds $NaNH_3$ and KNH_3.

The pressure of the systems sodium-ammonia and potassium-ammonia have been carefully investigated by Joannis.[1] He finds that in the case of both these systems, if ammonia is withdrawn from a solution of the metal, the vapor pressure falls until a solid phase makes its appearance, after which the pressure of the system remains constant until only free metal and gaseous ammonia are left. This would seem to show that the solid phase which initially separates from solution is free metal. Joannis, however, believes that such is not the case. He observed that the solid, which initially precipitates, appears to possess the same color of metallic reflection as does the solution itself, while, as is well known, the free metal possesses white metallic reflection. He therefore considers that this solid may be a compound of sodium with ammonia. We shall simply call this substance "solid compound" in order to avoid circumlocution. This substance is evidently a new phase; the question only remains to show whether it is a compound, as Joannis believes it to be, or, otherwise, free metal and saturated solution as the vapor pressure relations indicate. According to Joannis, free metal does not make its appearance until the saturated solution is completely converted into the solid compound, after which, on further withdrawal of ammonia, the free metal appears, without being accompanied by any change in

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[1] *Loc. cit.*: For details of the method described in this paragraph v. *Ann. chim. phys.*, **7**, 13–36 (1906).

the pressure. He assumes, therefore, that the dissociation pressure of the "solid compound" is exactly equal to the vapor pressure of its saturated solution. Analysis of the "solid compound" gave him a composition corresponding to the simple formula $MeNH_3$, where Me may be either Na or K.

According to the phase rule, the system, vapor, saturated solution, "solid compound," and free metal must be an invariant one and obtainable at a single temperature only, since two components and four phases are present. Roozeboom[1] first called attention to these facts and suggested that Joannis had carried out his experiments at the temperature of this invariant point. Joannis, however, showed that at a series of temperatures no change occurs in the pressure from the moment that a solid phase begins to separate until only free metal and gaseous ammonia are left. This proves conclusively that the solid phase initially separating out of the solution is identical with the solid phase which is finally left behind, namely, free metal, and that a solid compound is not formed between the metal and ammonia. The "solid compound" can consist only of free metal and saturated solution of the same in ammonia. Ruff and Geisel[2] have recently expressed this view and in addition they have adduced some evidence to show that the solid compound consists of a free metal covered with a film of solution, which adheres through the action of strong surface forces. Joannis,[3] replying to this paper of Ruff and Geisel, throws some doubt on the correctness of the conclusion which they have drawn from their experimental results. In the section dealing with lithium, whose behavior is in every way similar to that of sodium and potassium, I shall adduce independent evidence showing conclusively that, in accordance with the view of Ruff and Geisel, the so-called compound $LiNH_3$ contains solution and free metal. This evidence was not obtained primarily to show that compounds do not exist, for as to this point the thermodynamic evidence would seem to be sufficient in itself. Since, however, Joannis[4] believes that his hypothesis may be reconciled with the phase rule, it may be as well to give evidence which is quite independent of any theoretical considerations.

This reconciliation of his hypothesis with the phase rule Joannis[5] believes to have been effected by Moutier.[6] A careful examination of Moutier's paper fails to show, however, that such a reconciliation is possible. A consideration of the free energy of a system can lead to no results other than those obtainable by other thermodynamic methods.

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[1] *Compt. rend.*, 110, 134 (1890).

[2] *Ber.*, 39, 831 (1906).

[3] *Ann. chim. phys.*, 11, 101 (1907).

[4] *Loc. cit.*

[5] *Loc. cit.*, 103; *Ann. chim. phys.*, 7, 34 (1906).

[6] *Compt. rend.*, 110, 518 (1890).

The conclusions reached by Moutier are in fact applicable to a single temperature only and not to a series of temperatures, as be believes them to be.

Vapor Pressure of the System $LiNH_3$.

