

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY, AND UNIVERSITY OF CALIFORNIA RADIATION LABORATORY, LIVERMORE]

The Alkali Metal Salts of Arsine and their Ammoniates. The Reaction of Arsine with Alkali Metals and Alkali Metal Amides

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Sodium dihydrogen arsenide, NaAsH_2 , forms a diammoniate and a tetrammoniate. The equilibrium pressures of ammonia over the systems $\text{LiAsH}_2 \cdot 2\text{NH}_3$ – $\text{LiAsH}_2 \cdot 4\text{NH}_3$, NaAsH_2 – $\text{NaAsH}_2 \cdot 2\text{NH}_3$ and $\text{NaAsH}_2 \cdot 2\text{NH}_3$ – $\text{NaAsH}_2 \cdot 4\text{NH}_3$ have been determined as a function of temperature. The thermal decomposition of NaAsH_2 yields arsine, hydrogen and a residue of the approximate composition $\text{NaAs}_{0.60-0.70}$. An explanation is offered for the trends in stability and mode of decomposition for LiAsH_2 , NaAsH_2 and KAsH_2 . Reaction of arsine with alkali metals or sodium amide yields material of the approximate composition M_2AsH . The course of the reaction between arsine and lithium amide depends on the mole ratio of the reactants. The reaction proceeds in steps as the temperature is gradually raised.

Introduction

The hydrides of the heavy elements of Groups IV and V are much more unstable than those of the light elements of the same groups. Thus the heavier hydrides are more acidic, but the corresponding primary salts are unstable with respect to loss of hydrogen. For examples, NaSnH_3 readily loses hydrogen to form NaSn ,¹ and KAsH_2 , when heated, loses hydrogen to form "KAs."² Ammoniate formation seems to stabilize the salts.^{1,3,4} The purpose of this investigation was to characterize the alkali metal salts of arsine (and their ammoniates) and to see whether the salts could be prepared by the reaction of arsine with the pure alkali metals or alkali metal amides.

Results

Salts Prepared from Liquid Ammonia.—A liquid ammonia solution of the dihydrogen arsenide of lithium,⁴ sodium² or potassium² may be prepared by reaction of the appropriate alkali metal in liquid ammonia with arsine. Legoux⁴ isolated lithium dihydrogen arsenide as a tetrammoniate and as a diammoniate; removal of ammonia from the diammoniate at 0° resulted in decomposition to arsine, ammonia and lithium monohydrogen arsenide (Li_2AsH). Johnson and Pechukas² reported that potassium dihydrogen arsenide is stable at room temperature, and they found no evidence for ammoniate formation. They implied that sodium dihydrogen arsenide behaves similarly, but Albers and Schuler⁵ found that the latter salt darkens when kept at room temperature and suggested that it decomposes to trisodium arsenide.

This investigation showed that the sodium salt forms ammoniates at low temperatures and confirmed that the unammoniated salt is unstable at room temperature. The dissociation pressures of the ammoniates of the lithium and sodium salts were measured as a function of temperature and the thermal decomposition of all three salts was studied.

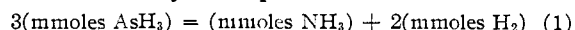
Reaction of Arsine with Alkali Metals.—Arsine reacts at room temperature with alkali metal films to form monohydrogen arsenides. In the cases of lithium and sodium, slight excesses of hydrogen are

evolved, probably corresponding to loss of hydrogen by the monohydrogen arsenides.

Reaction of Arsine with Amides of Sodium and Lithium.—The principal product from the reaction of arsine with excess sodium amide at room temperature is Na_2AsH , but the corresponding reaction with lithium amide is more complicated and will be discussed in some detail.

