$E = 0.1758$ v. Combining this with the value $E = 0.3351$ obtained by Lewis, Brighton, and Sebastian[9] for the 0.1 N calomel electrode, we obtain the potential of the electrode, Ag/AgSCN, KSCN (0.1 m); $E_{298} = -0.1593$ v.

In order to calculate the characteristic "normal electrode potential," E^0, of the thiocyanate electrode, that is, the potential of the electrode when immersed in a solution of unit activity with respect to potassium thiocyanate, we use the relation

$$E = E^0 - RT/nF \ln 1/a_{KSCN}$$

Substituting numerical values, $E^0_{298} = -0.1593 + 0.05915 \log 1/0.081$, we obtain the value -0.0947 volt.

The above value of E^0 has been verified as follows. Using data from an entirely different set of cells, made up and measured at a time several months previous to the above determination, the following calculations were made. Consider the value of the e. m. f. of the concentration cell with amalgam electrodes, Ag/AgSCN, KSCN (0.01 m)/KHg$_x$-KHg$_x$/KSCN (0.10 m), AgSCN/Ag, which is given by the expression $E = 2RT/nF \ln (a_{0.1}/a_{0.01})$, while the potential of the theoretical cell without ion transference, Ag/AgSCN, KSCN (0.01 m)//KSCN (0.1 m), AgSCN/Ag, is/ $E = RT/nF \ln (a_{0.1}/a_{0.01})$. It is apparent that the e. m. f. of the latter cell should be half that of the preceding one, or $E = -0.0561$ v. Combining this with the potential of the 0.1 m potassium thiocyanate electrode, we have, Ag/AgSCN, KSCN (0.01 m)// OH_3^+ / H_2, and making numerical substitutions, $E^0_{298} = -0.2154 + 0.05915 \log 1/0.0091$, we obtain the value 0.0947 for the normal electrode potential, which corresponds to the value obtained by comparing the 0.1 m electrode directly with the corresponding calomel electrode.

In these calculations, since suitable experimentally determined activity coefficients are not available, the modified Debye–Hückel equation of Scatchard[10] has been used to calculate the necessary values. This procedure seems to be justified by vapor pressure studies of solutions of potassium thiocyanate which show that this salt apparently deviates very little in behavior from an ideal solute.[11]

Summary

Electromotive force measurements have been made of a series of cells of the types, [Ag/AgSCN, KSCN (m)/KHg$_x$/KSCN (0.1 m), AgSCN/Ag], [Ag/AgSCN, KSCN (m) / KSCN (0.1 m), AgSCN/Ag], and [Hg/Hg2Cl$_2$, KCl (0.1 m)/KSCN (0.1 m), AgSCN/Ag], at 25°.

From these measurements transference numbers for the potassium ion have been calculated, and the potential of the electrode Ag/AgSCN, KSCN ($a = 1$) has been found to be $E^0_{298} = -0.0947$ volt.

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[9] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

[10] Scatchard, *ibid.*, **47**, 2098 (1925).

[11] Hopson, unpublished doctoral dissertation, 1935.

IOWA CITY, IOWA RECEIVED JULY 28, 1937

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrogen Compounds of Arsenic. I. Preparation of Arsine in Liquid Ammonia. Some Physical Properties of Arsine

BY WARREN C. JOHNSON AND ALPHONSE PECHUKAS

Due to the success in the preparation of the hydrogen compounds of germanium[1] and silicon[2] in liquid ammonia by the action of ammonium salts on magnesium germanides and silicides, respectively, an analogous method was chosen for the preparation of large amounts of arsine required for extensive investigations in this Laboratory. The liquid ammonia method gives high yields of arsine, eliminates objectionable impurities found in the aqueous method and does not produce any other hydrogen compounds of arsenic. In view of the conflicting data in the literature, it appeared advisable to redetermine some of the physical properties of arsine so as to have a control of the purity of the gas to be used in later studies.

Preparation of Arsine.—The arsine was prepared by treating sodium arsenides[3] with ammonium bromide in liquid ammonia by a procedure analogous to that previously described for the preparation of germanes and

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[1] Kraus and Carney, THIS JOURNAL, **56**, 765 (1934).

