equation giving 1160 and 1:2, respectively). The effect of a confining tube on the velocity of sound in a gas is found to be accurately given by the formula of Kirchhoff and Helmholtz. Neglect of that fact caused errors of over 10% in the sound velocity specific heat measurements of Partington and Shilling, making their work worthless unless recalculated. The velocity of sound in unconfined, dry, carbon dioxide-free air at 24° is found to be 345.66 meters per second and the velocity of sound in free hydrogen at 0° is found to be 1260.9 meters per second.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

DISPLACEMENT OF METALS FROM SOLUTIONS OF THEIR SALTS BY LESS ELECTROPOSITIVE ELEMENTS

IV. POTASSIUM AMMONO BERYLLATE AND SODIUM AMMONO BERYLLATE

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In attempting to prepare aluminum amide by the action of ammonium bromide—an acid in liquid ammonia—upon a solution of sodium ammono aluminate in accordance with the equation, $Al(NH_2)_2NHNa + NH_4Br = NaBr + NH_3 + Al(NH_2)_3$,[1] the author obtained precipitates which varied in composition approximately between the limits of $Al(NH)NH_2$ and $Al_2(NH)_3$. In explanation of this behavior it is suggested that these precipitates be regarded as indefinite compounds resembling the hydrous oxides in constitution, and therefore appropriately called ammonous aluminum nitrides, $AlN + xNH_3$. In view of the chemical similarity between aluminum and beryllium one might expect that beryllium amide would likewise prove to be an ammonous beryllium nitride. The present investigation was then undertaken primarily for the purpose of preparing beryllium amide or an ammonous beryllium nitride. As the potassium ammono beryllate required in the expected reaction, $Be(NHK)_2 + 2NH_4Br = Be(NH_2)_2 + 2NH_3 + 2KBr$, is unknown, the first experiments were directed toward the preparation of this compound.

Potassium Ammono Beryllate.—Since potassium hydroxide dissolves metallic beryllium to form potassium aquo beryllate, we should expect the analogous base of the ammonia system, potassium amide, to dissolve beryllium to form a potassium ammono beryllate. N. C. Jones and P. F. Frohring, at Western Reserve University in the summer of 1926, found that beryllium dissolves in solutions of sodium and potassium amides in liquid ammonia to form extremely soluble ammono beryllates

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[1] Bergstrom, *J. Phys. Chem.*, March, 1928. This reaction resembles the precipitation of aluminum hydroxide by the addition of an acid to a solution of an aquo aluminate in water.

which they were unable to analyze in the time at their disposal. It was for the added purpose of bringing to completion the preliminary work of Jones and Frohring that this portion of the present investigation was undertaken.

Beryllium reacts with potassium amide dissolved in liquid ammonia to form an opaque blue solution, which was shown to contain metallic potassium,[2] the reaction probably proceeding in accordance with the equation, $Be + 2KNH_2 \rightleftharpoons Be(NH_2)_2 + 2K$. The apparent anomaly of beryllium replacing the more electropositive element potassium can readily be understood if one recalls the fact that dilute solutions of the alkali metals in liquid ammonia are salt-like in character.[3] The (+) ions in such solutions are the normal ions of the alkali metal, while the (−) ion is the solvated negative electron, e^-. Now beryllium does not dissolve in liquid ammonia to form a solution sufficiently concentrated to exhibit a blue color such as characterizes solutions of the alkali and alkaline earth metals in this solvent. Nevertheless, one may ascribe an extremely slight solubility to beryllium in view of the fact that all of the very electropositive metals, including magnesium, dissolve, at least to some extent, in ammonia. One may assume, by analogy with the alkali metals, that beryllium dissolves to a slight degree in ammonia to form Be^{++} ions together with an equivalent number of solvated negative electrons. Since potassium amide forms K^+ and NH_2^- ions, the reaction of this base with beryllium will simply involve interaction between the ions Be^{++}, NH_2^-, K^+ and e^-. $Be(NH_2)_2$ is very slightly soluble in ammonia and so will form to some extent as a precipitate, leaving in solution equivalent quantities of K^+ and e^- ions, which constitute a solution of metallic potassium. Since $Be(NH_2)_2$ is not entirely insoluble in ammonia it is necessary to consider the above reaction as an equilibrium.

Potassium, formed in the reaction of the preceding paragraph, reacts with the solvent, in the presence of a catalyst such as beryllium, to form potassium amide and hydrogen, while the potassium amide thus formed dissolves the amphoteric base beryllium amide to form potassium ammono beryllate, in the sense of the equation, $Be(NH_2)_2 + KNH_2 = Be(NH_2)\text{-}NHK\cdot NH_3$. Aluminum has previously been found to react with potassium amide in an entirely analogous manner.[4]

Potassium ammono beryllate is, however, most conveniently prepared by the action of a solution of metallic potassium in liquid ammonia upon an excess of beryllium. The metallic beryllium, acting as a catalyst, first converts the potassium to potassium amide, which in turn reacts with the beryllium in accordance with the equations of the preceding paragraph.

