XLV.—*Sodium, Potassium, and Lithium Amides.*

By Arthur W. Titherley, B.Sc., 1851 Exhibition Scholar.

In the early part of this century, Gay Lussac and Thénard (*Recherches Physico-chimiques*, **1**, 337—356), and shortly afterwards Humphry Davy (*Phil. Trans.*, 1809, **1**, 39), discovered the amides of sodium and potassium whilst examining the behaviour of ammonia with a view to determining its ultimate composition. Since then, sodamide has been prepared and examined by Beilstein and Geuther (*Ann. Chem. Pharm.*, **108**, 88), and potassamide by Baumert and Landolt (*Ann. Chem. Pharm.*, **111**, 1).

The present work was undertaken with the view of examining especially the nitrides of sodium and potassium, described by Davy and by Gay Lussac and Thénard; and of preparing, if possible, compounds intermediate between the amides and nitrides. Lithamide has also been prepared and its properties examined.

The experiments fall under the following heads :—

1. Preparation, properties, and composition of sodamide.
2. Experiments disproving the alleged existence of nitride of sodium; and attempts to prepare disodimide.
3. Preparation, properties, and composition of potassamide.
4. Experiments disproving the alleged existence of nitride of potassium.
5. Preparation, properties, and composition of lithamide.
6. Action of the amides on inorganic oxides.
7. Sundry actions of the amides.

Preparation of Sodamide by the Action of Ammonia on Heated Metallic Sodium in Glass Vessels.

It is not possible to obtain this substance in a pure state if glass vessels are used, owing to its action on the latter; neither can large quantities be prepared at a time in this way, as the glass is so strongly attacked by the amide that it is finally corroded through. In preparing small quantities, it is best to use a silver boat, as the amide is practically without action on the metal; porcelain is attacked by it, though not very rapidly at 300°, but the action increases considerably as the temperature is raised; platinum is only slowly corroded, but after a few weeks' constant use the metal becomes friable and much corroded. For this reason, in all the later experiments a silver boat was used.

A polished iron retort, fitted with an adjustable head and capable of holding about 500 grams of sodium, may be used most advantageously, allowing of the ready preparation of several pounds of the amide in a comparatively short time. The ammonia must be completely dried by passing through several cylinders containing quick lime and fused caustic potash, and finally through a long tube packed with sodium in the form of wire, which serves to remove any oxygen and the last trace of moisture. The air in the retort is first displaced by a rapid current of ammonia, led in by a glass tube, the end of which nearly touches the surface of the sodium. The retort is then heated by a triple Bunsen burner to a temperature of 300—400°, and the action allowed to proceed rapidly during several hours until all the sodium has disappeared. So complete is the decomposition of the ammonia during the first three or four hours, that the evolved hydrogen may be burnt at the end of the exit tube in a flame some 6 or 7 inches in length, but after about five hours the action slackens, and a considerable excess of ammonia is necessary to convert the last portions of sodium into the amide. Finally, when no more hydrogen is evolved, indicating the complete conversion of the sodium into sodamide, it is allowed to cool down in a slow current of ammonia, and afterwards broken into lumps, and preserved under dry ether or benzene. In this way, it is possible to obtain an almost theoretical yield, the only loss that occurs being due to the small quantity which sublimes into the neck of the retort as a fine, white powder. Thus prepared sodamide forms a white, translucent mass, having a conchoidal fracture and a marked crystalline structure; it is pure and free from iron, the latter not being attacked by it. The olive-brown, green, yellow, or other tints ascribed to the substance by previous investigators, is due to impurity, derived either from traces of charred organic matter, from the naphtha or other liquid in which the sodium had been kept, or to the brown coloration produced by the action of the amide on the silica of the glass or other vessels in which it had been prepared.

When prepared in small quantities in a silver boat, from pure materials, it is white and of waxy appearance, but if pure sodium, freed from adhering organic matter, has not been used, the amide has an olive-brown or sometimes a pink shade. When prepared in quantity in an iron retort, it is also white and pure.

Composition.—The composition of sodamide was determined approximately by Beilstein and Geuther, who analysed a sample prepared in glass flasks, by decomposing it with hydrochloric acid and determining the relative amounts of sodium chloride and ammonium chloride formed. In this way, they did not obtain the percentage of sodium, as a known weight of the amide was not taken, but found the ratio Na : N to be as 26 : 14; that is approximately 1 atom to 1 atom; whence they deduced the formula $NaNH_2$.

As a more trustworthy means of ascertaining its composition, two synthetical methods were adopted, the results thus obtained confirming the generally accepted formula. The first of these consisted in determining the weight of amide formed from a known weight of sodium; whilst the second consisted in obtaining the ratios between the increase in weight on converting sodium into sodamide, and the weight of hydrogen liberated from the ammonia.