Arsine and lithium amide react vigorously at room temperature to form non-reproducible amounts of ammonia and hydrogen; thus it is clear that at least two different reactions take place. In addition to the observation of simple stoichiometric relations, the following techniques were employed to characterize the reactions: (1) the effect of the ratio of arsine to lithium amide on the products was noted; (2) the course of the reaction was followed as the temperature of the reaction vessel was raised gradually from low temperatures (*e.g.*, -60°) to high temperatures (*e.g.*, 90°); (3) in some cases, AsD_3 was employed and the gaseous products were analyzed for deuterium.

It was noted that, in the room temperature reaction with excess lithium amide, the millimoles of arsine reacted and the millimoles of ammonia and hydrogen formed may be related, within experimental error, by the expression



This information alone is insufficient to determine the reactions which take place. However, it will be noted that the reaction sequence described below (supported by other experimental data) is compatible with relation 1.

When arsine is allowed to react with excess lithium amide at -45° , the pressure in the reaction vessel gradually falls to a very small value (essentially zero) and remains at this low value as long as the temperature is held constant. Either of the following reactions is consistent with this observation.



It is believed that reaction 3 (or a similar reaction forming a lower ammoniate, such as a monoammoniate) takes place. For if ammonia is added to the products at -45° , there is no appreciable increase in pressure until the number of millimoles of ammonia added equals three times the original number of millimoles of arsine. It is presumed that, at this point, the lithium dihydrogen arsenide

(1) H. J. Emeléus and S. F. A. Kettle, *J. Chem. Soc.*, 2444 (1958).

(2) W. C. Johnson and A. Pechukas, *THIS JOURNAL*, **59**, 2068 (1937).

(3) C. A. Kraus and E. S. Carney, *ibid.*, **56**, 765 (1934).

(4) C. Legoux, *Bull. soc. chim.*, **7**, 549 (1940).

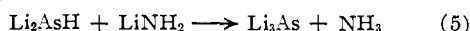
(5) H. Albers and W. Schuler, *Ber.*, **76B**, 23 (1943).

exists completely as the tetrammoniate. Beyond this point the pressure increases until a saturated solution of the products forms.

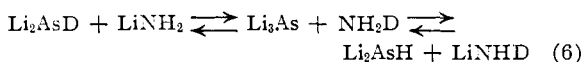
If, instead of adding ammonia, the reaction vessel is brought to room temperature, a complicated series of reactions takes place. The observed products are most easily explained by assuming that the lithium dihydrogen arsenide first reacts with lithium amide to form lithium monohydrogen arsenide



(For simplicity, the dihydrogen arsenide is written unammoniated.) It has not been possible to stop the reaction at this point, presumably because the lithium monohydrogen arsenide is very reactive when in intimate contact with lithium amide. Lithium monohydrogen arsenide, when alone, loses hydrogen at room temperature to form "Li₂As." In the present reaction, a small amount of the monohydrogen arsenide decomposes in this manner, but the remainder reacts as a protonic acid with lithium amide



It has been shown that, when AsD₃ reacts with LiNH₂, the evolved hydrogen contains large amounts of protium. This may be explained by assuming that reaction 5 is reversible, that is, proton-deuteron exchange may occur by a path such as



At temperatures in the neighborhood of -40°, excess arsine reacts with lithium amide according to equation 3. However, in order for the reaction to reach completion in a reasonable time, the temperature must be raised to 0°, and at this temperature the unammoniated dihydrogen arsenide and part of the diammoniate decompose to give both arsine and hydrogen. The principal net reaction at 0° is very approximately represented by equation 2. If the reaction products are subjected to a high vacuum at 0° or if they are warmed to room temperature, ammonia is released and all the dihydrogen arsenide decomposes to the monohydrogen arsenide. Finally, heating to *ca.* 300° yields a residue of "Li₂As."

Experimental

General.—All reactions were carried out in a conventional high vacuum line. Metal amides were prepared by the Fe₂O₃-catalyzed reaction between liquid ammonia and the metals. After evaporation of the ammonia, the samples were heated at 100° *in vacuo* for 15 minutes. The amount of amide was determined by measuring the evolved hydrogen. Deutero-arsine was prepared by the reaction of AsCl₃ with LiAlD₄ in ether solution.

