and oleates follows the order: cesium, potassium, sodium, calcium, silver, magnesium, zinc, aluminum, iron. This order is in accord with the valences and atomic diameters of the metals, as interpreted by the orientation theory.

6. It is suggested that the type of emulsion produced by a solid powder is determined by the angle of contact of the interface with the solid. In order for the powder to remain in the interface the angle must be finite, and unless the angle is 90°, the interface will be on one side or the other of the points of contact of the particles, and its tension will cause the film to be concave on that side.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 35]

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

I. THE REPLACEMENT OF SODIUM AND POTASSIUM BY MAGNESIUM AND ALUMINUM

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Introduction

Franklin[2] found that a solution of potassium amide in liquid ammonia reacts readily with magnesium to form an opaque blue solution, which disappears within a few hours leaving a precipitate of the sparingly soluble potassium ammono-magnesiate, $Mg(NHK)_2.2NH_3$.[3] During the preparation in an analogous manner of potassium and sodium ammono-aluminates the author observed the production of similar intermediate blue solutions. The present work, which was undertaken primarily for the purpose of accounting for the phenomena observed, and of establishing the equations for the reactions, is a portion of a general investigation dealing with the action of potassium and potassium amide upon the elements.

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[1] National Research Council Fellow.

[2] Franklin, THIS JOURNAL, **35**, 1463 (1913).

[3] Potassium and sodium amides are bases of the ammonia system, and behave in this solvent just as potassium and sodium hydroxides behave in water. Thus an aqueous solution of potassium hydroxide dissolves aluminum and zinc to form, respectively, potassium aquo-aluminate and potassium aquo-zincate, while a liquid ammonia solution of potassium amide dissolves aluminum to form a potassium ammono-aluminate, and reacts with zinc to form a sparingly soluble potassium ammono-zincate. Potassium ammono-magnesiate, on the other hand, has no analog in the water system, because the much greater solvolytic power of water relative to that of ammonia renders its existence impossible. Reactions thus occur in ammonia that cannot take place in water. For a further explanation of the ammonia system of acids, bases and salts, see *Am. Chem. J.*, **47**, 285 (1912); *Proc. Eighth Int. Cong. Appl. Chem.*, **6**, 119 (1912).

Discussion of the Reactions

The alkali and alkaline earth metals dissolve abundantly in liquid ammonia, yielding intensely colored blue solutions, which on concentration acquire a beautiful coppery luster. This behavior is characteristic of solutions of these elements alone, and so may be regarded as a positive test for their presence. Magnesium, if its surface is perfectly clean, dissolves to a slight extent in liquid ammonia, the saturated solution being light blue and readily transparent. Amalgamated aluminum does not dissolve under ordinary conditions, but might be expected to do so to a much less extent than magnesium if the surface were continually kept clean and free from amide as, for instance, by the action of a solution of sodium or potassium amide.

It is plain, therefore, that the opaque blue solutions obtained by the action of potassium amide on magnesium and aluminum, and of sodium amide on aluminum, must contain free alkali metal, for the strong color cannot possibly be due to either of the less electropositive elements. As a further and confirmatory test, these solutions, when evaporated almost to dryness, were found to assume the familiar coppery color characteristic of concentrated solutions of the alkali metals. After complete removal of the solvent, rather imperfect crystals of sodium or potassium were found to be deposited upon the walls of the reaction tube.

Kraus[4] has shown that dilute solutions of the alkali metals in liquid ammonia conduct the electric current in the same manner as ordinary salts. The positive carrier is the sodium ion, Na^+, while the negative carrier is the solvated negative electron, which may be represented by the symbol e^-. The conductance curve in these regions is similar in form to the curves obtained with solutions of the common salts, approaching asymptotically a limiting value as the dilution increases.[5]

In view of these facts one should expect dilute solutions of the alkali metals to exhibit salt-like properties in other respects. In fact, Kraus[6] has shown that the following metathetic reaction readily takes place because of the low solubility of one of the products, calcium chloride, in liquid ammonia: $\text{Ca (dslvd.)} + 2\text{KCl (dslvd.)} = \text{CaCl}_2\text{(ppt.)} + 2\text{K (dslvd.)}$.

Magnesium[7] is slightly soluble in ammonia, while aluminum probably dissolves under the proper conditions to a much less extent. Accordingly when either of these metals is treated with sodium or potassium amide, most of its ions are removed from solution by formation of the very slightly soluble magnesium or aluminum amide, and we have a virtual

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[4] Kraus, This Journal, **43**, 749 (1921), and previous articles.

[5] At a concentration above about 0.5 *N*, metallic conduction causes the curve to rise rapidly, a saturated solution conducting the current as well as many metals.