In the first series of syntheses the apparatus used consisted of a short, light piece of hard glass tubing, 6 inches in length, fitted with new rubber stoppers, through each of which a stopcock passed. The lower half of the glass tube was lined with platinum foil, on which the silver or platinum boat rested. The whole was first weighed full of gaseous ammonia, noting the temperature and barometric pressure. A piece of clean sodium was then introduced during the passage of a rapid current of the gas. After turning off the taps simultaneously and disconnecting from the ammonia supply, a second weighing was taken. Finally, the sodium was converted into amide by heating at nearly 300° in a steady current of ammonia. In less than an hour the conversion was complete, and when cold the apparatus was weighed; corrections were made for the amount of ammonia filling the tube. The results of two experiments were as follows:—

Weight of sodium taken.	Weight of sodamide formed.	Percentage of sodium.
0·1831 gram	0·3114 gram	58·80
0·1370 ,,	0·2334 ,,	58·70
	Mean	58·75
	Theory for $NaNH_2$	58·97

In the second series of experiments the exit end of the tube was connected to a Schiff's nitrometer, filled with hydrochloric acid and provided with a mercury trap, so that all the hydrogen liberated from the ammonia by the sodium was collected, the ammonia being absorbed. The experiment was conducted as before, weighing the tube with fittings and sodium, and the tube with fittings and sodamide.

In the interaction $2Na + 2NH_3 = 2NaNH_2 + H_2$, the ratio between the increase of weight of the sodium and the weight of hydrogen evolved is $NH_2 : H$ or $16 : 1$.

If $4Na + 2NH_3 = 2Na_2NH + 2H_2$, the ratio would be $NH : H_2$ or $15 : 2 = 7·5 : 1$.

If $6Na + 2NH_3 = 2Na_3N + 3H_2$ the ratio would be $N : H_3$ or $14 : 3 = 4·6 : 1$.

We thus have an accurate means of determining whether the sodium is wholly converted into $NaNH_2$ or partly also into Na_2NH and Na_3N.

The results obtained were as follows:—

Increase in weight.	Weight of hydrogen evolved.		Ratio of Increase : H.
0·1283 gram	0·081600 gram	=	16·00 : 1
0·0964 "	0·060032 "	=	16·05 : 1
0·1280 "	0·081063 "	=	15·92 : 1
	Mean.............		15·99 : 1

Theory for

$2Na + 2NH_3 = 2NaNH_2 + H_2$...... 16·00 : 1

The product is therefore entirely monosodamide.

Amongst the properties of sodamide not hitherto described its melting point is of interest, but as it is at once decomposed by the moisture in the air, the determination of its melting point is somewhat difficult. A small quantity was introduced into a fine capillary tube, either in the form of a fine powder ground under benzene, or whilst melted in a silver boat in a rapid current of ammonia. After sealing off each end, the melting point was observed in the usual way. It softened like wax at 149°, and was completely melted at 155°, forming a colourless liquid which set to a crystalline mass on cooling.

If, in preparing sodamide by passing ammonia over sodium contained in a boat, the temperature be kept at 400°, a quantity sublimes and is deposited, if passed through a narrow tube, as a feathery, white powder. When gently warmed, this powder melts, and on cooling crystallises on the interior of the tube in beautiful, transparent needles. Joannis has previously observed this crystalline form of the amide when produced in the spontaneous decomposition of sodammonium (*Compt. Rend.*, **112**, 392).

Experiments disproving the Existence of the alleged Nitride of Sodium and of Disodimide.—The decomposition of sodamide on heating is of interest, as several mis-statements have been made on this point in some of the more important treatises on chemistry. Gay Lussac and Thénard (*Recherches Physico-chimiques*, **1**, p. 354) state that when heated strongly in a glass tube, it behaves like potassamide, yielding a dark, infusible mass; this is described in the text-books as sodium nitride, the equation for its formation being written

$$3NaNH_2 = Na_3N + 2NH_3.$$

When not in contact with substances such as glass, which decompose it, sodamide behaves differently; at a little above its melting point, it becomes pale green, the depth of tint increasing as the temperature is raised, but on cooling it again becomes colourless. At 400°, it begins to volatilise, at the same time decomposing slightly, and condenses as a pale green liquid, which solidifies to a white mass on cooling. At a red heat, it distils more rapidly and decomposes into its elements, sodium, hydrogen, and nitrogen, although a certain quantity escapes decomposition by volatilising and condensing on the cool upper portion of the tube.

With the object of examining the behaviour of sodamide when heated alone, it was subjected to various temperatures in a vacuum. The amide, 0·4 gram, was prepared in a platinum boat placed in a short platinum-lined tube, drawn out at one end, and provided with a tap at the other; this end was subsequently sealed off, whilst the drawn-out end was bent at an obtuse angle, and connected with a Sprengel pump provided with a mercury trough and graduated tube for collecting the evolved gases. To prevent access of air, the joint between the tube and pump was immersed in mercury. The heating was very gentle at first, being applied by means of a spirit lamp held three inches below the tube. No change occurred beyond melting, but on heating to about 200° the sodamide commenced to distil slowly on to the upper surface of the tube, as an almost colourless liquid with a faint greenish tinge. At a higher temperature, it distilled more rapidly, and gas was evolved in small quantity, owing, as later experiments have shown, to the action of the distilled product on the glass. At 300—400° the liquid in the boat was dark green and apparently unchanged, but at 500—600° gas was evolved much more rapidly owing to the decomposition of the amide. Sodium was one of the products of decomposition, volatilising and collecting as a sublimate at the end of the tube. After keeping at this temperature during nearly an hour, the heating was discontinued and the products examined. The tube cracked into splinters on cooling, and was dark brown in places, like glass which has been strongly heated with sodium, the coloration being due to silicon. Some undecomposed amide had volatilised to the cooler parts of the tube, and also a quantity of sodium as lustrous globules. There was no residue in the boat, which was left clean, neither was there any other indication of the formation of sodium nitride. The gas evolved amounted to 81 c.c. at 0° and 760 mm., and consisted of 47·6 c.c. of hydrogen and 33·4 c.c. of nitrogen.