[2] Bergstrom, THIS JOURNAL, **45,** 2789 (1923), has described the test used.

[3] Kraus, *ibid.*, **44,** 1224 (1922).

[4] Bergstrom, ref. 2, p. 2788; **46,** 1548 (1924).

For the purpose, then, of preparing potassium ammono beryllate, a small tube containing about 0.35 g. of potassium is placed in one leg of a reaction tube[5] together with about two atomic equivalents of metallic beryllium.[6] Within a day or two after ammonia is distilled into the reaction tube the potassium is completely converted into a colorless solution of potassium ammono beryllate, which is then decanted into the other leg of the reaction tube to effect a separation from the residue of unused beryllium. Attempts to obtain crystals from a concentrated solution of potassium ammono beryllate at −40° having failed, analyses were made of the colorless solid remaining after evaporation of solvent ammonia from the reaction tube.

Potassium ammono beryllate is vigorously hydrolyzed by water to potassium hydroxide, ammonia and beryllium hydroxide, the latter remaining partly in solution as potassium aquo beryllate. In preparation for analysis the products of the hydrolysis were dissolved in dilute sulfuric or hydrochloric acid. Beryllium was determined on an aliquot portion of this solution as oxide, according to the method of Bleyer and Boshart.[7] Potassium was recovered as sulfate or chloride from the filtrate of the beryllium hydroxide. Nitrogen in a second aliquot portion was estimated volumetrically as ammonia.

Preparation 1, dried in a vacuum at 20°, weighed 0.8776 g. At 185° in a vacuum it lost 0.1071 g. of ammonia of crystallization. (The ammonia was not all pumped off.) One-fourth of the preparation gave 0.0736 g. of nitrogen. Another fourth gave 0.0582 g. of BeO and 0.1696 g. of KCl.

Preparation 2, dried in a vacuum at 20°, weighed 0.8478 g. Heated in a vacuum at 160° it lost 0.1388 g. of ammonia. One-fourth gave 0.0623 g. of nitrogen. A second fourth gave 0.0560 g. of BeO and 0.1674 g. of KCl.

Preparation 3, dried in a vacuum at −40°, weighed 0.8244 g. In a vacuum at 25° it lost 0.0067 g. and at 215° a further 0.1382 g. of ammonia. One-half gave 0.1080 g. of BeO. One-quarter gave 0.1584 g. of KCl. One-quarter gave 0.0603 g. of nitrogen.

Analyses.—Calcd. for $Be(NH_2)NHK \cdot NH_3$: Be, 9.4; N, 43.7; K, 40.7. Found, dried in a vacuum at room temperature: Be, 9.6, 9.5, 9.5; N, 43.6, 42.9, 43.4; K, 40.6, 41.4, 40.7. This salt, when converted into $Be(NH_2)NHK$, should lose 17.7% of ammonia. Specimens No. 2 and 3 lost, respectively, 16.4 and 17.6% of ammonia when heated in a vacuum above 160°.

Potassium ammono beryllate may be represented as a salt of the ammonia system, $Be(NH_2)NHK \cdot NH_3$, as a double compound of beryllium amide and potassium amide, $Be(NH_2)_2 \cdot KNH_2$, or, following Werner, as the coördination compound, $K[Be(NH_2)_3]$. In accordance with the

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[5] A description of the manipulations concerned in the preparation of compounds in liquid ammonia may be found in the following articles by Franklin and his students: THIS JOURNAL, **27**, 832 (1905); **29**, 1694 (1907); **35**, 1460 (1913); *J. Phys. Chem.*, **15**, 510 (1911); **16**, 694 (1912).

[6] The beryllium, which was in the form of small chips, was found to be practically free from other metals.

[7] Bleyer and Boshart, *Z. anal. Chem.*, **51**, 754 (1912).

fact that beryllium resembles aluminum more closely in properties than it does magnesium, potassium ammono beryllate was found to resemble potassium ammono aluminate, $Al(NH_2)_3{\cdot}KNH_2$, more closely in constitution and properties than it does potassium ammono magnesiate, $Mg(NH_2)_2{\cdot}2KNH_2$.[8] Both potassium ammono aluminate and potassium ammono beryllate are readily soluble in liquid ammonia and both melt in their ammonia of crystallization upon heating, each losing one molecule of ammonia. Potassium ammono magnesiate, on the other hand, is very slightly soluble in ammonia and does not readily lose ammonia when heated.

