## Art. XIII.—*The Behavior of Typical Hydrous Bromides when Heated in an Atmosphere of Hydrogen Bromide;* by J. Lehn Kreider.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxxxvii.]

In former papers from this laboratory* the results obtained in the dehydration of certain hydrous chlorides in air and in an atmosphere of hydrogen chloride have been studied and compared. In the present paper the effects of treating typical hydrous bromides in air and in an atmosphere of hydrogen bromide are described.

Hydrous barium bromide has been taken as a type of hydrous salts which when heated in air lose their water without much further decomposition; hydrous magnesium bromide as typical of salts which lose part of their water without much further decomposition and the remainder with simultaneous evolution of hydrogen bromide; and hydrous aluminum bromide as typical of salts which lose their water only with simultaneous loss of hydrogen bromide.

The method of experimentation was very similar to that followed by Gooch and McClenahan† in their experiments with hydrous chlorides.

For these experiments two combustion tubes $30^{cm}$ in length and $2^{cm}$ in diameter, set horizontally side by side in a tubulated paraffine bath, served as heating chambers. Each tube was fitted with a thermometer. Portions of the hydrous bromides to be treated were weighed into porcelain boats. One of these boats was inserted in each tube about midway in the bath (heated to a regulated temperature) and below the bulb of the thermometer, so that the temperature to which the material in the boat was submitted might be indicated by the thermometer as accurately as possible. Through one tube was drawn slowly a current of air purified by sulphuric acid, and through the other was sent a slow current of purified hydrogen bromide, generated in a flask by the action of bromine on a heated solution of naphthalene and kerosene, and passed through a purifying apparatus consisting of a tower containing successive layers of red phosphorus and glass wool and a wash bottle charged with a saturated solution of hydrobromic acid. At the end of a definite period, the boat was withdrawn, placed in a desiccator for a suitable interval to cool, and weighed. The residue in the boat was dissolved in water, and the bromine was precipitated by silver nitrate, the silver bromide being weighed on asbestos. In this way it was

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*Gooch and McClenahan, this Journal [4], xvii, 365. McClenahan, this Journal [4], xviii, 104.

† Loc. cit.

possible to determine the loss of water and hydrogen bromide from separate portions of the salt under examination, during definite intervals and at fixed temperatures, both in an atmosphere of hydrogen bromide and in air, and to find for each portion under examination what proportion of the total loss was hydrogen bromide and what was water. The tabular statements and the diagrams show the course of decomposition of the various salts for the temperatures indicated.

### *Hydrous Barium Bromide.*

For the experiments with hydrous barium bromide, a well crystallized specimen was prepared by taking commercially pure barium carbonate, dissolving it in hydrochloric acid, precipitating by ammonium carbonate, washing the precipitate, dissolving in hydrobromic acid, and crystallizing and drying the crystals by pressing between filter papers. The analysis of different portions of this salt showed a definite composition, corresponding very closely to theory.

| | Found. | Theory. |
|---|---|---|
| Ba | 41·69% | 41·60% |
| Br | 48·05 | 47·95 |
| $2H_2O$ | 10·26 | 10·45 |
| | 100·00% | 100·00% |

The progress of the decomposition of this salt in air and in hydrogen bromide when submitted for a half hour to the temperatures indicated is shown in the accompanying table and diagram.

Here may be noted a gradual loss of water from 70° C. to 160° C., at which point the water is entirely expelled, without an appreciable loss of hydrogen bromide, either in air or hydrogen bromide, and that hydrogen bromide influences the process of dehydration in no marked way. There is nothing to show that any part of the water sustains a peculiar relation to the salt.