It is thus obvious that on heating sodamide to redness it decomposes into its elements, and not, as previously stated, into sodium nitride and ammonia. The ratio of nitrogen to hydrogen is not 1 : 2 as might be expected ($2NaNH_2 = 2Na + N_2 + 2H_2$), the deficiency of hydrogen being very probably due to the reducing action of the gas on the glass, and also to some extent to its absorption by the metallic sodium.

At a temperature approaching dull redness the amount of decomposition is only very slight, whilst at 300—400° there is no decomposition whatever. In one experiment, a weighed quantity, 0·8791 gram, was prepared in a silver boat in a platinum-lined stopcock tube, and heated at various temperatures during known intervals of time. The experiment was conducted at the ordinary pressure in an atmosphere of purified dry hydrogen. On keeping the amide at a temperature of 300—350° for one hour, only 0·8 c.c. of gas was evolved, the sodamide remaining unchanged. Even when heated at 450° the decomposition was scarcely appreciable, gas being evolved extremely slowly, in an hour only 8·1 c.c. being given off; the gas consisted chiefly of ammonia, with a little hydrogen and nitrogen. This small amount of gas, which corresponds to a decomposition of only 0·09 per cent., was derived partly from the action of the small quantity of sodamide which had volatilised on to the upper surface of the tube, on the silica of the glass which was rendered brown (*vide* action of sodamide on silica).

At still higher temperatures, the decomposition and distillation take place more rapidly, the result being the same as that obtained in a vacuum. It is therefore possible to compare the decomposition of sodamide with that of ammonia, which is split up only very slowly at a red heat, except in the presence of substances which favour its decomposition, such as porous materials, porcelain, &c., but at higher temperatures decomposes into its elements more readily.

An interesting result is obtained on heating sodamide to dull redness in a boat contained in a hard glass tube, through which a current of ammonia is passing; the latter is continuously decomposed into its elements. At this comparatively low temperature, the amide is split up into nitrogen, hydrogen, and sodium, and the latter in presence of the ammonia re-forms sodamide, which is again split up. In this way an indefinite quantity of ammonia may be decomposed by a small quantity of amide; thus 0·4 gram of sodamide in the course of an hour or two gave nearly half a litre of the mixture of nitrogen and hydrogen, without showing any indication of loss of activity. The amide at the end of the experiment had mostly volatilised unchanged on to the cool upper surface of the tube.

Although neither disodimide, Na_2NH, nor sodium nitride could be obtained by the action of heat on sodamide, it appeared of interest to try whether by the further action of sodium on sodamide another atom of sodium could be introduced.

When a piece of sodium is half converted into the amide, and the mixture is then heated in a current of some indifferent gas, such as hydrogen, the sodamide in contact with the sodium becomes darker and darker blue as the temperature is raised, and if kept at 300—400° for about half an hour, the whole is converted into a dark Prussian-blue, almost black, mass. Although some of the sodium disappears in this way, it remains partly unchanged. On cooling, the thick blue mass turns grey and opaque, but on heating it regains its beautiful colour. When heated in ammonia, it quickly loses its blue tint, being converted into sodamide.

Thinking it probable that the blue compound consisted of disodimide, quantitative experiments were made to ascertain if hydrogen is evolved during its formation, for if it is simply a solution of sodium in the amide, no hydrogen would be evolved.

The method of procedure consisted in partially converting a known weight of sodium into amide, and heating the remaining sodium—the weight of which was ascertained by calculation—with the sodamide. Experiments were made under a variety of conditions, both in a vacuum and in atmospheres of hydrogen and nitrogen, but the results were negative; only a small quantity of gas was given off, but this corresponded to what would be obtained if sodamide alone were subjected to similar conditions. The sodium did not entirely disappear unless considerably more than the equivalent of amide was allowed to act on it. It is thus evident that there is no formation of an imide of sodium. The mixture behaves like sodamide, its properties being modified only in accordance with the quantity of sodium taken up; but it takes fire more readily than sodamide when heated in the air. When heated to about 300° in a vacuum, it distils as a beautiful dark blue liquid, changing to a grey solid on cooling. It is probably analogous to the sodammonium $(NaNH_3)_2$, which Joannis, (*Compt. rend.*, **115**, 820—823) has shown is contained in the dark blue solution formed by dissolving sodium in liquid ammonia. It is, therefore, possible that the solution of sodium in the mono-substitution derivative of ammonia, $NaNH_2$, contains a compound,

$$(Na{\cdot}NaNH_2)_2 \text{ or } Na_2H_2N{\cdot}NH_2Na_2,$$

that is, disodammonium, but as yet no further experiments have been made to ascertain if this compound is formed.