[2] Johnson and Isenberg, *ibid.*, **57**, 1349 (1935).

[3] Magnesium arsenides were found to give poor yields of arsine; not greater than 25%.

silanes.[1,2] The sodium arsenides were prepared by allowing a solution of sodium in liquid ammonia to react with freshly sublimed arsenic. Since an excess of arsenic was used, polyarsenides were undoubtedly present in addition to the normal arsenide, Na_3As.[4]

The reactions involved in the preparation of arsine may be expressed as follows

$$3Na + xAs = Na_3As_x$$

$$Na_3As_x + 3NH_4Br = 3NaBr + 3NH_3 + AsH_3 + (x - 1)As$$

The liberated gases, arsine and hydrogen, were collected over water to remove ammonia, dried over phosphorus pentoxide, and then fractionally distilled at low pressure at −112° after the hydrogen had been removed by the pumps. The molecular weight of the gas was calculated from vapor density determinations on several samples and was found to range from 77.6 to 77.9 (calculated value for arsine is 77.9). The yield of arsine based upon the amount of sodium initially combined with arsenic was found to range from 60 to 90%. Arsine was the only gas liberated found to contain arsenic. In addition, no arsenic–hydrogen compound remained in the reaction tube after the ammonia had been allowed to evaporate. Evidence for this fact was obtained by heating the residue in the reaction tube to 300°. Since hydrogen was not liberated in this treatment it may be assumed that no solid hydrogen compounds of arsenic were present.

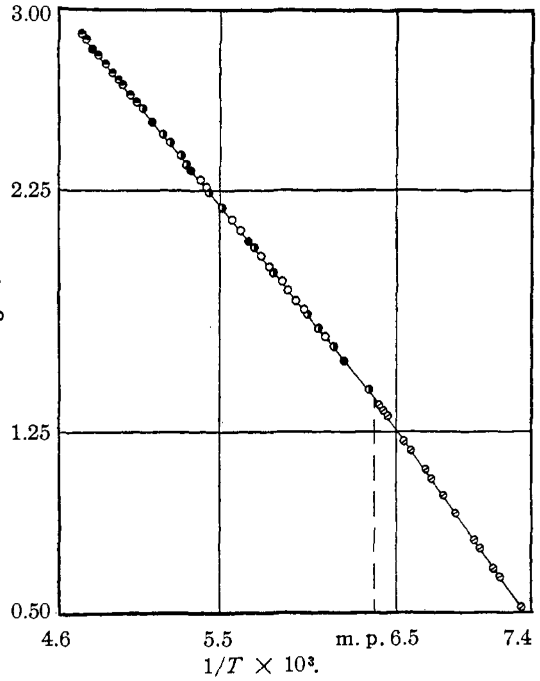

Fig. 1.—Vapor tension of liquid and solid arsine.

Vapor Tension of Liquid and Solid Arsine.—Arsine, obtained by the method described above, is a colorless gas which condenses to a water-clear liquid and freezes to a white crystalline solid.[5] To determine the vapor tension a purified sample of arsine of molecular weight 77.8 was used. The arsine was condensed into a small bulb connected to a mercury manometer. The volume of the entire system was about 22 cc. The bulb was surrounded by constant temperature baths consisting of solid chloroform, ethyl acetate, isopropyl acetate and carbon disulfide in equilibrium with their respective liquids. The liquids from which these baths were prepared were not purified since their freezing points were not used as standards, but merely as a means of maintaining a constant temperature over a reasonably long period of time. The temperature of each bath was determined by a vapor tension thermometer.[6]

As a check upon the fixed point measurements a solution of alcohol in ether was cooled to −120° with liquid nitrogen and was then placed about the arsine bulb and allowed to warm slowly. Readings of the vapor tension were taken at convenient temperature intervals. The temperature was determined either with calibrated vapor tension thermometers or with a copper–constantan thermocouple which had been standardized against the thermometers. A Leeds and Northrup Type K potentiometer was employed in the measurement of the thermocouple potentials. The vapor tensions determined in this manner are plotted in Fig. 1 as log p against $1/T$ and are found to be in good agreement with the fixed point values.[7]

The results show the normal boiling point of arsine to be −62.4°.[8,9] The heat of vaporization is calculated to be 416_5 cal./mole and Trouton's constant, 19.8 cal./mole/degree. Durrant, Pearson and Robinson[9] give 434_0 cal./mole for the heat of vaporization at the boiling point and a value of 20.26 for Trouton's constant.