According to Moissan,[1] the compound $LiNH_3$ is formed. Since he employed the same method as did Joannis in the case of sodium and potassium and since confirmatory vapor pressure measurements were lacking, it seemed advisable to determine the pressure relations of the system $Li–NH_3$.

The apparatus employed need not be described in detail. It consisted essentially of a tube permanently attached to a manometer and containing the solution. Provisions were made for connecting this tube with a source of pure ammonia vapor or a vacuum pump as desired. After introducing the metal into the containing tube, it was placed in a bath at —10° and ammonia vapor was introduced under a pressure slightly greater than one atmosphere. The process of condensation and solution takes place with great facility in the case of lithium, even at ordinary temperatures. When the process of solution was complete the container was placed in a bath at 20° and the excess of ammonia was allowed to escape under a pressure of about 100 cm. of mercury. On withdrawing ammonia by means of the pump, the pressure fell until it reached a value of about 10 centimeters, after which it remained constant. At this point a solid phase began to separate out and on continuing the withdrawal of ammonia the amount of solid increased. The solid phase appeared to have the same color as the solution and the solution apparently disappeared long before all the ammonia had been completely withdrawn. The pressure, however, remained constant until only free metallic lithium was left behind. When but very little ammonia was present the color distributed appeared uniformly over the entire surface of metal, giving it a slight tinge of color. On adding more ammonia the color became more pronounced while, at the same time, the crystals of metal, which previously were very sharply defined, lost their sharp outline, their edges becoming indistinct. The phenomenon is such as we should expect if the crystals were covered by a film of highly colored metallic solution.

The equilibrium pressure of the saturated solution of lithium in ammonia was measured at a number of temperatures with the following results:

Temperature.	Pressure.	Mean.	Temperature.	Pressure.	Mean.
19.3°	9.48 cm. 9.58 "	9.53 cm.	9.75°	5.68 cm. 5.72 "	5.70 cm.
0°	3.31 " 3.31 "	3.31 "	20.3°	9.91 " 10.06 "	9.98 "
0°	3.31 " 3.32 "	3.31 "	20.3°	9.90 " 10.06 "	9.98 "

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[1] *Compt. rend.*, **127**, 685 (1898).

The pressures first recorded were obtained after abstracting, the second after adding ammonia.

From the pressure data the heat evolved when one gram-molecule of ammonia vapor combines with metal under equilibrium conditions to form a saturated solution may be calculated from the equation:

$$Q = 4.6 \frac{T_1T_2}{T_2-T_1} \, log. \frac{p_2}{p_1}.$$

Using the values of p at 0° and 20.3°, respectively, we thus obtain Q = 8698 calories. The value of P at 9.75° calculated from this value of Q is 5.699 cm. while the value 5.70 was found.

Independent Evidence Showing that the Solid Compound $LiNH_3$ is Not Formed.

The pressure relations recorded above show conclusively that a compound is not formed between lithium and ammonia. It seemed worth while to examine the behavior of lithium solutions somewhat further in order to determine, if possible, the sources of the error in the result of Moissan. In common with other investigators who have adopted the method of Joannis, he finds that so long as the amount of ammonia present exceeds that corresponding to the formula $LiNH_3$, that is, when saturated solution is present, any free bit of metal at once absorbs ammonia from the saturated solution to form the compound. On the other hand, when the amount of ammonia is less than that which corresponds to the formula $LiNH_3$, a free surface of metal remains permanently free from ammonia. This is, in fact, the criterion which these investigators employ in determining when the saturated solution disappears and the supposedly "solid compound" begins to dissociate. Since no change occurs in the pressure when the composition passes through the point corresponding to the composition $LiNH_3$, it is difficult to understand why there should be any difference in the behavior of the system on one side and the other of this point. The following experiments were undertaken for the purpose of obtaining more light on this question.

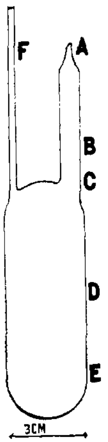

Fig. 1.—Apparatus employed in studying lithium solutions.