Potassium behaves in exactly the same way when heated with potassamide, forming a similar beautiful dark blue product, but with even greater ease. It may always be noticed during the conversion of potassium into the amide if the supply of ammonia be deficient. As soon, however, as a rapid current is passed over the heated mass it is at once decolorised, forming potassamide.

Action of Ammonia on Sodium Oxide.—Thinking it possible that ammonia and sodium monoxide might interact to form disodimide according to the equation

$$Na_2O + H_2NH = Na_2NH + H_2O,$$

experiments were made to ascertain if this was the case.

When ammonia is passed over gently heated sodium oxide, a violent action takes place, accompanied by incandescence, the solid quickly fusing to a frothing mass; and if the temperature is kept at 200—300°, nothing remains but sodium hydroxide. If, however, the heating be discontinued immediately the mass has commenced to grow incandescent, and the whole quickly cooled, a white semifused product remains, which, on examination, is found to consist of a mixture of sodamide and sodium hydroxide, there being nothing to point to the existence of a substituted ammonia other than sodamide. The change may be expressed thus—

$$Na_2O + 2NH_3 = 2NaNH_2 + H_2O.$$

The water at once decomposes the amide, forming sodium hydrate and ammonia, unless the action is stopped at once, in which case the secondary decomposition is only partial.

Lastly, with the view of preparing sodium nitride, it appeared interesting to try if sodamide and sodium monoxide would interact.

Several experiments were made in which the two were heated together under varying conditions, but in all cases with negative results. The two merely fuse and mix together, but it is possible, by heating strongly, to distil off the unaltered amide from the sodium oxide.

Potassamide.

This has been previously described by Gay Lussac, Davy, and Baumert and Landolt (*Annalen*, **111**, 1); it is very similar to sodamide. Baumert and Landolt, who prepared it in small glass flasks, analysed it, and deduced the formula KNH_2. Their results were approximately accurate, and agree with my determination of its composition by synthesis. This method, which was precisely similar to that used in the case of sodamide, did not give as good results, owing to the difficulty of getting a piece of potassium into the boat without the surface undergoing slight oxidation. The results of two experiments were as follows.

Weight of potassium taken.	Weight of potassium amide formed.	Percentage of potassium.
0·4160 gram	0·5826 gram	71·41
0·1680 „	0·2345 „	71·63
	Mean	71·52
Theory for KNH_2		70·96

Potassamide has hitherto been described as dark olive-green or brown, and Davy says that it is "in colour and lustre not unlike protoxide of iron." When prepared pure, however, in a silver boat, it is white and of a waxy appearance; on heating, it melts to a nearly colourless liquid of a faint greenish tinge, which, as in the case of sodamide, increases in depth as the temperature is raised. It resembles sodamide very closely in many of its physical and chemical properties. Its formation from the metal by the action of ammonia is very much more rapid than that of its sodium analogue, whilst its action on hard glass is considerably less marked; so much so, that it is possible to make several preparations of about 10 grams of the substance in the same flask. Thus prepared, however, it is contaminated with a small quantity of potassium silicate.

Potassamide is softer and less brittle than sodamide, and melts at a considerably higher temperature, namely, 270—272°; it begins to soften like wax a few degrees below this. It may be obtained in several forms, such as massive crystalline lumps, feathery powder (deposited as a sublimate in its ordinary method of preparation when the temperature is kept at 400°), or as a fine white powder by grinding under benzene, and drying in any indifferent gas, such as dry air. It is decomposed rapidly in presence of moist air, forming potassium hydroxide and ammonia; carbon dioxide also quickly decomposes it (*vide* action of inorganic oxides).

Experiments disproving the alleged Existence of the Nitride of Potassium.—In 1808, Humphry Davy, while carrying out an investigation on the composition of ammonia and its action on potassium, was led to examine the "fusible substance," potassamide, thus obtained. He describes experiments on the behaviour of the amide on heating, and states that when the temperature is raised to dull redness, it yields a black, infusible substance, which, in all the more important treatises and dictionaries of chemistry, is described as potassium nitride, K_3N. As the present investigation points conclusively to the non-existence of this substance, it will be necessary to briefly recapitulate the details of some of Davy's experiments as well as those of Gay Lussac and Thenard (*Recherches Physico-chimiques*, **1**, 337—356), which were also carried out with the view of ascertaining the effect of heat on potassamide. Gay Lussac and Thénard considered the "green material" (potassamide) to be a combination of ammonia and potassium nitride, and state that when heated to redness it gives up the former constituent, leaving a black residue. In their experiments, the amide was prepared by heating a pellet of potassium in a glass tube bent at the upper end and filled with ammonia, the whole being placed in a mercury trough; but the ammonia was not dry, and the amide was impure. The tube containing the potassamide was filled with mercury, which was afterwards displaced by hydrogen, and "la matiere verte-olivâtre" heated to dull redness in contact with the glass. Much gas was evolved, and the amide frothed up and finally solidified, leaving a greyish-black infusible substance. "Dans tous les cas, après la calcination la matière étoit noirâtre, et avoit perdu la propriété de se fondre." The evolved gases varied very much both in quantity and composition, and consisted of ammonia, nitrogen, and hydrogen, of which the two latter were in the ratio in which they exist in ammonia, namely, 1 : 3. This remarkable result led them to believe that the green material had given up its ammonia, part of which had been decomposed into its elements by the high temperature, which varied from that of a dull red to an ordinary red heat. The error is obvious, when it is remembered that ammonia undergoes no appreciable decomposition at this temperature. According to Ramsay and Young (Trans., 1884, **45**, 88) the extent to which ammonia is decomposed at a red heat, even in the presence of such substances as iron and broken porcelain, which assist the decomposition considerably, is only 1—5 per cent., whilst in an ordinary plain glass combustion tube it is only 0·24 per cent. at 780°.

