ether–borine has been obtained. The relative stability of the series of ether–borines is probably: $C_4H_8O:BH_3 > (CH_3)_2O:BH_3 >> (C_2H_5)_2O:BH_3$, the order which would be expected if steric factors in the $—BH_3$ group were comparable to those in the $-BF_3$ group.[4] The interpretation of the compounds of diborane with ethers as ether–borines and the order of the stability as given above have been further confirmed by a detailed study[5] of the Raman spectra, to be published elsewhere, of ether solutions of diborane at low temperatures.

### Experimental

**Materials.**—Diborane was prepared by the reaction[6] of $LiBH_4 \cdot O(C_2H_5)_2$ and copper(I) chloride in chlorobenzene and purified by fractional condensation at −140°. The product had a sharp melting point at −168.0° and a vapor pressure at −112° of 225 mm. The procedure used has the advantage of minimizing the diethyl ether concentration and thus contamination of the diborane with ether and its cleavage products. Diborane of exceptional purity results. Tetrahydrofuran was purified by refluxing over $LiAlH_4$, followed by fractionation. The purified material gave a sharp melting point at −107.8°.

**Procedure.**—The freezing points of tetrahydrofuran–diborane solutions were determined from cooling curves in the region 0 to 34 mole per cent. diborane. The quantities of tetrahydrofuran were measured as the liquid in a calibrated tube and the quantities of diborane were measured as the gas in a calibrated volume. The materials were transferred into the freezing point cell by condensation with liquid nitrogen. Liquid nitrogen was used as the coolant and the rate of cooling was regulated by variation of the gas pressure in a jacket interposed between the cell and the cooling bath. Temperatures were determined by a thermocouple calibrated against a platinum resistance thermometer and their over-all reliability is estimated to be ±0.5°. The results are given in the table above and graphically in Fig. 1.

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[4] H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942).

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[6] R. Toeniskoetter, Master's Thesis, St. Louis University, June 1955.

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## Ammoniates of Guanidine and Guanidinium Chloride[1]

BY GEORGE W. WATT AND WILLIAM R. MCBRIDE

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The experiments described below are concerned with a method for the preparation of pure guanidine, and with the detection of ammoniates of guanidine and guanidinium chloride through the study of pressure–composition isotherms for the systems guanidine–ammonia and guanidinium chloride–ammonia.

### Experimental

Guanidine was prepared by the interaction of guanidinium carbonate and potassium amide by an adaptation of equipment and procedures described previously.[2] The apparatus was modified to the extent that the reaction vessel was provided with a side-arm addition bulb from which guanidinium carbonate was added in slight excess to potassium amide solution previously prepared in the reaction vessel by the iron-catalyzed interaction of potassium and ammonia. After about two hours, the liquid ammonia solution of guanidine was separated from the insoluble potassium carbonate and excess guanidinium carbonate by filtration, the ammonia was evaporated, and the guanidine was collected in ampoules in the manner previously described.[2] Guanidinium chloride was prepared by treating guanidinium carbonate with hydrochloric acid, and was purified by recrystallization from absolute ethanol.

The purity of both the free base and the salt was determined by precipitation of guanidinium picrate using a procedure based upon the work of Vozarik.[3] To 25 ml. of aqueous solution of guanidinium chloride (or guanidine neutralized to the phenolphthalein end-point with hydrochloric acid), 50 ml. of 1.4% ammonium picrate solution was added slowly and with stirring. The resulting mixture was maintained at 25°, stirred occasionally over a period of at least 30 min., filtered, and the crystals of guanidinium picrate washed with two 5-ml. portions of ice-water, and dried to constant weight at 120°. To the weights of guanidinium picrate thus found there was added a predetermined correction factor to compensate for the solubility of the picrate under the conditions specified. On the basis of analyses of solutions of known guanidinium salt content, the solubility loss was found to be linear with respect to observed weights of guanidinium picrate over the range 120 to 500 mg.; the corresponding corrections amount to 10.6 to 21.0 mg., respectively. The maximum error in the determination of the solubility loss in this range is 0.5 mg. and the maximum percentage error in the analytical determinations would vary from about 0.5 to 0.1% as the observed weight of guanidinium picrate varies from 120 to 500 mg. As determined by this method, the purity of guanidinium hydrochloride was found to be 99.9% while that of guanidine was found to be 98.3 ± 0.6%. The purity of the latter