A quantity of lithium was introduced into a tube of the form outlined in Fig. 1. Ammonia was condensed at 0° until the metal had all dissolved, after which ammonia was withdrawn by means of the pump until a portion of the metal had been precipitated. A portion of the solution spattered along the walls of the tube EC, while a few isolated drops of solution could be seen clinging to the walls of the smaller tube AC.

On immersing the tube as far as E in a bath at 15°, 10° below room temperature, the solvent at once evaporated from the isolated drops in AC, leaving metal behind, while along the walls of the tube EDC the metal retained ammonia. This portion of the tube was then warmed with the hand, whereupon the ammonia evaporated. As soon as this heating process was discontinued, the solution from the bottom could be seen creeping up over the walls of the tube. The solution passed from crystal to crystal, tracing out characteristic figures, such as would naturally result if a liquid were to creep over a surface covered with irregularly spaced particles. Isolated particles of metal like those in the tube AC underwent no change whatever. On plunging the entire tube in the bath the particles in AC remained unaffected.

After repeating the above operation a number of times, it was observed that the amount of metal in the space DC had greatly increased. This is evidently due to the fact that the metal on the walls of the tube acts as a wick by means of which solution is drawn from the colder portion of the tube in the bottom to the warmer portions above. Here the solvent evaporates to condense again in the bottom, while the metal is left behind in the warmer portion of the tube. To test this further, the tube was left immersed as far as E in a bath at 12°. At the end of 45 minutes the metal had crept up the tube AC over a distance of more than a centimeter, forming a very heavy deposit. The deposit of metal in CD had now become so heavy that it could not be freed from ammonia by warming with the hand. The tube was left immersed as far as D in a bath at 0° for some time, after which all the ammonia was withdrawn. On examination it was found that no metal was left in the bottom, it having collected in the warmer portion of the tube DC.

A small quantity of ammonia was now introduced, sufficient to form only a thin film on the surface of the metal. The tube was placed in ice-water as far as C, while the metal deposit extended about 1.5 cm. above C in AC. On warming the tube at B with the hand, the metal deposit crept up the tube with visible speed, and at the end of about ten minutes the entire surface of the tube AC was coated with metal. The tube AC was kept warm for some time, after which the ammonia was again withdrawn. Nearly all the metal now appeared collected in the tube AC.

It is remarkable that this process should take place so rapidly against a temperature difference of nearly 30°. No better illustration could be given of the strength of the surface forces coming into play between the metal and its solution. It is to be remembered that the amount of ammonia was but a small fraction of that required to form a compound of the composition $LiNH_3$. This experiment, therefore, shows conclusively that liquid is present in the system even when, according to Moissan, only the compound $LiNH_3$ should be present. *These experi*ments show, moreover, that the behavior of the system is the same irrespective of the amount of ammonia present so long as this is less than that necessary to form a saturated solution of all the metal present. Those phenomena which Moissan employed in isolating the supposed compound $LiNH_3$, I have been quite unable to reproduce. It is clear, then, that in accordance with the vapor pressure relations, the properties of lithium in the presence of small quantities of ammonia, are such as to preclude the possibility of a compound being formed at the temperatures of the present experiments.

The behavior of other alkali metals is doubtless similar to that of lithium. In the case of sodium I have observed this experimentally. Caesium and rubidium have not been investigated as regards their vapor pressure relations. Moissan[1] obtained what he believed to be the compounds $CsNH_3$ and $RbNH_3$. It seems not improbable, however, that the same errors underlie the results obtained with these metals as has been shown to underlie those obtained with the remaining alkali metals.

The Vapor Pressure of the System Ca-NH_3.