Humphry Davy, in 1808, controverted the opinion of the two French chemists regarding the behaviour of potassamide on heating, and proved that the amount of ammonia evolved varied with the extent to which precautions had been taken to dry the materials used; and that, if moisture were excluded, the amount of ammonia which could be generated by the action of heat was only one-tenth of that originally absorbed by the potassium to form the amide. He further showed that nitrogen and hydrogen were the chief gases evolved, the relative amounts of which never reached the ratio 1 : 3, that observed by Gay Lussac and Thénard.

In one experiment, the amide was heated to redness in a green glass retort filled with hydrogen, and the evolved gas collected and analysed. He says: "When the retort containing the fusible substance is exhausted, filled with hidrogen and exhausted a second time, and heat gradually applied, the substance soon fuses, effervesces, and, as the heat increases, gives off a considerable quantity of elastic fluid, and becomes at length, when the temperature approaches nearly to dull redness, a dark gray solid, which by a continuance of this degree of heat does not undergo any alteration." A considerable quantity of gas was evolved, containing ammonia, though it consisted chiefly of a mixture of nitrogen and hydrogen in the ratio of about 1 : 2·5. The dark grey solid or "black residuum" which has always been regarded as potassium nitride, K_3N, was described by Davy as a brittle, opaque powder, which sometimes took fire in the air, and was violently acted on by water, giving hydrogen and ammonia. He considered it to be a "combination of a suboxide of potassium and nitrogen," thinking that ammonia probably contained some oxygen. The equation for its formation is always written

$$3KNH_2 = K_3N + 2NH_3.$$

With the object of examining the behaviour of potassamide when heated to various temperatures out of contact with bodies that decompose it, and, if possible, of preparing the supposed nitride, I have made a series of experiments similar to those with sodamide, the results showing that the nitride does not exist. On the contrary, potassamide at a dull red heat is a comparatively stable substance, decomposing only very slowly directly into its elements, and not into ammonia and potassium nitride. This decomposition increases considerably when the temperature is raised, and varies with the length of time during which the substance is heated, in this resembling ammonia whose decomposition is a function of temperature and time. The results of three experiments are tabulated below. Of these, the first was similar in principle to Davy's, in which potassamide was heated in a vacuum. In the second, the heating, which was sustained for several hours, was conducted in an unglazed porcelain boat, in an atmosphere of nitrogen at the ordinary pressure, the evolved gases being collected in nitrometers filled with dry mercury placed at either side of the tube containing the boat. As far as the gaseous products are concerned, the results of these two experiments are somewhat similar to Davy's; but in no stage of the heating was there any indication whatever of the formation of a black solid such as he describes.

The porcelain was considerably attacked at about 350—400°, and it was found that the residue in the boat at the conclusion of the experiment consisted mainly of potassium silicate and aluminate, if the heating had been continued for several hours. This remarkable result led to the investigation of the action of the amides on silica and alumina, the results of which throw considerable light on the nature of the decomposition which occurred in the experiments of Davy, and of Gay Lussac and Thénard. The behaviour of the amides with silica is described later, but, as it has a direct bearing on the results given in the following table, it is necessary to state here that the action gives rise to the evolution of a large quantity of ammonia; and alumina acts somewhat similarly, though it occasions the evolution of nitrogen and hydrogen also, as will be seen from Experiment *c*.

It will be obvious, from a comparison of Experiments *a*, *b*, and *c* with *d*, that the evolution of gas at a temperature of 350° is entirely due to the action of the material in contact with the amide, and not to the decomposition of the amide by heat alone. At higher temperatures, also, most of the gas originates in the action occurring between the amide and the alumina or silica, although it is partly due to the simple decomposition of the amide into its elements. When potassamide and alumina are heated together, they readily interact, the amide apparently exerting a reducing action, although,

Weight of potassamide.	Time of heating.	Total gas evolved N. T. P.	Ammonia.	Nitrogen.	Hydrogen.	Loss in weight.	Temperature.	Conditions.
grams.	hours.	c.c.	c.c.	c.c.	c.c.	per cent.	C°.	
(*a.*) 0·2345	1·5	35·6	26·64	8·96		11·37	350	Porcelain boat; in a vacuum.
(*b.*) 0·4620	2·5	142·5	13·3	44·9	81·3	16·03	350—500	Porcelain boat; in an atmosphere of nitrogen.
(*c.*) 0·7758 (Heated with Al_2O_3)	1	80·0	65·0	15·0	5·0	20·48	300	Silver boat; in an atmosphere of hydrogen.
	2	142·0	51·2	37·4	53·4		450	
	Total..	222·0	116·2	52·4	58·4			
(*d.*) 0·5825	0·5	0	0	0	0	0	350	Silver boat; alone, in an atmosphere of hydrogen.
	0·5	27·0	10·6	13·4	3 0	4·2	500	

as yet, there has been no evidence of the formation of the lower oxide, AlO, described by Clemens Winkler as being formed on reducing alumina by magnesium (*Ber.*, **23**., 780—787).