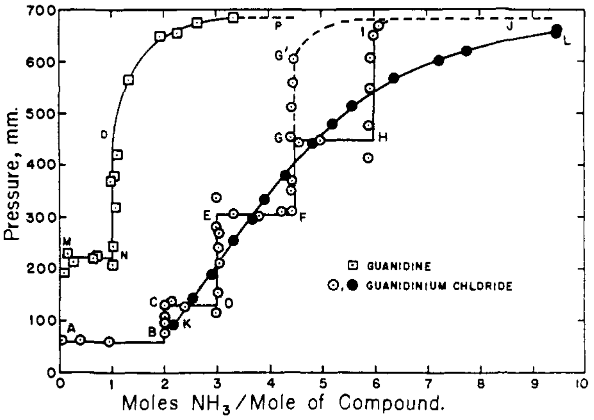

Fig. 1.—Pressure–composition isotherms for the systems guanidine–ammonia and guanidinium chloride–ammonia at −35.5°.

TABLE I

COMPOSITION OF PHASES IN EQUILIBRIUM

| Curve | Phases |
|---|---|
| AB | A(s),[a] A·$2NH_3$(s), $NH_3$(g) |
| BC | A·$2NH_3$(s), $NH_3$(g) |
| CD | A·$2NH_3$(s), A·$3NH_3$(s), $NH_3$(g) |
| DE | A·$3NH_3$(s), $NH_3$(g) |
| EF | A·$3NH_3$(s), A·$4.5NH_3$(s), $NH_3$(g) |
| FG | A·$4.5NH_3$(s), $NH_3$(g) |
| GG | A·$4.5NH_3$(s), $NH_3$(g)[b] |
| GH | A·$4.5NH_3$(s), A·$6NH_3$(s), $NH_3$(g) |
| HI | A·$6NH_3$(s), $NH_3$(g) |
| IJ | A·$6NH_3$(s), satd. soln., $NH_3$(g) |
| KL | Supersatd. soln., $NH_3$(g)[b] |
| MN | B(s),[c] B·$NH_3$(s), $NH_3$(g) |
| NO | B·$NH_3$(s), $NH_3$(g) |
| OP | B·$NH_3$(s), satd. soln., $NH_3$(g) |

[a] A = guanidinium chloride. [b] Metastable. [c] B = guanidine.

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[1] This work was supported in part by the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

[2] G. W. Watt and W. R. McBride, THIS JOURNAL, **77**, 2088 (1955).

[3] A. Vozarik, *Z. angew. Chem.*, **15**, 670 (1902).

was also determined by direct titration with hydrochloric acid; this method gave a value of 100.5 ± 0.9%. The yields of guanidine prepared by the above procedure were essentially quantitative and the melting point of the product was 47.5–48.5°, which is to be compared with the previously reported melting point of approximately 50°.[4]

The quartz helix balance and the procedures employed in the establishment of pressure–composition isotherms for the systems guanidine–ammonia and guanidinium chloride–ammonia (Fig. 1) are described elsewhere.[5] The phases coexistent at equilibrium are listed in Table I.

**Discussion.**—Earlier efforts to prepare pure guanidine have been concerned with the interaction of guanidinium salts with barium hydroxide[6,7] in aqueous solution and potassium hydroxide[8] or calcium hydroxide[4] in alcohol. All of these procedures involve the difficult dehydration of guanidinium hydroxide at low temperatures and the exclusion of carbon dioxide. Apparently only Markwald and Struwe[4] succeeded in preparing even reasonably pure guanidine. Franklin[9] has shown that guanidinium nitrate and potassium amide in liquid ammonia react to form a soluble monopotassium salt and an insoluble dipotassium salt of guanidine. The present method for the preparation of guanidine in high purity and substantially quantitative yield takes advantage of the insolubility of potassium carbonate in liquid ammonia,[10,11] the ease of elimination of water and carbon dioxide, and the ease of complete elimination of the solvent owing to its volatility.

As shown by Fig. 1, guanidine forms a 1-ammoniate which has a dissociation pressure of 220 mm. at −35.5°. This solvate is isomeric with the tetramide of carbon(IV),[9] $C(NH_2)_4$; also, this solvate may be looked upon as either guanidinium amide or ammonium guanide. In aqueous solutions guanidine is a very strong base ($pK_a = 13.65$ at 25°[12]), but Franklin[9] has pointed out that guanidine behaves as a weak acid in *liquid* ammonia solutions. In the *solid–gas reaction* observed in the present work, the guanidine molecule most likely acts as a Lewis acid to form an intermediate which could lead to either of the products suggested above.