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

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

metathesis, which may be represented by the equations: $Mg + 2KNH_2 \rightleftharpoons Mg(NH_2)_2 + 2K$; $Al + 3NaNH_2 \rightleftharpoons Al(NH_2)_3 + 3Na$.

In view of the slight solubility of both magnesium and aluminum, and in view of the fact that their amides cannot be completely insoluble, although, being weak bases, they must be but very slightly ionized in solution,[8] it is necessary to assume an equilibrium to exist. This is being continually displaced toward the right because of the interaction of the alkali metal solutions with the solvent, in which process magnesium and aluminum play the part of catalytic agents: $3K + 3NH_3 \longrightarrow 3KNH_2 + \frac{3}{2}N_2$; or $3Na + 3NH_3 \longrightarrow 3NaNH_2 + \frac{3}{2}H_2$.

Aluminum and magnesium amides are both amphoteric in their properties and therefore react with the excess of potassium or sodium amide present to give the ammono salts finally obtained. In this manner aluminum and magnesium ions are practically completely removed from solution and the equilibrium is further displaced toward the right. The complete equations for the formation of sodium ammono-aluminate may then be written: $Al + 3NaNH_2 \rightleftharpoons Al(NH_2)_3 + 3Na$; $Al(NH_2)_3 + NaNH_2 = Al(NH_2)_2NHNa.NH_3$; $3Na + 3NH_3 = 3NaNH_2 + \frac{3}{2}H_2$; and for the formation of potassium ammono-magnesiate: $Mg + 2KNH_2 \longrightarrow Mg(NH_2)_2 + 2K$; $Mg(NH_2)_2 + 2KNH_2 \longrightarrow Mg(NHK)_2.2NH_3$; $2K + 2NH_3 \longrightarrow 2KNH_2 + H_2$.

In view of the relative rapidity of formation of potassium ammono-aluminate and magnesiate, and of sodium ammono-aluminate according to the above type equations, it is probable that the equilibria of which the first equation is an example rest far over on the right hand side. In the first example above, sodium amide has a solubility of approximately 1 g. per liter,[8a] yet the blue solution obtained on interaction with aluminum is quite opaque and contains sodium in fairly high concentration.

Evidence for the intermediate formation of aluminum amide has been obtained during a previous study of the action of potassium amide on aluminum. Aluminum, although a very reactive metal, is quickly covered in air with an adherent protective coating of oxide which hinders further action. Consequently in order that reaction with the alkali metal amides might take place at all, it was necessary to amalgamate the surface. It will be shown later that the mercury plays no essential part in the course of the reactions, although it may in some measure increase the velocity.

This work suggests that the reactions between potassium or sodium hydroxide and aluminum may partially take place in an analogous manner,

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[8] Even the relatively strong ammono bases, sodium and potassium amides, are ionized only to a small extent in solution. Nevertheless, aluminum and magnesium amides are weak enough to exhibit amphoteric properties toward them. Kraus, "Properties of Electrically Conducting Systems," **1922,** p. 59. American Chemical Society Monograph, Chemical Catalog Co.

[8a] E. C. Franklin, unpublished work.

that is, the evolution of hydrogen may be due to a secondary action of potassium or sodium on water rather than to a direct replacement of the hydrogen of the hydroxyl group. Certain experiments already carried out favor this view, but further discussion will be reserved for a future paper.

Action of Solutions of Sodium and Potassium on Aluminum

Potassium[9] and sodium ammono-aluminates are formed by the action of solutions of the alkali metals alone on amalgamated aluminum. It seems probable that the potassium or sodium is first converted to amide by the combined catalytic action of the aluminum and mercury, and this in turn reacts as previously described. It was found, curiously enough, that the formation of sodium ammono-aluminate by either of the methods mentioned was two to three times more rapid than the formation of the potassium analog, undoubtedly because of difference in the rapidity of the initial stage of the reaction.

Potassium amide, due to its superior solubility, probably reacts at first much more rapidly on aluminum, quickly coating the amalgamated areas over with a thick and relatively adherent layer of aluminum amide and preventing for the time being direct contact between portions of the metal and the solution. Experiments[9a] with potassium amide and slightly amalgamated aluminum have shown that the amalgamated surfaces may be covered up so as to stop the reaction completely, although only temporarily, causing a periodic production and disappearance of the blue potassium solution. With sparingly soluble sodium amide, aluminum amide is undoubtedly formed at a slower rate, and thus has no tendency to form a retarding layer, that is, contact exists between the active areas of the metal and solution at all times. The resultant reaction is, therefore, more rapid.

That the mercury is inert, aside from possible catalytic effects, is shown in the two following experiments.