Preparation of Dihydrogen Arsenides.—Liquid ammonia solutions of the dihydrogen arsenides were prepared by allowing excess arsine to react with ammonia solutions of the appropriate alkali metals. The evolved hydrogen was taken as a measure of the dihydrogen arsenide formed. Lithium was cut under benzene and quickly added to the reaction vessel. Sodium and potassium were freshly distilled into the reaction vessel. In some cases, sodium was electrolyzed into the reaction vessel.⁶

Lithium dihydrogen arsenide with approximately four ammonias of crystallization was prepared by allowing an ammonia solution to evaporate to near-dryness at -20°

and one atmosphere followed by 4 hr. of pumping at -78°. The sodium and potassium salts were prepared by pumping the ammonia from the solutions at *ca.* -20°.

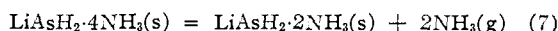
The LiAsH₂·4NH₃-LiAsH₂·2NH₃ Equilibrium.—Enough ammonia was removed from the tetrammoniate so that the empirical composition was LiAsH₂·3NH₃. The equilibrium ammonia pressures were then measured over the range -30 to +20°. The observed pressures agree (with an average deviation of 4%) with those calculated from the equation

$$\log P_{\text{mm.}} = 22.661 - \frac{2815}{T} - 4.530 \log T$$

From this equation one calculates

$$\begin{aligned} \Delta H_{298}^0 &= 20.4 \text{ kcal./mole} \\ \Delta S_{298}^0 &= 60 \text{ e.u.} \end{aligned}$$

for the reaction



The experimental data for the main experiment are presented in Table I. The data are numbered in the chronological order of observation. In another experiment, the dissociation pressure at 0° was found to be 20.9 ± 0.1 mm., in good agreement with the main experiment. Legoux⁴ reported a 0° dissociation pressure of 25 mm.

TABLE I

DISSOCIATION PRESSURE OF LiAsH₂·4NH₃

Observation	t, °C.	Pressure, mm.	
		Obsd.	Calcd.
12	-30.1	2.1	1.9
1	-23.7	3.1	3.3
2	-22.5	3.3	3.7
3	-18.6	4.7	5.1
4	-15.6	6.4	6.5
5	-12.2	8.3	8.5
6	- 8.8	10.6	11.0
13	- 6.0	13.0	13.5
14	- 2.0	17.1	18.1
9 ^a	0.0	21.2	20.9
10 ^a	.0	20.9	20.9
11 ^a	.0	21.0	20.9
22	.0	22.0	20.9
7	1.6	22.7	23.3
8	3.0	25.3	25.7
15	5.0	28.5	29.4
16	8.5	36.2	37.1
17	10.1	40.2	41.3
18	12.5	47.0	48.2
19	14.9	54.8	55.9
20	16.7	61.4	62.6
21	19.2	72.0	72.9

^a Vapor was removed after each of these measurements to remove any arsine which might have formed from thermal decomposition.

Thermal Decomposition of LiAsH₂·4NH₃.—The tetrammoniate was warmed to 0° and held at this temperature for 1 hr. while pumping the evolved gases through a liquid nitrogen trap with a Toepler pump. During this process the material turned from a pale yellow to a chocolate color. The material was then warmed to room temperature and held there for 45 hr., after which the evolved gases were pumped off and analyzed. The residue then was held at 90° for 1 hr. while pumping off the evolved gases. The empirical compositions of the solids, as calculated from the evolved gases, were as follows: after pumping at -78° 4 hr., LiAsH₂·3.78NH₃; after pumping at 0° 1 hr., Li₂As_{1.04}H_{1.08}·0.02NH₃; after standing at *ca.* 25° two days, Li₂As_{1.04}H_{0.87}; after pumping at 90° 1 hr., Li₂As_{1.03}H_{0.14}. The compound Li₂AsH was found to lose hydrogen even at 0°. Evidence was found for ammoniate formation, but quantitative measurements were prevented both by the decomposition and by extremely slow equilibration. The data extend the observations of Legoux by indicating that Li₂AsH is unstable at 0° and yet that temperatures greater than 90° are

(6) W. L. Jolly, *J. Phys. Chem.*, **62**, 629 (1958).

required in order to dehydrogenate it completely in a reasonable time.