It having been shown that the alkali metals do not form compounds with ammonia, it seemed important to examine at least one member of the group of the alkaline earths. For this purpose calcium was selected. According to Moissan, the compound $Ca(NH_3)_4$ is formed, the method employed being that of Joannis, which has been shown to be untrustworthy. Pressure data were not obtained by Moissan, but he states that above 0° calcium combines with ammonia without liquefaction, while at lower temperatures liquefaction takes place. This indicates that a solid compound is formed whose dissociation pressure lies below one atmosphere, while the vapor pressure of its saturated solution lies above one atmosphere at temperatures in the neighborhood of 0°. That this is correct, follows from the experiments about to be described.

Observations on the phase relations in the more dilute solutions of calcium in ammonia were made in connection with some conductivity experiments. Solutions of calcium, like those of sodium, separate into two liquid phases. The point of complete miscibility of these two phases lies at much higher temperatures in the case of calcium than it does in that of sodium. Even at room temperatures, the concentration of the two phases differs very widely. At $-33°$ the concentration of the dilute phase does not exceed 1/10 gram-atom per liter, while that of the concentrated phase is such that pronounced metallic reflection results. Owing to the tendency of the concentrated phase to cling to the walls of the containing tube and also, perhaps, because of the small difference in the specific gravity of the two phases, it was not possible to separate them into two layers, one above the other. The fact that the concentra-

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[1] *Loc. cit.*

ted solution clings to the walls of the container made it very difficult to determine the nature of the system. However, on using very large quantities of solvent and small quantities of metal the concentrated phase could be plainly seen adhering at intervals to the walls of the tube or floating about in the dilute solution.

In studying the concentrated solutions of calcium, a tube of the form outlined in Fig. 2 was employed. The tube G serves as a receptacle for the metal or its solution. At F it is joined to the manometer system C by means of a bit of rubber tubing. The stop-cocks D and E are provided so that at any time G may be detached and weighed, the cocks being closed beforehand. When G is again attached, the air is exhausted from the tube ED before opening E. The cocks A and B make connection with a source of pure ammonia and a vacuum pump, respectively.

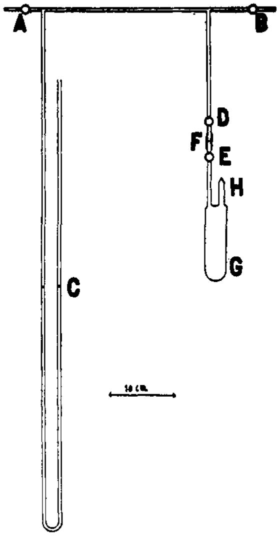

Fig. 2.—Apparatus employed in analyzing calcium compounds.

A piece of metal, freshly cleaned, is introduced into G through H, which is immediately sealed off, after which G is exhausted. The tube G having been weighed beforehand, the weight of metal is obtained by detaching G and weighing. The amount of ammonia present in G at any time may be obtained in a similar manner.

After having introduced a quantity of metal according to the method described above, G was placed in a bath at 20° and ammonia vapor was introduced under a pressure slightly greater than one atmosphere. At the end of 10 minutes appreciable absorption of ammonia had not taken place. Even at 0°, absorption was inappreciable at the end of 5 minutes. The containing tube was then placed in a bath at —33° and ammonia was condensed. It was noticeable that calcium dissolves at a much slower rate than do the alkali metals. When the metal was all in solution, the tube was allowed to warm up, the excess of ammonia being allowed to escape under a pressure of 1 1/3 atmospheres. In the neighborhood of 0°, the liquid disappeared, leaving behind what appeared to be a solid metallic substance identical in color with the solution from which it was precipitated and possessing the mechanical properties of a solid.

The tube was now placed in a bath at 22° and ammonia was withdrawn by means of the pump. The pressure fell rapidly and reached a constant value at 10 centimeters. Pressure readings were carried out at different temperatures with the following results:

Temperature.	Pressure.
10.8°	4.60
0°	2.28
21.7°	9.07
21.7°	9.07
43.7°	30.67

The last two determinations were made at different times. The equilibrium pressure could be reached from one side only. This was due to the extreme slowness with which ammonia combines with calcium. Such combination does take place, however, as will be seen below. In the last experiment a slow increase in pressure was noted, due, without doubt, to the formation of amide and hydrogen from the two constituents.