### *Hydrous Magnesium Bromide.*

Similar experiments were performed with hydrous magnesium bromide, prepared by dissolving magnesium ribbon in hydrobromic acid and crystallizing the salt over sulphuric acid. The analysis of the salt gave a definite constitution corresponding fairly to theory.

| | Found. | Theory. |
|---|---|---|
| Mg | 08·68 | 08.27 |
| Br | 54·61 | 54·69 |
| $6H_2O$ | 36·71 | 37·04 |
| | 100·00 | 100·00 |

### *Dehydration of Hydrous Barium Bromide.*

$BaBr_2 \cdot 2H_2O$.

| Atmosphere. | | Weight taken. | Loss on heating. | | Bromine in residue. | | | Water evolved. | Time. | Temperature. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | grm. | grm. | per cent. | grm. | per cent. | Variation from theory. | per cent. | hrs. | |
| 1 | HBr | ·2377 | ·0165 | 06·94 | ·1130 | 47·56 | −0·39 | 06·55 | ½ | 70°C. |
| | Air | ·2364 | ·0107 | 04·52 | ·1141 | 48·24 | +0·29 | 04·81 | | |
| 2 | HBr | ·2309 | ·0147 | 06·36 | ·1105 | 47·82 | −0·13 | 06·23 | ½ | 80°C. |
| | Air | ·2247 | ·0125 | 05·56 | ·1082 | 48·16 | +0·21 | 05·77 | | |
| 3 | HBr | ·2299 | ·0121 | 05·26 | ·1115 | 48·49 | +0·54 | 05·80 | ½ | 90°C. |
| | Air | ·2311 | ·0127 | 05·49 | ·1115 | 48·26 | +0·31 | 05·80 | | |
| 4 | HBr | ·2413 | ·0121 | 05·01 | ·1173 | 48·58 | +0·63 | 05·64 | ½ | 100°C. |
| | Air | ·2416 | ·0134 | 05·54 | ·1167 | 48·33 | +0·38 | 05·92 | | |
| 5 | HBr | ·2399 | ·0118 | 04·91 | ·1157 | 48·26 | +0·31 | 05·22 | ½ | 110°C. |
| | Air | ·2342 | ·0128 | 05·50 | ·1162 | 48·09 | +0·14 | 05·64 | | |
| 6 | HBr | ·2296 | ·0115 | 05·00 | ·1111 | 48·41 | +0·46 | 05·46 | ½ | 120°C. |
| | Air | ·2287 | ·0127 | 05·50 | ·1095 | 47·91 | −0·04 | 05·46 | | |
| 7 | HBr | ·2501 | ·0157 | 06·27 | ·1208 | 48·32 | +0·37 | 06·64 | ½ | 130°C. |
| | Air | ·2472 | ·0135 | 05·46 | ·1195 | 48·37 | +0·42 | 05·88 | | |
| 8 | HBr | ·2389 | ·0198 | 06·58 | ·1147 | 48·03 | +0·08 | 06·66 | ½ | 140°C. |
| | Air | ·2304 | ·0148 | 06·42 | ·1113 | 48·31 | +0·36 | 06·78 | | |
| 9 | HBr | ·2491 | ·0258 | 10·36 | ·1190 | 47·78 | +0·17 | 10·19 | ½ | 150°C. |
| | Air | ·2438 | ·0251 | 10·29 | ·1167 | 47·86 | −0·09 | 10·20 | | |
| 10 | HBr | ·2460 | ·0269 | 10·93 | ·1190 | 48·37 | +0·42 | 11·35 | ½ | 160°C. |
| | Air | ·2416 | ·0242 | 10·01 | ·1166 | 48·26 | +0·31 | 10·32 | | |

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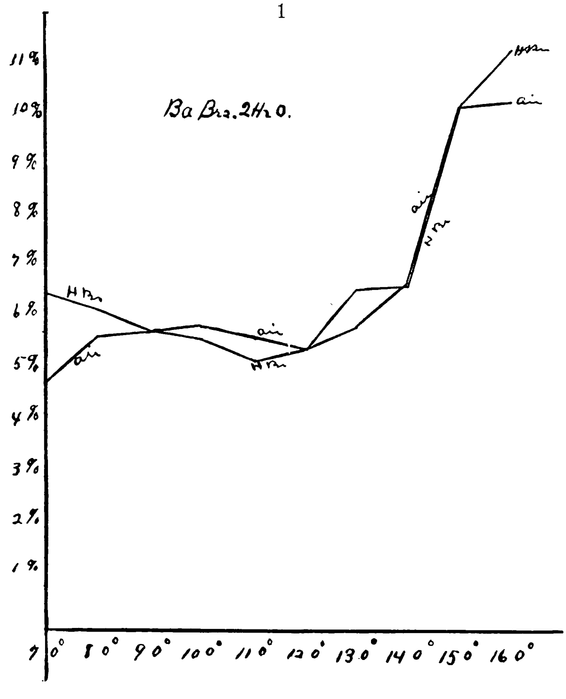