(1) A piece of sheet aluminum was well amalgamated in a liquid ammonia solution of mercuric iodide,[10] washed with the same solvent, and then sealed up in one leg of a two-legged reaction tube.[11] The other leg contained a few tenths of a gram of sodium. Ammonia was distilled into the reaction tube, a portion of the sodium solution was poured upon the aluminum and allowed to remain until the mercury of the amalgam was saturated, after which the metal strip was washed and allowed to remain in contact with fresh solvent for a day. No evidence of the formation of sodium ammono-aluminate could be obtained, even after the mercury had been treated again with sodium.

(2) A moderately concentrated sodium amalgam was prepared by agitating a solution of sodium in liquid ammonia with mercury in a three-legged reaction tube. This together with the ammonia was then poured upon a small, well-amalgamated slab of

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[9] (a) Unpublished work of the Author. (b) See *C. A.*, **16,** 3822 (1922).

[10] To prevent oxidation.

[11] See Expt. 4.

aluminum prepared as in the preceding experiment. At the end of $4^1/_2$ months no sodium ammono-aluminate had been formed.

Sodium Ammono-Aluminate

Sodium ammono-aluminate, obtained by either of the methods mentioned, is readily soluble in liquid ammonia at ordinary temperatures, and may be obtained in the form of small white needles by cooling a moderately concentrated solution to —40°.[12] The solubility at 0° is only a little less than at room temperature. Curiously enough, large crops of blunt prisms were obtained in two cases by cooling (in ice water) the solution obtained immediately after the disappearance of the blue color of the sodium. After these solutions had stood for a day, only the small needles, previously described, were obtained when the liquid was cooled to —40°. The existence of two crystalline modifications of this salt is not surprising in view of the fact that aluminum cyanide behaves in a somewhat similar manner.[9a]

Sodium ammono-aluminate when dried in a vacuum at either —33° or room temperature corresponds in composition to $Al(NH_2)_2NHNa.NH_3$, $Al(NH_2)_3.NaNH_2$ or $Na[Al(NH_2)_4]$. When heated in a vacuum it melts near 90° with a large increase of pressure, giving off one molecule of ammonia and forming $Al(NH_2)_2.NHNa$, a solid of the nature of a glass, and possessing no crystalline structure.

Water reacts very vigorously with either of the above compounds, a great deal of heat being developed. The resulting products of hydrolysis are for the most part soluble in the water introduced into the reaction tube. Hydrochloric acid then reacts with this solution of sodium aquo-aluminate and with the remaining precipitate to form aluminum, ammonium, and sodium chlorides.

Experimental Part

The general methods used for the preparation of compounds in liquid ammonia solution and their subsequent analysis have been described in previous articles.[13]

In this work analyses were made on aliquot portions of the hydrochloric acid solution of the specimen.

Preparation 1.—In one leg of a two-legged reaction tube were placed 0.35 g. of sodium and an excess of commercial sheet aluminum, the other leg remaining clean and empty for subsequent crystallization of the aluminate. The sodium was completely converted after 24 hours into a colorless solution of sodium ammono-aluminate, which was then separated from a small quantity of residue by decantation into the other leg. On cooling to 0°, a large crop of blunt thick needles was obtained, although only the fine needles could be isolated in the succeeding experiments. When this stood for a day,

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[12] In an open ammonia bath.

[13] This Journal, **27**, 831 (1905); **29**, 1694 (1907); **35**, 1460 (1913). *J. Phys. Chem.*, **15**, 915 (1911); **16**, 694 (1912).

partial ammonolysis took place with the deposition of some amorphous white precipitate. Accordingly, the solution was merely evaporated to dryness and then analyzed.

Analyses. Subs., dried in a vacuum at —40° (1–2 mm.), 1.3055 g. Wt., dried in a vacuum at room temperature, (1 mm.), 1.3053 g. One-fifth gave 0.1650 g. of sodium sulfate; two-fifths gave 0.2346 g. of Al_2O_3.

Preparation 2.—The reaction between 0.34 g. of sodium in the form of amide with an excess of pure amalgamated aluminum was complete at the end of a day. The resulting salt was crystallized once by cooling the moderately concentrated solution in an open liquid-ammonia bath, and ammonia of crystallization at —33° was determined by the method outlined by Franklin.[13] Unfortunately, a small quantity of sodium amide lodged in the stopcock tube and could not be removed, helping to make the sodium analysis run a little high. The analytical results for the first and fourth experiments are more satisfactory, even though impure aluminum was used. The larger surface of metal exposed in these cases undoubtedly accounts for the facts.

Analysis. Subs., dried in a vacuum at —33°, 0.9335 g. Wt., dried in a vacuum at room temperature, 0.9323 g. Two-fifths gave 0.1633 g. of Al_2O_3; one-fifth gave 0.08989 g. of nitrogen; one-fifth gave 0.0813 g. of Al_2O_3 and 0.1026 g. of NaCl.