Calculating, as above, the value of Q from the pressures at 0° and 21.7° we find Q = 10,230 calories for the heat evolved when one gram-molecule of ammonia combines with calcium to form the compound in question. This value of Q gives the pressures 4.66 cm. and 30.20 cm. at 10.8° and 43.7°, respectively. The corresponding values found are 4.60 cm. and 30.67 cm.

The tube was now cooled to —33°, and ammonia was again condensed until the metal was dissolved. Leaving the tube G in its bath of boiling ammonia, solvent was withdrawn with the pump. The pressure soon reached a constant value at about 50 centimeters and a solid substance apparently crystallized from solution. Evidently a compound precipitates out of solution at this pressure, which in turn loses ammonia at a much lower pressure.

A fresh piece of calcium weighing 0.4189 gram was introduced into G, and ammonia was condensed until the process of solution was complete. Leaving the tube in its bath, ammonia was withdrawn until the pressure became constant and solid began to precipitate. The following pressure observations were then made:

Temperature.	Pressure.	Approached from
—32.5°	47.42 cm.	higher pressure
—32.5°	46.98 "	lower "
—32.5°	47.28 "	higher "
—50°	19.28 "	higher "
—50°	19.28 "	lower "
—32.5°	47.18 "	higher "
—32.5°	47.08 "	lower "
—32.5°	47.42 "	higher "

As may be seen, the pressure reading differs slightly according as the equilibrium is approached from higher or from lower pressures. This is due to the slowness with which equilibrium establishes itself. Taking the mean of these observations, we obtain the following values for the pressure of the saturated solution, namely: $t = 50°$, $p = 19.28$ cm., $t = -32.5°$, $p = 47.18$ cm.

For the heat of solution, we obtain from these data, by calculation, the value Q = 5458 calories when one gram-molecule of gaseous ammonia *dissolves the compound under equilibrium conditions to form a* saturated solution.

The pressure-composition curve for calcium and ammonia at —32.5° is represented in Fig. 3, where the ordinates represent pressures in centimeters and the abscissae composition in mols of calcium per 100 mols of calcium and ammonia. Portions of the curve are exaggerated in order to bring out certain points. The correct pressures, however, appear on the margin. Along AB we have the change in pressure of a dilute solution with concentration. At B, a second liquid phase of concentration *c* appears, and the pressure remains constant until the dilute phase of concentration *b* disappears. This pressure is within a millimeter of the atmospheric pressure, since *b* is very small. Along CD the pressure falls to 47.18 cm., when the solid compound of composition $Ca(NH_3)_6$ (see below) appears. The pressure now remains constant until the saturated solution of composition *d* disappears, when the pressure falls abruptly to 1.8 mm. (calculated) and metallic calcium appears. This pressure is maintained as long as the solid compound remains. That