The melting point of arsine was determined by a method described by Stock.[10] An ethylene vapor tension thermometer was used for the temperature measurements. Five determinations gave the following values for the melting point: −116.3, −116.5, −116.2, −116.3, −116.3°. From these values −116.3° may be taken as the melting point. Durrant, Pearson and Robinson give −111.2° for the melting point of arsine.

The vapor tension of solid arsine was determined at a series of temperatures by condensing the gas in a small

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[4] Hugot [*Compt. rend.*, **129**, 603 (1899)] describes the normal alkali metal arsenides as brick-red in color, and a polyarsenide of the composition $K_2As_4 \cdot NH_3$ as orange. In the present work, both the red and orange solids were observed in every experiment. Zintl, Goubeau and Dullenkopf [*Z. physik. Chem.*, **154**, 1 (1931)] have found Na_3As, Na_3As_3, Na_3As_5 and Na_3As_7 to exist in ammonia solutions. They show a relatively low solubility in ammonia and undoubtedly separate from solution with ammonia of crystallization.

(5) Natta and Casazza [*Gazz. chim. ital.*, **60**, 851 (1930)] have studied the crystal structure of solid arsine.

(6) A carbon dioxide vapor tension thermometer was used for the range, −112 to −78°, while an ammonia thermometer was used for the range, −74 to −60°.

(7) The vapor tension values obtained with the use of the fixed point baths are indicated in Fig. 1 by solid black circles; those obtained with the carbon dioxide vapor tension thermometer, by solid white circles; with the ammonia vapor tension thermometer, by horizontal half circles; with the copper–constantan thermocouple, by vertical half circles; and the crossed circles represent values for solid arsine obtained with the aid of an ethylene vapor tension thermometer.

(8) Values for the boiling point of arsine ranging from −40 to −70° have been reported in the literature. See Mellor, "Comprehensive Treatise on Inorganic Chemistry," Vol. IX, p. 53.

(9) Recent work by Durrant, Pearson and Robinson [*J. Chem. Soc.*, 730 (1934)] shows a value of −58.5° for the boiling point of arsine.

(10) Stock, *Ber.*, **50**, 156 (1917).

TABLE I

VAPOR TENSION OF SOLID AND LIQUID ARSINE

Temp., °C.	−138.0	−135.3	−134.0	−133.1	−132.0	−131.2	−129.0	−127.0	−124.5
Press., mm.	2.0	3.0	3.7	4.05	4.5	4.95	6.4	8.1	10.9
Temp., °C.	−123.0	−121.2	−120.2	−119.0	−116.7	−116.1	−115.4	−112.5	−111.9
Press., mm.	12.4	14.7	16.1	18.5	22.8	25.0	27.0	33.7	35.0
Temp., °C.	−111.0	−110.2	−109.0	−108.3	−106.3	−104.3	−103.3	−102.2	−100.8
Press., mm.	40.0	42.3	44.1	47.4	54.0	62.8	68.5	74.7	80.7
Temp., °C.	− 99.7	− 98.7	− 97.5	− 96.6	− 95.8	− 94.8	− 93.7	− 92.7	− 92.0
Press., mm.	88.5	95.3	103.5	109	113	124	134	148	151
Temp., °C.	− 90.7	− 89.4	− 88.7	− 87.7	− 86.6	− 85.7	− 84.3	− 83.5	− 81.8
Press., mm.	164	177	184	198	213	219	246	257	283
Temp., °C.	− 79.9	− 78.9	− 77.5	− 76.6	− 75.4	− 74.3	− 73.6	− 72.2	− 71.1
Press., mm.	316	330	350	370	397.5	419	432	467	496
Temp., °C.	− 70.0	− 68.8	− 68.0	− 66.9	− 65.6	− 64.3	− 62.8		
Press., mm.	523	556	577	613	647	694	734		