The true behaviour of potassamide on heating may be readily ascertained by using a silver boat. It will be seen from Experiment *d* that no decomposition occurs at 350°. The amide melts like wax to a greenish-blue, transparent liquid which commences to volatilise very slowly about 400°. It mostly condenses as a fine mist consisting of minute greenish drops, in the region immediately above the boat, a little condensing as a nearly colourless liquid on the cool surface of the glass. At 500°, the amount distilling increases considerably, and the amide remaining in the boat during the distillation at this temperature forms a dark, very mobile liquid, which, if the heating be discontinued, sets quite unchanged to a colourless solid. In Experiment *d*, more than a third of the gas evolved (10·6 c.c. ammonia) arose from the distilled portion of the amide acting slowly on the glass, which was kept as cool as possible in order to reduce the action. The total loss in weight of the amide was only 4·2 per cent.; the amount of nitrogen given off, representing as it does the actual decomposition of the amide alone, amounted to 2·8 per cent. only, at this temperature. At a full red heat, the amide distils rapidly, partially decomposing into its elements, the potassium being deposited in the cool parts of the tube as a mirror. Nitrogen and hydrogen are evolved, approximately in the ratio of 1 : 2, together with some ammonia formed by the action of the volatilised amide on the glass. Even at this temperature, when distillation and decomposition are rapidly taking place, the amide remaining in the silver boat forms a quiescent, very mobile liquid. In one experiment, after heating for 20 minutes, a small quantity was left in the boat and, when cool, had the form of a colourless, glassy solid, not unlike fused borax. This consisted entirely of potassamide; and in no stage of the heating was there ever the slightest evidence of the formation of any infusible black solid, as described by the earlier investigators, this substance no doubt arising from the impurities in the amide used and from contact with materials which decompose it. It is probable that the potassium employed in its preparation contained small quantities of organic matter, which invariably renders the amide black, and it is likely that Davy's "black residuum," which, he stated, gave hydrogen and ammonia with water, consisted essentially of a mixture of potassamide, potassium oxide, and potassium, together with charred organic matter; for he found that on heating to cherry redness in a platinum tube, potassium sublimed as a mirror, leaving caustic potash.*

---

* Davy considered this evidence of the existence of oxygen in ammonia.

As further showing the stability of potassamide at a dull red heat, it is interesting to note that it may be completely distilled in a current of hydrogen without undergoing decomposition. The experiment may be conducted in a silver boat in which the amide is kept at 400—500°, while a rapid current of the gas is passed through the tube. It distils entirely, and condenses as a bluish-green liquid, which, on cooling, changes to a pearly-white solid, a small portion being deposited as a white sublimate on the cooler portions of the tube.

Although potassium nitride is not formed by heating potassamide, it appeared of interest to try whether it would be formed by the action of the latter on potassium oxide. Experiments were made under a variety of conditions in which the oxide and amide were heated together in molecular proportion. No action whatever took place, and it was found possible to distil the amide unchanged from the mixture at high temperatures.

As potassium nitride is not formed by the direct action of nitrogen on potassium at high temperatures, as Gay Lussac and Thénard have shown, and taking into account the above results, it may justly be considered that the compound does not exist.

Lithamide.

As sodium and potassium readily yield amides when heated in ammonia, lithium, which is closely related to both these metals, would *à priori* be expected to behave similarly, but no experiments with this metal have been recorded. When dry ammonia is led over a bright surface of metallic lithium, the lithium loses its lustre and becomes coated with a bluish-white crust, on which excrescences of a gold colour appear in places; and until the temperature is sufficiently high to melt this crust, and allow it to flow off and expose the metallic surface, little conversion into amide takes place.

When lithium is very gently heated during the passage of a steady current of ammonia, it melts, and is at the same time violently attacked by the gas, swelling up considerably and glowing; so complete is the decomposition of the ammonia, that when a rapid current is passed over only 0·25—0·3 gram of lithium, the hydrogen which is evolved is nearly free from ammonia, and may be burnt at the exit tube. After the lapse of a few minutes, however, the violence of the action quickly diminishes, and if the temperature be not raised considerably, the action will stop altogether, owing to the fact that the amide has a high melting point and consequently solidifies over the metal, protecting it from further change. It is, therefore, necessary to keep the temperature at about 400°, so that the amide remains fused; in this way the whole of the lithium may be converted into amide, though the last globule disappears very slowly. During the formation of the lithamide, a small quantity is volatilised and deposited along the tube as a very finely divided, white powder, similar in appearance to sublimed sodamide or potassamide.