Preparation 3.—The preparation was carried out as in Expt. 1, using, however, small pieces of pure amalgamated aluminum. The sodium solution was changed to sodium ammono-aluminate within a day. The product was crystallized twice at —40° without the appearance of insoluble ammono basic residues. (Compare Expt. 1.) On heating in a vacuum, the salt melted at 85–90° and on continued evacuation finally solidified to a voluminous froth.

Analysis. Subs., dried in a vacuum at room temperature, 0.7736 g. Wt., heated in a vacuum at 110°, 0.6528 g. (Probably a little overheated.) One-quarter gave 0.06929 g. of nitrogen; one-quarter gave 0.0879 g. of Al_2O_3 and 0.1032 g. of NaCl.

Preparation 4.—This experiment was performed primarily to see whether the mercury of the amalgam took any essential part in the reaction. After completion of the tests described previously in this article, the sodium solution was poured upon the aluminum, and allowed to react with it. The salt was crystallized twice at 40°, then dried in a vacuum at room temperature and 105°.

Analysis. Subs., dried in a vacuum at room temperature, 1.0004 g. Wt., dried in a vacuum at 105°, 0.8513 g. One-quarter gave 0.1145 g. of Al_2O_3 and 0.1274 g. of NaCl; one-quarter gave 0.09206 g. of nitrogen. One-quarter gave 0.1147 g. of Al_2O_3.

SUMMARY OF ANALYSES

Dried in a vacuum at —33° or room temperature.						Heated in a vacuum above 100°			
	Calc. for $Al(NH_2)_2NHNa.NH_3$	Found					Calc. for $Al(NH_2)_2NHNa$	Found	
		No. 1	No. 2	No. 3	No. 4			No. 3	No. 4
Al	23.7	23.8	23.1	24.0	24.2	Al	27.9	28.5	28.5
N	49.2	. .	48.2	48.7	49.1	N	43.3	42.4	43.3
Na	20.2	20.5	21.6	21.0	20.0	Na	23.7	24.9	23.6

In conclusion the author wishes to thank Dr. Charles A. Kraus for his kind and helpful interest in this work.

Summary

1. Sodium amide and amalgamated aluminum react to form a definite crystalline compound, sodium ammono-aluminate, to which any one of the following formulas may be given: $Al(NH_2)_2NHNa.NH_3$, $Al\ (NH_2)_3.NaNH_2$,

or $Na[Al(NH_2)_4]$. This compound loses one molecule of ammonia on heating in a vacuum above 90°. The equations for the reaction have been shown to be $Al + 3NaNH_2 \rightleftharpoons Al(NH_2)_3 + 3Na$; $Al(NH_2)_3 + NaNH_2 = Al(NH_2)_2NHNa.NH_3$; $3Na + 3NH_3 = \frac{3}{2}H_2 + 3NaNH_2$.

The action of potassium amide on amalgamated aluminum and on magnesium are analogous in character. An explanation is given which depends upon the fact previously pointed out by Kraus that dilute solutions of the alkali metals in ammonia are salt-like in character. The initial stages may be regarded as metatheses, although actually involving equilibria which suffer continual displacement because of secondary reactions.

2. A solution of sodium in liquid ammonia reacts with amalgamated aluminum to form the same sodium ammono-aluminate described above. Sodium amide is probably first formed, and this in turn reacts according to the equations given. The mercury of the amalgam does not play an essential part in the reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE DIELECTRIC CONSTANTS OF ORGANIC LIQUIDS AT THE BOILING POINT

BY F. V. GRIMM AND W. A. PATRICK

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The following study was undertaken with the idea of finding some relationship between the dielectric constant of liquids and other physical properties. It was thought that the dielectric constant would be found to be related to those properties of liquids that depend upon the force of molecular attraction, namely, latent heat of vaporization, surface tension, etc. That such relationships do exist is shown by the parallelism that is exhibited in the case of organic homologs.[1,2,3] The conclusion was, however, reached that no simple relationship exists between the dielectric constant and the latent heat of vaporization although in the case of closely related liquids there was unmistakable evidence to show that the contrary is true. Walden[4] connects several physical properties of liquids with the following function of the dielectric constant: $\frac{D.C. - 1}{D.C. + 2}, \frac{1}{\delta}$ which according to the Clausius-Mossotti theory involves the volume actually occupied by the molecules. All of these relations give different values for associated and non-associated liquids. Walden uses values of surface tension, latent heat of vaporization, etc., at the boiling temperature, while the values of

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[1] Hesehus, *Physik. Z.*, [2] 750 (1900).

[2] Campbell, "Modern Electrical Theory," Cambridge University Press, **1913.**

[3] Obach, *Phil. Mag.*, [5] **32,** 113 (1891).

[4] Walden, *Z. physik. Chem.*, **70,** 569 (1910).