## *Dehydration of Hydrous Magnesium Bromide.*

$MgBr_2 \cdot 6H_2O$.

| Atmosphere. | | Weight taken. | Loss on heating. | | Bromine in residue. | | HBr lost. | Water lost. | Time. | Temperature. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | grm. | grm. | per cent. | grm. | per cent. | per cent. | per cent. | hrs. | |
| 1 | HBr | ·2389 | ·0000 | 00·00 | ·1310 | 54·81 | 00·12 | 00·12 | ½ | 70° C. |
| | Air | ·2400 | ·0000 | 00·00 | ·1319 | 54·98 | 00·29 | 00·29 | | |
| 2 | HBr | ·1370 | ·0000 | 00·00 | ·0751 | 54·85 | 00·16 | 00·16 | ½ | 80° |
| | Air | ·1380 | ·0012 | 00·86 | ·0752 | 54·55 | 00·14 | 00·72 | | |
| 3 | HBr | ·1259 | ·0019 | 01·50 | ·0693 | 54·96 | 00·27 | 01·77 | ½ | 90° |
| | Air | ·1482 | ·0023 | 01·95 | ·0813 | 54·87 | 00·18 | 02·13 | | |
| 4 | HBr | ·1220 | ·0053 | 04·34 | ·0664 | 54·46 | 00·23 | 04·11 | ½ | 100° |
| | Air | ·1448 | ·0048 | 03·31 | ·0797 | 55·07 | 00·38 | 03·69 | | |
| 5 | HBr | ·1345 | ·0070 | 05·20 | ·0736 | 54·76 | 00·07 | 05·27 | ½ | 110° |
| | Air | ·1384 | ·0103 | 07·44 | ·0752 | 54·33 | 00·36 | 07·80 | | |
| 6 | HBr | ·1374 | ·0115 | 08·36 | ·0751 | 54·69 | 00·00 | 08·36 | ½ | 120° |
| | Air | ·1353 | ·0120 | 08·86 | ·0737 | 54·50 | 00·19 | 08·67 | | |
| 7 | HBr | ·1331 | ·0114 | 08·56 | ·0724 | 54·41 | 00·28 | 08·28 | ½ | 130° |
| | Air | ·1317 | ·0128 | 09·71 | ·0714 | 54·28 | 00·41 | 09·30 | | |
| 8 | HBr | ·1345 | ·0140 | 10·40 | ·0734 | 54·58 | 00·11 | 10·29 | ½ | 140° |
| | Air | ·1369 | ·0183 | 13·37 | ·0733 | 53·59 | 01·11 | 12·26 | | |
| 9 | HBr | ·1375 | ·0216 | 15·71 | ·0748 | 54·47 | 00·22 | 15·49 | ½ | 150° |
| | Air | ·1358 | ·0251 | 18·48 | ·0727 | 53·58 | 01·12 | 17·36 | | |
| 10 | HBr | ·1313 | ·0140 | 10·66 | ·0714 | 54·46 | 00·23 | 10·46 | ½ | 160° |
| | Air | ·1311 | ·0324 | 24·71 | ·0698 | 53·26 | 01·44 | 23·27 | | |
| 11 | HBr | ·1366 | ·0170 | 12·44 | ·0744 | 54·39 | 00·31 | 12·13 | ½ | 170° |
| | Air | ·1379 | ·0159 | 11·53 | ·0744 | 54·00 | 00·69 | 10·84 | | |
| 12 | HBr | ·1399 | ·0220 | 15·72 | ·0760 | 54·35 | 00·34 | 15·38 | ½ | 180° |
| | Air | ·1358 | ·0232 | 17·08 | ·0723 | 53·27 | 01·43 | 15·65 | | |
| 13 | HBr | ·1285 | ·0217 | 16·89 | ·0696 | 54·75 | 00·06 | 16·95 | ½ | 190° |
| | Air | ·1324 | ·0275 | 20·77 | ·0702 | 53·06 | 01·65 | 19·12 | | |
| 14 | HBr | ·1345 | ·0284 | 21·11 | ·0731 | 54·42 | 00·27 | 20·84 | ½ | 200° |
| | Air | ·1382 | ·0312 | 22·57 | ·0730 | 52·87 | 01·84 | 20·73 | | |
| 15 | HBr | ·1349 | ·0282 | 20·90 | ·0731 | 54·19 | 00·50 | 20·40 | ½ | 210° |
| | Air | ·1350 | ·0331 | 24·51 | ·0704 | 52·20 | 02·51 | 22·00 | | |
| 16 | HBr | ·1337 | ·0297 | 22·21 | ·0722 | 54·01 | 00·68 | 21·53 | ½ | 220° |
| | Air | ·1320 | ·0379 | 28·71 | ·0686 | 52·03 | 02·69 | 26·02 | | |
| 17 | HBr | ·1354 | ·0340 | 25·11 | ·0731 | 54·02 | 00·67 | 24·47 | ½ | 230° |
| | Air | ·1373 | ·0606 | 44·13 | ·0649 | 47·43 | 07·35 | 36·78 | | |
| 18 | HBr | ·1376 | ·0401 | 29·14 | ·0740 | 53·69 | 01·01 | 28·13 | ½ | 240° |
| | Air | ·1360 | ·0555 | 40·80 | ·0665 | 48·93 | 05·80 | 35·00 | | |