Sodium Ammono Beryllate.—This salt is best prepared in the same manner as potassium ammono beryllate, that is, by the action of a liquid ammonia solution of sodium upon an excess of metallic beryllium.

Preparation 1, dried in a vacuum at 20°, weighed 1.2017 g. One-quarter gave 0.0950 g. of BeO and 0.2743 g. of Na_2SO_4. One-quarter gave 0.1537 g. of nitrogen.

Preparation 2, dried in a vacuum at 20°, weighed 1.0378 g. One-half gave 0.2696 g. of nitrogen. The other half gave 0.1646 g. of BeO and 0.3847 g. of NaCl.

Preparation 3, dried in a vacuum at $-40°$, weighed 0.8035 g. When heated in a vacuum at room temperature, 0.0038 g. of ammonia of crystallization was lost. One-quarter gave 0.1032 g. of nitrogen. Another quarter gave 0.0633 g. of BeO and 0.1497 g. of NaCl.

Analyses.—Calculated for $Be(NH_2)NHNa{\cdot}NH_3$: Be, 11.2; N, 52.5; Na, 28.8. Found, dried in a vacuum at room temperature: Be, 11.4, 11.4, 11.4; N, 51.2, 52.0, 51.6; Na, 29.6, 29.2, 29.5. These analyses indicate that sodium ammono beryllate has lost a little of its ammonia of crystallization in a vacuum at room temperature. When heated in a vacuum between 150 and 200°, sodium ammono beryllate melts and loses approximately one molecule of ammonia.

Sodium ammono beryllate resembles the corresponding potassium salt closely in physical and chemical properties.

Beryllium Amide.—It was hoped that beryllium amide would be formed, in accordance with the equation, $BeI_2 + 2KNH_2 = 2KI + Be(NH_2)_2$, when potassium amide is added to a solution of a salt of beryllium in liquid ammonia. Unfortunately, potassium amide precipitates ammonobasic mixtures from solutions of both beryllium iodide and thiocyanate.

When a solution of ammonium bromide is slowly poured into a solution of sodium ammono beryllate, a flocculent, white precipitate containing much sodium is thrown down instead of the expected beryllium amide.

Magnesium amide may be formed by the action of a liquid ammonia solution of sodium chloride or iodide upon magnesium.[9] An attempt to prepare beryllium amide by the analogous action of a solution of sodium chloride on beryllium failed.[10]

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[8] Franklin, This Journal, **35,** 1463 (1913).

[9] Bergstrom, *ibid.*, **48,** 2849 (1926).

[10] Since beryllium chloride is very soluble in liquid ammonia at room temperature, there is no tendency for the reaction $Be + 2NaCl \rightleftharpoons BeCl_2 + 2Na$ to take place.

Notes.—Since a solution of sodium ammono magnesiate attacks magnesium to form magnesium amide,[9] it was expected that a solution of sodium ammono beryllate would likewise react with magnesium to form magnesium amide. The anticipated reaction does not take place. Magnesium amalgam, however, reacts with a solution of sodium ammono beryllate to form a very impure magnesium amide and sodium amalgam.

Addition of a solution of sodium ammono beryllate to a solution of magnesium thiocyanate throws down a flocculent precipitate of the composition $Mg(NH_2)_2 \cdot Be(NH_2)_2$, which may be a mixture of beryllium and magnesium amides and not a definite compound.

A solution of sulfur in liquid ammonia reacts slowly with beryllium to form a yellow precipitate of an ammonated beryllium mono- or polysulfide. This precipitate slowly dissolves in an excess of sulfur solution to form soluble polysulfides of beryllium.

Beryllium, the surface of which has been cleansed by the action of a liquid ammonia solution of ammonium chloride,[11] does not dissolve in pure liquid ammonia to form a visibly colored solution. Under similar conditions it will be remembered that magnesium dissolves to form a light blue solution.[12]

In conclusion, the author wishes to express his thanks to Dr. E. C. Franklin for his interest in this work and for reading the manuscript prior to publication.

Summary

(1) Potassium and sodium ammono beryllates of the general formulas $Be(NH_2)NHK \cdot NH_3$ and $Be(NH_2)NHK$ have been prepared by the action of solutions of the corresponding alkali metal or alkali metal amide upon metallic beryllium.

(2) Attempts to prepare beryllium amide, $Be(NH_2)_2$, have failed.

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[11] Ammonium chloride is an acid in liquid ammonia. Franklin and Kraus, *Am. Chem. J.*, **23**, 305 (1900); THIS JOURNAL, **27**, 822 (1905).

[12] Cottrell, *J. Phys. Chem.*, **18**, 96 (1914).