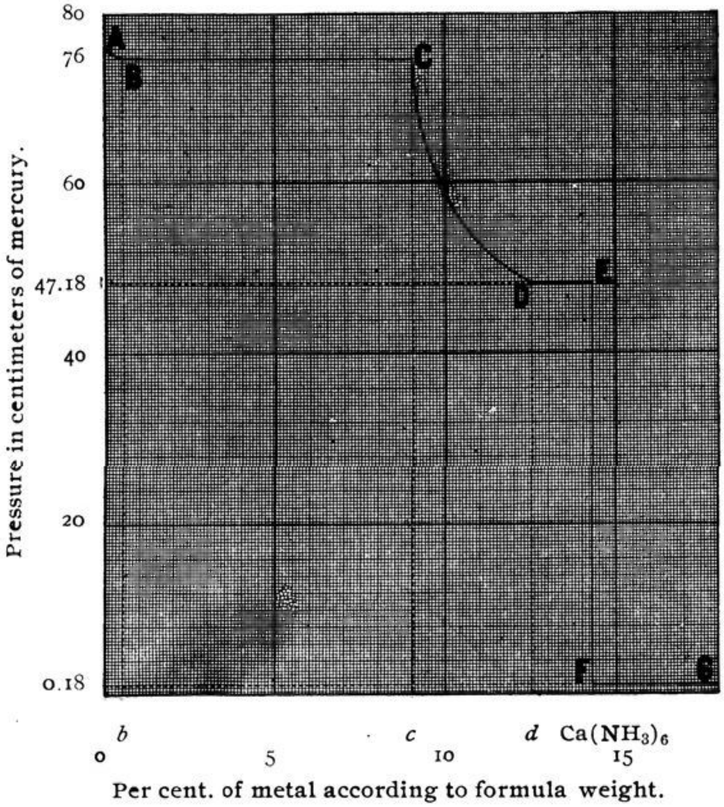

Fig. 3.—Vapor pressure—composition curve for calcium in ammonia.

the solid compound does not lose its ammonia in two steps instead of one was shown by measuring the pressure: first when the compound had lost but a little ammonia, and second when only a small amount of ammonia was present in the system. This result will be referred to below in connection with the possible formation of the compound $Ca(NH_3)_4$.

Moissan[1] states that calcium does not absorb ammonia above 20°. As already stated, calcium in the massive form absorbs ammonia very slowly even at 0°. This is to be expected, since a compound is formed which does not liquefy in the presence of ammonia. By employing very finely divided calcium, as it may be obtained by completely withdrawing the ammonia from a solution of the same, it was found that at temperatures above 20° ammonia combines with calcium, although the process is a very slow one.

Composition of the Compound of Calcium and Ammonia.

Experiment 1.—In the preceding experiment in which the vapor pressure of a saturated solution of the compound of calcium in ammonia was determined, 0.4198 gram of metal was employed. At the end of the pressure experiments, which occupied in all about 8 hours, the solution was placed in a bath at 0° and ammonia was withdrawn until a pressure of about 10 centimeters was reached. The tube was then weighed. The contents of the tube weighed 0.9873 gram in excess of that of the metal present. Assuming that this excess in weight is due to ammonia combined with calcium, we may calculate n the number of molecules of ammonia per atom of calcium. We thus have

$$n = \frac{0.9873 \times 40.1}{0.4198 \times 17.06} = 5.529.$$

The correct value is probably either 5 or 6. In view of the fact that the solution was prepared eight hours before analysis was made, it is not improbable that a portion of the metal reacted with the solvent according to the equation: $Ca + 2NH_3 = Ca(NH_2)_2 + H_2$.

Experiment 2.—To avoid errors due to possible formation of amide the following experiments were carried out as rapidly as possible. In this experiment 0.2489 gram of metal was employed. Ammonia was withdrawn at 0° until the pressure nearly reached the dissociation pressure of the compound. There was found a gain of 0.6218 gram, corresponding to $n = 5.874$.

Experiment 3.—The calcium introduced weighed 0.2075 gram. After pumping off the excess solvent at 20°, there was found a gain of 0.5142 gram, giving $n = 5.825$.

Experiment 4.—In this experiment 0.5142 gram of metal was employed. The excess solvent was removed at 0° as in Experiment 2.

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[1] *Loc. cit.*

There was found a gain of 1.2830 grams, from which n may be calculated to be 5.864.

After weighing, the tube was again attached to the pump and the ammonia was completely eliminated. The contents of the tube now weighed 0.0116 gram in excess of the weight of metal initially present. This indicates that amide is formed during the experiment. It was accordingly decided to carry out several experiments in which the solvent should be withdrawn at lower temperatures. It is to be mentioned, however, that at lower temperatures a longer time is required in removing the excess of solvent.

Experiment 5.—Employing 0.3888 gram of calcium from which the excess solvent was withdrawn at —33°, a gain of 0.9772 gram was obtained. This gives $n = 5.909$.