The System NaAsH₂-NH₃.—Samples of NaAsH₂ were held at either -63.5° or -45.2° and measured amounts of ammonia were added and removed, allowing the systems to come to equilibrium between additions and removals of ammonia. When the observed pressures are plotted against the amounts of ammonia in the solid phases, two plateaus are observed, corresponding to a diammoniate and a tetrammoniate. The -63.5° isotherm indicates the existence of a 5.5- or 6-ammoniate, but the system was found to equilibrate extremely slowly in this composition range and this phase was not further characterized. The last traces of ammonia were very difficult to remove; it was necessary to warm the samples to room temperature in order to recover all the ammonia. The data for three runs are presented in Fig. 1.

The dissociation pressure of ammonia over a mixture of NaAsH₂ and NaAsH₂·2NH₃ was measured over the temperature range from -23 to -45°. The data are presented in Table II and may be represented by the equation

$$\log P_{\text{mm.}} = 9.90 - \frac{2120}{T}$$

From this equation one calculates

$$\Delta H^0 = 19.4 \text{ kcal./mole}$$

$$\Delta S^0 = 64 \text{ e.u.}$$

for the reaction

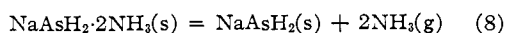


TABLE II
DISSOCIATION PRESSURE OF NaAsH₂·2NH₃

t, °C.	Pressure, mm.	
	Obsd.	Calcd.
-45.2	3.8	4.0
-44.5	4.8	4.3
-44.1	4.8	4.5
-43.5	5.3	4.7
-40.2	6.3	6.3
-38.2	7.8	7.6
-36.4	9.2	8.9
-31.5	13.6	13.5
-23.4	25.2	25.7

The dissociation pressure of ammonia over a mixture of NaAsH₂·2NH₃ and NaAsH₂·4NH₃ was measured over the temperature range from -67 to -36°. The data are presented in Table III and may be represented by the equation

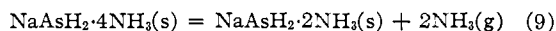
$$\log P_{\text{mm.}} = 22.193 - \frac{2330}{T} - 4.524 \log T$$

From this equation one calculates

$$\Delta H_{220}^0 = 17.4 \text{ kcal./mole}$$

$$\Delta S_{220}^0 = 62 \text{ e.u.}$$

for the reaction



Thermal Decomposition of NaAsH₂.—Unsolvated sodium dihydrogen arsenide is a white solid which may be kept at 0° indefinitely without decomposition. At room temperature it turns red-brown and both hydrogen and arsine are evolved slowly. Two samples after standing overnight at room temperature had empirical compositions NaAs_{0.93}H_{1.53} and NaAs_{0.96}H_{1.73}. When samples were heated for about 0.5 hr. at 90°, they darkened; the empirical compositions of the residues were consistently very close to NaAs_{0.96}H_{0.50}, but no significance is attached to this formula inasmuch as there was no evidence for stepwise loss of hydrogen when a sample was warmed gradually from room temperature to 120°. The material is completely dehydrogenated by heating to 250°, the empirical composition of the black residue usually falling within the range NaAs_{0.90-0.70}. Arsenic may be sublimed from the residue* by flaming. When samples were heated up *gradually* to 250°, no arsine evolution occurred above 90°.