It is of particular interest to note that guanidinium chloride is not ammonolyzed upon exposure to gaseous ammonia at −35.5°, but rather forms 2-, 3-, 4.5- and 6-ammoniates (Fig. 1, Table I). The dissociation pressures of these solvates in equilibrium with the next lower ammoniate or the deammoniated salt and ammonia gas are 60, 130, 305 and 450 mm., respectively. The 6-ammoniate of guanidium chloride is apparently analogous to the 6-ammoniate of ammonium chloride.[5] The extent to which supersaturation may occur in such systems is illustrated by Fig. 1, curve KL, which indicates metastability with respect to four invariant systems.

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## Synthesis of Anhydrous Metal Halides[1]

BY GEORGE W. WATT, PHILIP S. GENTILE AND E. P. HELVENSTON

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In connection with other studies in progress in these laboratories we have devised a new method for the synthesis of anhydrous metal halides that offers considerable promise of generality of application. By this procedure, pure halides are produced in essentially quantitative yield by the interaction of the appropriate hydrated metal acetate and acetyl halide in benzene, in accordance with the general equation

$$M(C_2H_3O_2)_y \cdot zH_2O + (y + z)CH_3COX \longrightarrow MX_y + y(CH_3CO)_2O + zHC_2H_3O_2 + zHX$$

where M is a metal and X is chlorine, bromine or iodine.

**Experimental.**—All chemicals employed in this work were reagent grade and were not further purified.

In a typical case, 4.0 g. of finely ground hydrated metal acetate was placed in a Pyrex test-tube (18 × 200 mm.) fitted with a rubber stopper bearing a dropping funnel and a filter stick. Following addition of 15 ml. of benzene, the mixture was slurried with a magnetic stirrer and treated slowly with a 10% excess of the appropriate acetyl halide. The reaction mixture was stirred for 30 min., the precipitated metal halide was allowed to settle, and the mother liquor was drawn off through the filter stick. The residue was retreated with benzene and acetyl halide to ensure complete conversion, after which the supernatant liquid was removed by filtration and the solid product was washed three or four times with 20-ml. portions of dry benzene. The product contained in the reaction vessel in an atmosphere of dry oil-pumped nitrogen was transferred to an oven and dried for 3 hr. at 200° in a nitrogen atmosphere and thereafter transferred to a dry-box for sampling and analysis. The results obtained with ten different halides are given in Table I.

TABLE I

ANALYTICAL DATA

| | Anal. for halide[b] | | | |
|---|---|---|---|---|
| | Chloride | | Bromide | |
| Halide[a] | Found | Calcd. | Found | Calcd. |
| $CuX_2$ | 51.6 | 52.8 | 71.2[e] | 71.7 |
| $CdX_2$ | 38.4 | 38.7 | 58.6 | 58.8 |
| $MnX_2$[c] | 56.0 | 56.4 | 73.7 | 74.4 |
| $CoX_2$ | 54.2 | 54.6 | 72.7 | 73.0 |
| $NiX_2$[d] | 54.0 | 54.8 | 72.9 | 73.1 |

[a] The starting materials were the 1-hydrate of the acetate of copper(II), the 2-hydrate of the acetate of cadmium(II), and the 4-hydrates of the acetates of manganese(II), cobalt(II) and nickel(II). [b] Determined by the Volhard method. [c] Slow reaction; acetyl chloride added first; mixture boiled for 5 min. after second addition of acetyl chloride. [d] Same as footnote *c* except that reaction mixture was finally stirred for 12 hr. at room temperature. [e] Bromide decomposes slowly at 200°; hence, drying for 2 hr. at 150° was used.

In a similar experiment, bismuth(III) chloride was converted quantitatively to the corresponding iodide by treatment with acetyl iodide. *Anal.* Calcd. for $BiI_3$: Bi, 35.4. Found[2]: Bi, 34.9.

**Discussion.**—Although complete data on yields and purity are not available, similar use of the acetates of aluminum(III), chromium(III), thallium(I), neodymium(III) and samarium(III) indicates that the reactions lead to the corresponding an-

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(1) This work was supported in part by the U. S. Atomic Energy Commission, Contract AT-(40-1-)-1639.

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