Experiment 6.—This experiment is a duplicate of No. 5. There was employed 0.4491 gram of metal and found a gain of 1.1255 grams. From these results n is found to be 5.891 molecules of ammonia per atom of calcium.

Collecting the results of the last five experiments we have:

Experiment No.	n.	Temperature.
2	5.874	0°
3	5.825	20°
4	5.864	0°
5	5.909	—33°
6	5.891	—33°

The temperatures here given are those at which the excess of ammonia was withdrawn. It is plain that at lower temperatures the value of n is consistently larger than at higher ones, while at the same temperature the results are in good accord. That a portion of the metal reacts with ammonia is indicated by the fact that a slow but steady increase in pressure may be observed, particularly at higher temperatures. We may conclude, therefore, that the composition of the compounds of calcium is represented by the formula $Ca(NH_3)_6$.

As already stated, Moissan describes a compound $Ca(NH_3)_4$. It might be though that the compound $Ca(NH_3)_6$ breaks down in two steps, in which case $Ca(NH_3)_4$ should appear as an intermediate product. The experiments described above show conclusively, however, that the compound dissociates according to the equation

$$Ca(NH_3)_6 \rightleftarrows Ca + 6NH_3 .$$

Compounds of Barium and Strontium.

A compound of barium, whose composition is $Ba(NH_3)_6$, has been described by Mentrel.[1] Systematic pressure determinations were not carried out for the purpose of determining the phase relations, but it is stated

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[1] *Loc. cit.*

that above certain temperatures a solid compound is obtained which does not liquefy in excess of ammonia. It can scarcely be doubted, therefore, that a compound is formed. Employing the method of Joannis, he finds the decomposition decreasing from 6.97 molecules of ammonia per atom of metal at —50° to 6.10 at 0°. He believes the compound $Ba(NH_3)_6$ to be formed, the excess ammonia being present as a solid solution in this compound. There seems to be need of further evidence on this point.

Roederer[1] has investigated the action of ammonia on strontium. His results are in every way similar to those of Mentrel in the case of barium. He believes the compound $Sr(NH_3)_6$ to be formed. Here also the composition is a function of the temperature and a solid solution is suggested by way of explanation.

Nature of the Compound $Ca(NH_3)_6$.

It was stated at the beginning of this paper that Weyl, on discovering the solutions of sodium and potassium in ammonia, concluded that compounds resulted, to which he assigned an ammonium structure. Joannis, believing that he had isolated compounds of sodium and ammonia, retained these conceptions of Weyl as to the constitution, and other investigators have, for the most part, accepted this view. In the case of compounds containing a considerable number of ammonia molecules, the structural formulae advanced are rather complex to say the least, and they lack for support a single physical property or a single reaction that would indicate a structure such as has been proposed. How little this theory of constitution was based upon facts is well illustrated by the fact that those compounds which first led to the ammonium theory have now been shown to be non-existent. In the case of the metals of the alkaline earths where six molecules of ammonia are present per atom of metal and where all are given off at the same pressure, it is no longer necessary to take the ammonium theory into consideration. The term metal-ammonium should therefore be dropped from the literature as Ruff and Geisel have suggested.[1]

Before discussing further the question of the constitution of the compound $Ca(NH_3)_6$ it will be necessary to consider, briefly, the properties of this substance. It has already been mentioned that the compound is identical in appearance with the solution from which it is precipitated, *i. e.*, that it possessed the same optical properties. To whatever molecular condition these optical properties may be due, it is plain that they obtain in both solid and solution and are therefore not dependent on the physical state of the system. Now the compound and its solution not only possess the same optical properties but they likewise possess the same electrical properties, for both the solid and its solution exhibit

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[1] *Loc. cit.*

metallic conduction. It seems possible, therefore, that the same factors which govern the optical properties of these two substances also govern their electrical properties. This suggests that if the factors governing the electrical and optical properties may be determined they will lead to some knowledge as to the state of the compound $Ca(NH_3)_6$ in its solid state. A further discussion of this point cannot be undertaken, however, until the data relating to the properties of the solutions in ammonia have been pesented.