From these results it appears that approximately a third of the water may be removed from the hydrous magnesium bromide, submitted at once to the temperatures indicated, either in air or in an atmosphere of hydrogen bromide, without considerable simultaneous loss of hydrogen bromide from the salt, the trifling loss being somewhat less in the atmosphere of hydrogen bromide than in air, Thereafter the loss of hydrogen bromide when the salt is heated in air increases generally with the temperature and is inhibited, as is the loss of water,

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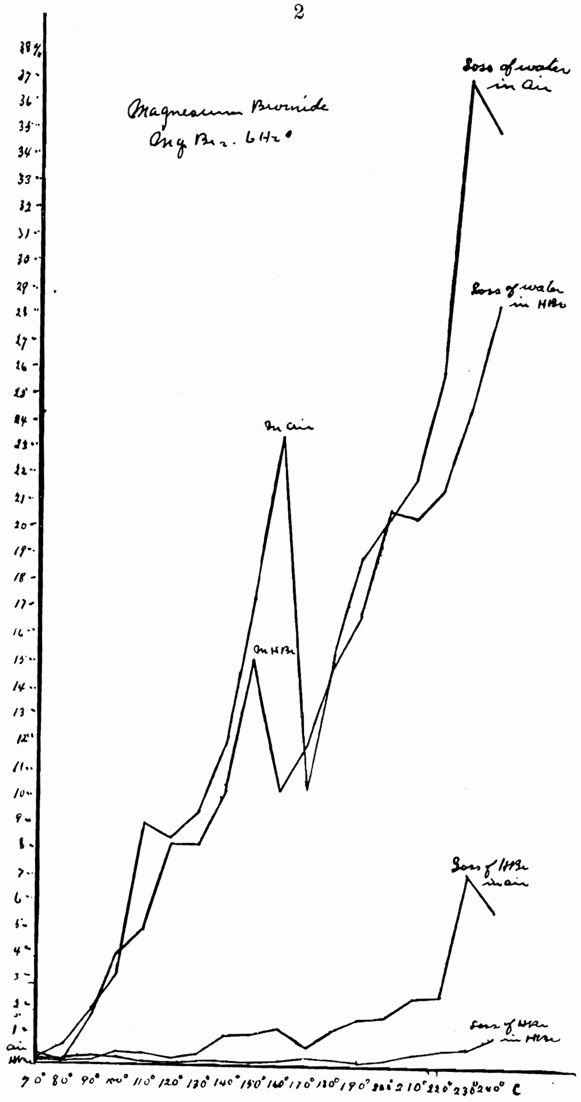

by the atmosphere of hydrogen bromide. It appears that about a third of the water of magnesium bromide bears a relation to the salt different from that of the remainder.