The System KAsH₂-NH₃.—Potassium dihydrogen arsenide was prepared in liquid ammonia and the ammonia

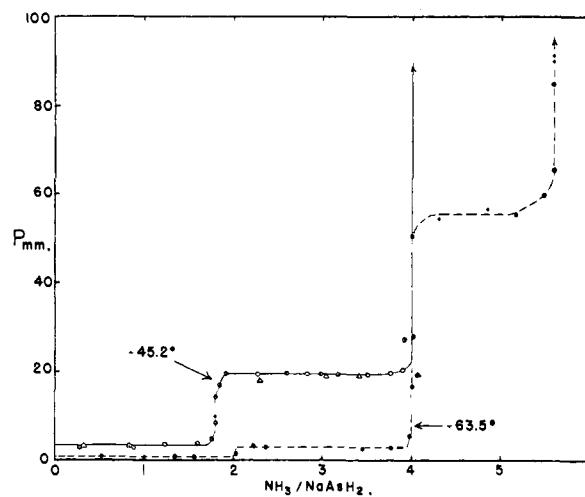


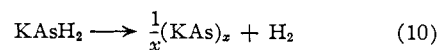
Fig. 1.

was then completely evaporated, leaving the unammoniated salt. In two different experiments, at -63.8° and -78.5°, measured amounts of ammonia were added stepwise to the salt. In both cases, the equilibrium pressures of ammonia over the condensed phases remained constant for several additions of ammonia and then increased *very slowly*. This behavior is explained by assuming that the unammoniated salt was in equilibrium with its saturated solutions. The non-existence of an ammoniate at these temperatures is further borne out by the observation that the molar ratios of ammonia to KAsH₂ in the condensed phase at the points where the pressures began to rise were different in the two experiments. These ratios and the equilibrium pressures were, at -63.8°: 3.5 and 32.6 mm.; at -78.5°: 4.5 and 9.4 mm.

TABLE III
DISSOCIATION PRESSURE OF NaAsH₂·4NH₃

t, °C.	Pressure, mm.	
	Obsd.	Calcd.
-67.4	2.4	2.5
-66.0	2.6	2.9
-64.3	3.5	3.5
-63.3	3.9	3.9
-62.0	4.6	4.4
-61.3	4.9	4.7
-60.5	5.4	5.1
-58.9	5.7	6.0
-54.9	8.9	8.5
-52.2	11.1	11.1
-45.6	19.8	19.6
-42.8	24.9	24.7
-41.8	26.0	26.8
-40.3	29.8	30.2
-39.1	33.4	33.2
-38.6	34.9	34.5
-36.8	41.5	39.7

Thermal Decomposition of KAsH₂.—Potassium dihydrogen arsenide is thermally stable up to about 80°. Hydrogen is evolved slowly at 90° and rapidly at 110°, but it was found necessary to apply a flame in order to carry the reaction to completion

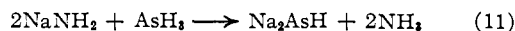


There was no evidence for stepwise loss of hydrogen or for evolution of arsine.

Reaction of AsH₃ with Li and Na.—Lithium metal was dispersed on glass wool by wetting the glass wool with a lithium-ammonia solution and then evaporating the ammonia. Sodium and potassium were distilled to form thin films on the reaction vessel wall. Although excesses of the

alkali metals were used, complete reaction of the arsine at room temperature was achieved only with potassium. From the amounts of arsine consumed and hydrogen evolved, the product compositions given were calculated: lithium: $\text{Li}_{2.13}\text{AsH}_{0.87}$; sodium: $\text{Na}_{1.93}\text{AsH}_{1.02}$, $\text{Na}_{2.12}\text{AsH}_{0.87}$, $\text{Na}_{2.13}\text{AsH}_{0.87}$; potassium: $\text{K}_{1.96}\text{AsH}_{1.04}$.

Reaction of Arsine with Excess Sodium Amide.—In a typical experiment, arsine (0.241 mmole) was allowed to react with sodium amide (4.3 mmoles) at room temperature for two days. Ammonia (0.452 mmole) and hydrogen (0.021 mmole) were evolved, corresponding closely to reaction 11.