On removing the flame when the conversion is complete, the contents of the boat quickly solidify, forming a beautifully crystalline mass, long, transparent, colourless needles shooting across the silver boat. In mass, lithamide is pure white, though it is darkened by heating with very slight traces of organic matter. When fused, it has a very light greenish tinge, but on cooling it again becomes white. It differs from both its analogues in several respects, notably in its more marked crystalline nature and absence of waxy appearance, and in its much higher melting point, which lies between 380° and 400°. It decomposes comparatively slowly in the air, and when a crystal is placed in cold water it slowly dissolves without any energetic action taking place, forming an alkaline solution; when dropped into hot water, however, it effervesces, giving off ammonia and forming lithium hydrate. Hydrochloric acid decomposes it scarcely more rapidly than water, lithium chloride and ammonium chloride being formed. When a crystal of lithamide is moistened with a drop of strong hydrochloric acid, it slowly disappears, giving off ammonia; this partly escapes in the gaseous condition, forming a small cloud of ammonium chloride with the acid vapour. Lithamide dissolves with difficulty in absolute alcohol, being decomposed as by water, but if boiled with the alcohol, it is decomposed more quickly, giving off ammonia. These properties of lithamide are very interesting when compared with those of its analogues, both of which are violently decomposed by acids, water, and alcohol. Further, when heated strongly in the air, unlike sodamide and potassamide, it does not take fire, although it is rapidly decomposed. When heated strongly in contact with glass, some of it sublimes, partly as a white powder and partly as beautiful crystals, whilst the remainder attacks the glass, giving off ammonia and forming lithium silicate. The experiment has not yet been conducted quantitatively. When heated strongly in a silver boat, in an atmosphere of hydrogen, it decomposes but slightly and volatilises very slowly, being deposited as a fine, white powder on the cooler portions of the tube. Even when kept at a full red heat for 20 minutes, a considerable portion remains in the boat unaltered.

Composition.—This has been determined by synthesis and by analysis. In the former case, the method employed was precisely similar to that adopted for sodamide and potassamide. Owing to the violence of the action at first, and to the comparatively high temperature at which it was necessary to keep the contents of the boat during the formation of the amide, a small quantity was lost by volatilisation. This renders the percentage of lithium higher than it should be, but the result of the following experiment is sufficient to show that the composition of lithamide corresponds to formula $LiNH_2$.

Weight of lithium taken.	Weight of amide formed.	Percentage of lithium.
0·2410 gram	0·7382 gram	32·6
	Theory for $LiNH_2$	30·4

It is unlike its analogues, inasmuch as a more accurate result may be obtained by analysis. The method used consisted in decomposing a known weight with water in a flask, and distilling off the ammonia, which was then determined in the usual way. The lithium hydrate remaining was then determined, (1) volumetrically by titration with standard acid, and (2) by weighing as lithium sulphate after ignition in a platinum dish. The results were as follows:—

Weight of lithamide.	Nitrogen found.		Lithium found.
0·5305 gram	0·3197 gram ..	(1)	0·1626 gram
		(2)	0·1638 ,,
	Mean........		0·1632 ,,

Found—

		Theory for $LiNH_2$.
Lithium	30·76 per cent.	30·43 per cent.
Nitrogen	60·26 ,,	60·87 ,,
Hydrogen (by diff.)...	8·98 ,,	8·70 ,,
	100·00 ,,	100·00 ,,

The behaviour of lithamide towards organic compounds is similar to that of sodamide and potassamide, complex organic matter being readily charred, but the action is less marked, as might be expected from its greater stability (see p. 521).

Action of Sodamide and Potassamide on Inorganic Oxides.

In all my previous experiments, I had observed that glass was much attacked by these compounds, even when they were not heated much beyond their melting point; moreover, that during the corrosion effervescence occurred, due to the evolution of a gas which consisted chiefly of ammonia. This showed that the oxygen of one or more of the constituents of the glass had combined with the hydrogen of the amide, and in order to ascertain which of the oxides was acted on, a series of comparative experiments were made with the view of observing the volume of gas given off on heating known weights of the amides in a silver boat at various temperatures, during definite intervals of time, in an atmosphere of hydrogen (1) alone; (2) with lime; (3) with silica. In this way, it is possible to detect even a slow action by the evolution of ammonia attending it. Using pure (artificially prepared) lime, no action whatever occurred, even when the substances were heated together at 450° during an hour. The lime acts like a sponge, absorbing the melted amide and forming a mixture which is olive-green while hot, but becomes white on cooling. The amide in this mixture does not decompose readily on exposure to air; a sample which had been left for two days still effervesced on adding water, giving off ammonia, and forming sodium hydroxide and calcium hydroxide.

Silica and sodamide or potassamide interact very readily, evolving a large quantity of ammonia. Pure, amorphous silica, which had been ignited for several hours over the blast, was used in excess; the mixture froths up considerably as soon as the amide melts, most of the action being over after the first few minutes, though it is necessary to heat the mass to 300—400° for an hour before the change is approximately complete. At higher temperatures, nitrogen and hydrogen are slowly evolved, along with the ammonia resulting from the decomposition of the amide, this doubtless being assisted by contact with the heated silica. The product, which generally contains a little unchanged amide, is greyish white, and consists of silicate of sodium or potassium and silicon nitride. The latter, about which there is not much known, was obtained by this method as an amorphous, brown powder, which remained undissolved on lixiviating the mixture with water. It is not decomposed appreciably by boiling with caustic potash, but, on fusion with the latter, gives ammonia and potassium silicate. The composition and properties of silicon nitride, as prepared by this method, are still under investigation.