bulb connected to a short mercury manometer of wide bore, and placing an alcohol–ether bath at −140° around the solid. The bath was then allowed to warm slowly and the vapor tension was read on the manometer with the aid of a precision cathetometer reading to 0.04 mm. The temperature was determined with an ethylene vapor tension thermometer. The results for the solid are also plotted in Fig. 1. A straight line plot is obtained which is found to intersect the line for liquid arsine at the melting point, −116.3°. This is a good confirmation of the melting point obtained in the direct determination. The heat of sublimation calculated from the slope of the log p–$1/T$ plot is 484_0 cal./mole. The heat of fusion of the solid is therefore 67_5 cal./mole. The vapor tension at the triple point has a value of 24.4 mm. The equation for the vapor tension of the liquid is

$$\log_{10} p_{\text{mm.}} = -(910.6/T) + 7.198$$

while that for the solid is

$$\log_{10} p_{\text{mm.}} = -(1057/T) + 8.141$$

Table I gives the vapor tension values for both the solid and liquid arsine.

The Density of Liquid Arsine.—Using a pycnometer consisting of a small bulb with a capillary stem, the density of liquid arsine was determined by comparison with the density of liquid ammonia. Values for the latter have been determined accurately.[11] Ammonia which had been dried thoroughly over metallic sodium was distilled into the bulb and maintained at constant temperature by means of a well-stirred bath of solid chloroform in equilibrium with its liquid in a transparent Dewar vessel. The level of the liquid in the capillary stem of the pycnometer was determined with respect to a reference mark with the aid of a cathetometer. The ammonia was allowed to evaporate into a known volume after the cooling bath had been removed and the pressure of the ammonia gas was then determined. In this manner, the volume, and therefore the weight, of the gaseous ammonia could be calculated assuming the gas to obey the perfect gas laws. After correcting for the amount of ammonia vapor above the liquid in the pycnometer (about 2 mg.), the weight of liquid ammonia was obtained. With the density of liquid ammonia known, the volume of the pycnometer to the reference point on the stem could be determined readily. The volume so obtained was 0.849 ± 0.002 cc.

The ammonia was then replaced by arsine and the same procedure was employed to determine the density of the latter. Constant temperature baths corresponding to those used in the vapor tension measurements likewise were employed. The measurements were made at several temperatures ranging from −64 to −112°. The values given in Table II represent the average of not less than four, nor more than seven, determinations at each temperature.

TABLE II

DENSITY OF LIQUID ARSINE AT DIFFERENT TEMPERATURES

Temp., °C.	−64.3	−76.9	−85.4	−96.0	−111.8
Density, g./cc.	1.640	1.670	1.692	1.723	1.766
Deviation, g./cc.	0.001	0.002	0.002	0.006	0.001

A plot of the density of liquid arsine against the temperature gives a smooth curve, the equation for which may be expressed as

$$d = 1.516 - 0.00150t + 0.00000663t^2$$

where d is the density in g./cc. and t, the temperature in °C. From this equation the density of arsine at the normal boiling point, −62.4°, is found to be 1.635 g./cc. Extrapolating to −60°, the density is 1.629 g./cc., which value is in substantial agreement with that obtained by Durrant, Pearson and Robinson,[9] who have reported a value of 1.625 g./cc. at this temperature.

Solubility of Arsine in Liquid Ammonia.—An attempt was made to determine the solubility of arsine in liquid ammonia through a study of the pressure–composition relationships for the two-component system. However, considerable difficulty was found in establishing equilibrium conditions and, in addition, the arsine was observed to be only slightly soluble. Qualitative measurements indicated the solubility of liquid arsine in liquid ammonia to be less than 1%. The saturated solution appears yellow in color, even at temperatures as low as

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(11) Cragoe and Harper, *Sci. Papers of the Bur. of Stand.*, No. 420, p. 313 (1921).

$-80°$, and according to its chemical behavior the arsine must be appreciably ionized.[12]

We wish to acknowledge the aid of a grant from the National Research Council for the liquid nitrogen used in this study.