The slightly low yield of ammonia may be explained by assuming that some of the intermediate NaAsH_2 decomposed with evolution of hydrogen.

Reaction of AsH_3 with Excess LiNH_2 .—In a series of experiments, arsine was allowed to react with lithium amide for several days, after which time the evolved ammonia and hydrogen were measured. Heating the solid reaction product to 90° caused no further hydrogen evolution and only a small amount of ammonia evolution. The results are summarized in Table IV. It will be noted that, in accord-

TABLE IV
REACTION OF AsH_3 WITH EXCESS LiNH_2
(Bracketted terms refer to millimoles)

Run	$\frac{[\text{LiNH}_2]_{\text{init.}}}{[\text{AsH}_3]}$	$[\text{NH}_3]$	$\frac{3[\text{AsH}_3] - 2[\text{H}_2]}{2[\text{H}_2]}$	$[\text{H}_2]$
1	3.8	3.06	3.15	0.265
2 ^a	5.1	1.73	1.71	.180
3 ^b	5.2	1.12	1.17	.235
4	7.0	1.425	1.477	.056
5	8.3	2.39	2.34	.219
6	15	0.902	0.860	.116
7 ^a	17	0.686	0.687	.059
8	32	1.131	1.147	.035
9	48	0.293	0.291	.039

^a AsD_3 used. ^b Added and removed NH_3 several times.

ance with relation 1, the entries in columns 3 and 4 are, within experimental error, equal. In runs 6 and 9, the pressure in the reaction vessel was followed as the temperature was allowed to rise gradually. These data are plotted in Fig. 2. The minima in the curves correspond to

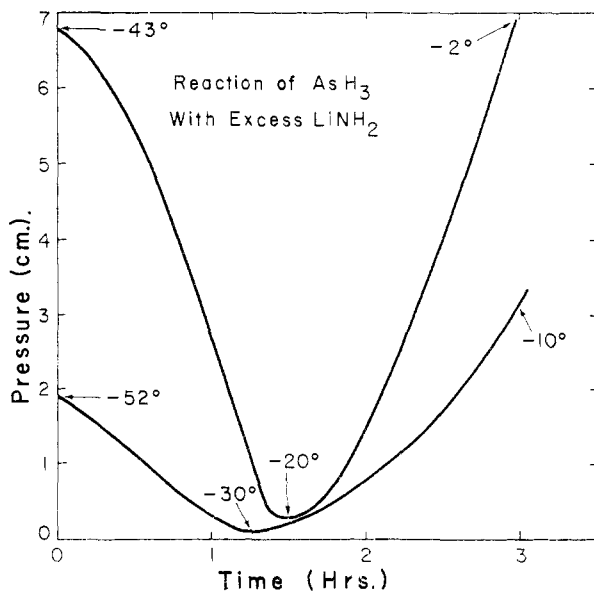


Fig. 2.

completion of reaction 3. In another experiment, the reaction vessel was held at -45° for 4.5 hr., at which time the pressure fell to a negligible value. Equilibrium pressures

were then measured after adding various amounts of ammonia to the system. In Fig. 3, the observed pressures are plotted as a function of the ratio of added ammonia (in the solid phase) to reacted arsine. It will be noted that the pressure rises abruptly when $\text{NH}_3/\text{AsH}_3 = 3$, corresponding to formation of $\text{LiAsH}_2 \cdot 4\text{NH}_3$.

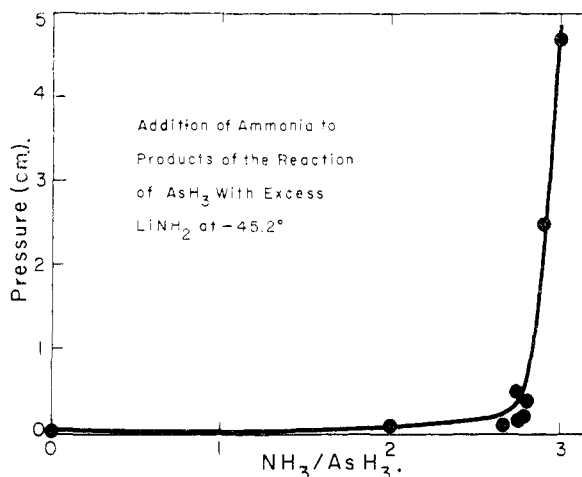


Fig. 3.