That the compound $Ca(NH_3)_6$ is capable of existence is an important fact. We have here for the first time a compound in which a metal appears combined with a solvent without at the same time being combined with a strongly electronegative element or group of elements, as is commonly the case in solvated salts. The nature of the forces coming into play when calcium combines with ammonia must be quite different from those involved in the combination of a metal with a negative element to form a salt, for, while in the latter case all metallic properties are lost, in the former the metallic properties persist. The salts are usually considered to be valence compounds, and their formation is supposed to involve forces of an electric nature. The compound $Ca(NH_3)_6$ belongs to the class of compounds which, like the solvates, are commonly grouped under the head of molecular compounds. That electrical forces play only a minor part in the compound $(CaNH_3)_6$ is indicated by the persistence of the metallic properties.

It seems probable that the ammonia present in the calcium compound is combined with the metal in the same manner as in the case of ammoniated salts or solvated ions. Indeed the thought lies near that $Ca(NH_3)_6$ is simply a free positive ion which is present to some extent when a calcium salt is dissolved in ammonia. It is interesting, also, to note that this compound corresponds with both Abegg's theory of contravalences and Werner's co-ordination number.

Since the compound $Ca(NH_3)_6$ appears to be a solvate of the metal calcium, the name calcium, hexammoniate may be suggested as a consistent nomenclature.

Incidentally, attention may be called to the fact that the presence of a large number of nitrogen and hydrogen atoms in the compound does not interfere with its properties as a metal. The presence of non-metallic elements in a compound does not necessarily preclude the existence of metallic properties. Further examples of compounds of this character will be discussed later.

Summary.

The existing experimental data relating to the supposed formation of the compounds $NaNH_3$ and KNH_3 are examined in the light of the phase rule and the conclusion is reached that these compounds do not exist.

In a similar manner the non-existence of the compound $LiNH_3$ is established. In this case independent evidence is given which shows conclusively that in a system containing lithium and a small molecular per cent. of ammonia a saturated solution of the metal in ammonia is formed. This result is in agreement with the phase relationships existing in the system and demonstrates the inapplicability of the method employed by Moissan in obtaining and identifying the supposed compound of lithium and ammonia.

It is shown that calcium forms a solid compound with ammonia whose composition is represented by the formula $Ca(NH_3)_6$. The optical properties of this compound are apparently identical with those of its saturated solution in ammonia, and like its solution, the compound exhibits metallic conduction.

The vapor pressures of saturated solutions of lithium and of $Ca(NH_3)_6$ in ammonia have been determined, as well as the dissociation pressures of the compound itself. The heats of formation of the corresponding solutions and of the compound from metal and gaseous ammonia are calculated to be 8700, 10230, and 5460 calories per gram-molecule of ammonia, respectively.

The constitution of the compound $Ca(NH_3)_6$ is discussed. It appears that this compound is of the nature of a solvate, corresponding, perhaps, to an ammoniated calcium ion. It is suggested that the compound be called calcium hexammoniate in order to take account of these relations in the nomenclature.

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THE OSMOTIC PRESSURE OF CONCENTRATED SOLUTIONS, AND THE LAWS OF THE PERFECT SOLUTION.

BY GILBERT NEWTON LEWIS.

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The laws of the infinitely dilute solution have been thoroughly established. There can be no reasonable doubt as to the accuracy of Henry's law for the vapor pressure of the solute, Raoult's law for the vapor pressure of the solvent, or van't Hoff's law for the osmotic pressure, in the case of an infinitely dilute solution. In fact if any one of these laws is shown to be correct, the other two must follow as a direct consequence of the laws of thermodynamics.

Unfortunately, we never work with an infinitely dilute solution, and too little attention has been given to the question of the validity or even the mutual compatibility of the laws just mentioned in concentrated solutions and even in the so-called dilute solutions.