Summary

Arsine has been prepared in good yields by the action of ammonium bromide on sodium arsenides in liquid ammonia. Arsine was found to be the only arsenic containing gas liberated in the reaction. No solid arsenic hydrogen compounds are formed.

The vapor tension of solid and liquid arsine has been determined over a considerable range of temperature. From the measurements the boiling point has been found to be $-62.4°$; the melting point, $-116.3°$; the heat of vaporization, 416_5 cal./mole; the heat of sublimation, 484_0 cal./mole; and the heat of fusion, 67_5 cal./mole.

The density of liquid arsine has been determined at temperatures ranging from the melting point to the boiling point.

Liquid arsine is only slightly soluble in liquid ammonia.

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[12] In connection with this problem a rapid method of separation and determination of arsine in an arsine–ammonia gas mixture was found. Ammonia may be removed quantitatively from a mixture of the two gases without loss of arsine by liquefying the mixed gases on anhydrous calcium chloride which has been previously heated in a vacuum to 400°. The ammonia combines with the calcium chloride to form a solid ammonate but the arsine does not produce a similar combination possessing any appreciable stability at temperatures as low as $-78°$. If the calcium chloride and its ammonate are kept at this temperature, the arsine may be distilled into a suitable container and condensed at the temperature of liquid nitrogen. Two such treatments were found to remove the ammonia quantitatively from 200 cc. of a mixture of the gases containing 90% ammonia by volume, without loss of arsine.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrogen Compounds of Arsenic. II. Sodium and Potassium Dihydrogen Arsenides

BY WARREN C. JOHNSON AND ALPHONSE PECHUKAS

Ammonia is known to exhibit some acidic properties since it conducts electricity to an appreciable extent and reacts with strongly electropositive metals to form dihydrogen nitrides (amides). Joannis[1] has shown that phosphine reacts with the common alkali metals in liquid ammonia to produce dihydrogen phosphides (phosphamides). In the case of potassium the reaction may be expressed as

$$K + PH_3 = KPH_2 + 0.5H_2$$

Since arsenic shows a greater tendency than phosphorus to become electropositive one would expect the arsenic–hydrogen bonds of arsine to be weaker than the phosphorus–hydrogen bonds of phosphine. If the reaction between the alkali and alkaline earth metals and the hydrogen compounds of the fifth group elements is dependent upon the lability of the hydrogen atoms, arsine would be expected to react with these metals more readily than does phosphine and, in turn, ammonia. Gay-Lussac and Thenard[2] observed that hydrogen is liberated from arsine when the latter is treated with sodium or potassium and that the arsenic probably enters into combination with the metal. Lebeau[3] investigated this reaction further, both with the pure alkali or alkaline earth metals and their liquid ammonia solutions. He prepared calcium arsenide (Ca_3As_2) by the action of liquid arsine on solid calcium; in liquid ammonia solution arsine was found to react with calcium rapidly to give a yellow compound which decomposes at 150° to produce a brown arsenide of calcium. Using sodium instead of calcium, he obtained a bright yellow solution when arsine was passed into a liquid ammonia solution of the metal. Evaporation of this solution produced a red solid to which Lebeau ascribed the composition $Na_3As(NH_3)_x$.

Since arsine is appreciably soluble in liquid ammonia[4] and appears to be somewhat ionized in this medium, it appeared advisable to prepare some of the alkali metal salts and study the chemistry of these substances.

The Reaction of Arsine with Sodium and Potassium.—Gaseous arsine, of known purity,[4] was passed into a solution containing a weighed amount of sodium or potassium in liquid ammonia at $-78°$. The type of apparatus used has been described elsewhere.[5] The arsine was found to react very rapidly with the ammonia solution of the metal, changing the color of the latter from

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[1] Joannis, *Compt. rend.*, **119**, 557 (1894).

[2] Gay-Lussac and Thenard, *Ann. chim. phys.*, [1] **73**, 229 (1810).

[3] Lebeau, *Bull. soc. chim.*, [3] **23**, 251, 340 (1900); *Ann. chim. phys.*, [7] **25**, 470 (1902).

[4] Johnson and Pechukas, THIS JOURNAL, **59**, 2065 (1937).

[5] Kraus and Brown, *ibid.*, **52**, 4031 (1930).