Reaction of LiNH_2 with Excess AsH_3 .—The experiments with excess arsine differ from those with excess lithium amide in that, in the former, the solid reaction product liberates hydrogen when heated above room temperature. The experimental results are summarized in Table V. It will be noted that, excepting run 10 (where the arsine was not really in excess), $[\text{LiNH}_2] \approx [\text{NH}_3]_{\text{total}} \approx 2[\text{AsH}_3]_{\text{reacted}}$. In run 14, the reaction mixture was allowed to gradually warm up from -35° to 0° over a period of 20 hr. and was then held at 0° for 6 hr. The reaction vessel was then cooled to -50° and 0.105 mmole of hydrogen, 0.772 mmole of arsine and 0.096 mmole of ammonia were pumped from the vessel. While holding at room temperature for 20 hr., 0.100 mmole of hydrogen, 0.251 mmole of arsine and 1.645 mmoles of ammonia were evolved. The empirical composition of the solid at this point was $\text{Li}_2\text{As}_{1.10}\text{H}_{1.08} \cdot 0.035\text{NH}_3$. After heating at 300° , the empirical composition was $\text{Li}_2\text{As}_{1.04}\text{H}_{0.02}$.

Reaction of AsD_3 with LiNH_2 .—The experimental data are summarized in Table VI. The hydrogen samples were analyzed for deuterium directly with a mass spectrometer. Arsine was pyrolyzed to the elements at 500° and ammonia was converted to uranium nitride and hydrogen by hot uranium; the hydrogen samples were then analyzed mass-spectrometrically.

Discussion

The decreasing tendency toward ammoniation on going from lithium dihydrogen arsenide to potassium dihydrogen arsenide parallels the observed trends of ammoniate stability for most other lithium, sodium and potassium salts.⁷ The observed entropies of dissociation of ammonia (about 31 e.u. per mole of ammonia) also agree closely with values found for most other ammoniates.^{7,8}

A distinct progression is apparent in the stabilities and modes of decomposition of the dihydrogen arsenides of lithium, sodium and potassium. Decomposition commences at 0° or lower for LiAsH_2 , at about 10° for NaAsH_2 and at 80° for KAsH_2 . The solid residues remaining after complete dehydrogenation of the salts are " Li_2As ," $\text{NaAs}_{0.60-0.70}$ and " KAs ."

(7) W. Biltz, *Z. anorg. Chem.*, **130**, 93 (1923).

(8) A. B. Hart and J. R. Partington, *J. Chem. Soc.*, 104 (1943).

TABLE V
REACTION OF EXCESS AsH_3 WITH LiNH_2
(Bracketted terms refer to millimoles)

Run	[AsH_3] (initial)	[AsH_3] (reacted)	[LiNH_2]	[NH_3]			[H_2]		
				~25°	~80°	~300°	~25°	~80°	~300°
10	2.41	2.41	8.7	2.943	0.024	...	0.175	0	...
11	2.335	2.335	4.65	4.52647	...	0.606
12	1.36	1.33	~2.4	2.332	0.054	0.032	.560	0.134	0.146
13 ^a	1.750	0.462	0.908	0.885	0.015092	0.090	...
14	2.000	0.920	1.772	1.741	...	0.030	.205	...	0.280

^a AsD_3 used.