The interesting behaviour of the amides towards silica led to the investigation of their action on boric anhydride, the method of procedure being precisely similar to that adopted in the previous experiment, and similar results were obtained. The boric anhydride was fused and finely powdered in an agate mortar, and gently heated with the amides. As soon as the latter melted, the oxide was attacked, effervescence taking place, the action being so rapid that water condensed in the cool part of the tube. After a short time, however, the action proceeded more gently, ammonia being slowly evolved, together with a little nitrogen and hydrogen, when the temperature was raised to about 400°.

The solid product was greenish whilst hot, and white on cooling, and always contained a little unchanged amide, unless a considerable excess of the oxide was used. It consisted of sodium borate and boron nitride, the latter being left as an insoluble, light, flocculent, white powder on treating the mass with water; it was freed from traces of unchanged boric anhydride by boiling with dilute hydrochloric acid and washing. It exhibited the usual properties of boron nitride, and evolved ammonia on fusion with caustic potash. When fused with potassium carbonate, it yielded potassium cyanate and carbon dioxide. The equation for the formation of boron nitride by this method may be represented thus:

$$2NaNH_2 + B_2O_3 = 2BN + 2NaOH + H_2O.$$

Amongst the other oxides which act on the amides of sodium and potassium, the behaviour of alumina has been alluded to in connection with the decomposition which potassamide undergoes when heated in contact with glass and porcelain. The action of the oxides of carbon on sodamide has previously been investigated by Beilstein and Geuther (*Annalen*, **108**, 91), who found that carbon dioxide gave the sodium derivative of cyanamide, whilst carbon monoxide yielded sodium cyanide. I have repeated the former of these experiments, with similar results; ammonia is always formed by a secondary action occurring between the liberated water and the unchanged amide, and hence, in presence of excess of carbon dioxide, a sublimate of ammonium carbonate and carbamate is also formed, whilst the non-volatile solid product consists of sodium cyanamide and sodium carbonate.

Sundry Interactions with other Compounds.

The action of nitrosyl chloride is interesting. When a current of the pure gas is passed over cold sodamide or potassamide, no change is apparent, but, on warming very gently by means of a spirit lamp, a sudden action occurs, nitrogen being quickly evolved, whilst a small quantity of ammonium chloride is deposited in the tube; water is also formed, and condenses as large drops. The action is soon over, and the residue consists of potassium or sodium chloride; the primary action is, therefore, as follows:—

$$KNH_2 + NOCl = KCl + N_2 + H_2O.$$

The behaviour of the amides with organic haloïds is different from what might be expected. Experiments made with several haloïd derivatives under varying conditions show that the displacement of the halogen by the amido-group only takes place to a very small extent. Thus, when the vapour of ethylic iodide is passed over sodamide, no action occurs till the temperature rises to about 200°, when a somewhat violent decomposition takes place, the mass becomes carbonised, and vapours of iodine make their appearance, whilst the gaseous products consist of a little ammonia with traces of ethylamine; the solid residue consists chiefly of sodium iodide and carbon. Several experiments were also made with ethylenic bromide with similar results. In one case the vapour was passed over the heated amide, but only traces of a diamine were formed; in another experiment the amide, which had been finely powdered under absolute ether, was heated gently in a flask during three hours with an ethereal solution of ethylenic bromide. Only a very slight action had occurred, although a little ethylenediamine appeared to have been formed, but the quantity was far too small for analysis. Finally, the two were heated together in a sealed tube at 190° for 2½ hours. Considerable charring had occurred, and the solid matter consisted of potassium bromide, ammonium bromide, and charcoal. There was no unchanged amide, and the mixture had a distinct fishy smell, whilst some gas had been evolved during the action. The amount of diamine, or other amine formed was inappreciable, however.

Sodamide acts violently on nitrobenzene. No change occurs in the cold, but, if the two be gently warmed, a very energetic action takes place, the mass becoming incandescent and carbonised; phenyl isocyanide and other products are formed.

Hydrocarbons and organic bases, such as aniline, quinoline, &c., do not act on the amides; but the general behaviour of other organic compounds is to act violently, secondary decompositions occurring at the same time, which mar the results considerably. It is interesting to note that when complex organic matter is charred by the amides, sodium or potassium cyanide is found amongst the products of the decomposition.

The marked activity of the hydrogen of the NH_2 group of the metallic amides, as shown by the preparation of the nitrides of boron and silicon, affords a ready means of preparing inorganic nitrides, and I wish to reserve the investigation of these substances from this point of view. Moreover, many oxygenated organic compounds, such as ketones and aldehydes, interact readily with the amides, yielding interesting products, which are also under investigation.

In concluding this paper, I desire to express my thanks to Dr. Charles A. Kohn, at whose suggestion the work was commenced, for the interest he has taken in it throughout its progress; and also to Professor J. Campbell Brown, for the kindly advice he has at all times afforded me.

Chemical Laboratories,
University College, Liverpool.