TABLE VI
REACTION OF AsD_3 WITH LiNH_2

Run	AsH ₃	D/H ratios			
		H ₂ evolved at 25°	H ₂ evolved at 90°	NH ₃ evolved at 25°	NH ₃ evolved at 80°
2	24.0	0.53	..	0.53	0.19
7	5.85	0.83	..	0.38	0.16
13	24.0	2.10	2.15

The decreasing tendency toward elimination of arsine on going from the lithium salt to the potassium salt may be explained in terms of the increasing cation size. If we postulate that the mechanism of arsine evolution involves migration of a proton from one AsH_2^- ion to another, then we would expect this process to occur more readily when the AsH_2^- ions are next to smaller, more polarizing ions. The first step in the decomposition of LiAsH_2 is presumably



The proton may re-unite with the AsH^{-2} ion or it may unite with some other AsH_2^- ion to form arsine, which may escape. The stability of $\text{LiAsH}_2 \cdot 4\text{NH}_3$

at room temperature bears out this polarization concept. In this compound, the ammoniated lithium ion is relatively large and weakly polarizing; hence no decomposition of the AsH_2^- ion occurs.

The hydrogens in Li_2AsH , Na_2AsH and KAsH_2 have very little protonic character; therefore little or no arsine is evolved when these compounds are heated. Another type reaction takes place, probably involving hydrogen atom or hydride ion transfer. The behavior of NaAsH_2 is between that of LiAsH_2 and that of KAsH_2 . Arsine is lost until the remaining hydrogens have lost their protonic character; this occurs before the composition Na_2AsH is reached. However, the protonic character of the hydrogen in Li_2AsH is manifested in its implied reaction with lithium amide to form Li_3As . The corresponding sodium salt, Na_2AsH , does not react with sodium amide at room temperature.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Stability of Metal Chelates of 8-Quinolinol-5-sulfonate¹

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The interaction of Mn(II) , Co(II) , Ni(II) , Cu(II) , Zn(II) , Mg(II) , Fe(III) , $\text{UO}_2(\text{VI})$ and Th(IV) ions with 8-hydroxyquinoline-5-sulfonate has been investigated by potentiometric and spectrophotometric methods. Formation constants have been calculated for chelates containing 1:1, 2:1 and in some cases 3:1 and 4:1 ratios of ligand to metal ion. Comparison of these stability constants with those obtained for 8-quinolinol itself shows that the observed differences are essentially the result of the lower basicity of the sulfonated ligand. The hydrolytic behavior of Fe(III) , $\text{UO}_2(\text{VI})$ and Th(IV) chelates containing two unfilled coordination positions has been investigated quantitatively. The hydrolysis and olation tendencies of the 3:1 thorium and 2:1 uranyl and ferric chelates were found to follow the order $\text{Fe(III)} > \text{Th(IV)} > \text{UO}_2(\text{VI})$.

In view of the relatively high stabilities of the uranyl(VI) and thorium(IV) chelates of pyrocatechol-3,5-disulfonate (Tiron), it was decided to investigate the interaction of these and other metal ions with 8-quinolinol-5-sulfonate. Both of these ligands form five-membered rings with metals, the essential difference between the two being that the Tiron contains two phenolic groups as donors, while the latter ligand contains one phenolic group and one heterocyclic nitrogen atom. Both ligands would be expected to form chelates solubilized by sulfonate groups. The soluble 8-hydroxyquinoline-5-sulfonate is of further interest as a ligand

because of the well-known affinity of the parent compound, 8-hydroxyquinoline itself, for the thorium(IV) ion and for many other metal ions.

The stabilities of the chelate compounds formed by this ligand and some of the metals studied in the present investigation have been reported by Näsänen² and others³⁻⁵ for somewhat different reaction conditions. A more important difference between the present and previous work, however, is a study of the interactions between metal and ligand under conditions such that the maximum

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(2) R. Näsänen and E. Uisatalo, *Acta Chem. Scand.*, **8**, 112 (1954).

(3) A. Albert, *Biochem. J.*, **54**, 646 (1953).

(4) L. E. Maley and D. P. Mellor, *Austral. J. Sci. Res.*, **2**, A, 579 (1949).

(5) A. Albert and A. Hampton, *J. Chem. Soc.*, 505 (1954).