When submitted at once, without preliminary heating, to a temperature of 170° in air and 160° in hydrogen bromide, the hydrous salt melts and in the melted condition loses water less rapidly than the solid salt at a somewhat lower temperature. This is what makes the break in the curves which indicate the losses of water and hydrogen bromide. When the salt was heated successively, for intervals of a half hour, at temperatures varying by ten degrees, the progress of dehydration was more uniform, as is shown in the accompanying diagram, all the water being lost at 160° in air and 220° in hydrogen bromide, the inhibiting action of hydrogen bromide upon the dehydration being more marked as the temperature rises from the point at which the first third is lost.

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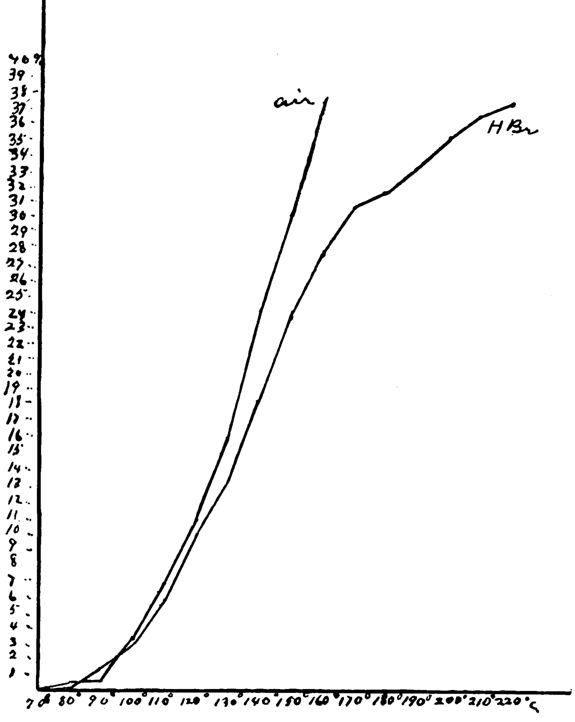

*Hydrous Aluminum Bromide.*

The hydrous aluminum bromide used was prepared by dissolving pure aluminum chloride in water, precipitated aluminum hydroxide by ammonium hydroxide, filtering off the aluminum hydroxide, and washing until free from impurities. This precipitate was then dissolved in hydrobromic acid, and the solution thus formed allowed to crystallize by evaporation in vacuum over sulphuric acid: the crystals thus formed were of nearly normal constitution.

| | Found. | Theory. |
|---|---|---|
| Al | 07·25% | 07·20% |
| $Br_3$ | 63.90 | 63·95 |
| $6H_2O$ | 28·85 | 28·85 |
| | 100·00 | 100·00 |

The course of dehydration of hydrous aluminum bromide in air and in an atmosphere of hydrogen bromide is shown in the accompanying table and diagram.

*Dehydration of Aluminum Bromide.*

$AlBr_3 \cdot 6H_2O$.

| | Atmosphere. | Weight taken. | Loss on heating. | | Bromine in residue. | | HBr lost. | Water lost. | Time. | Temperature. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | grm. | grm. | per cent. | grm. | per cent. | per cent. | per cent. | hrs. | |
| 1 | HBr | ·1308 | ·0000 | 00·00 | ---- | ---- | ---- | ---- | ½ | 70° C. |
| | Air | ·1306 | ·0000 | 00·00 | ---- | ---- | ---- | ---- | | |
| 2 | HBr | ·1394 | ·0000 | 00·00 | ---- | ---- | ---- | ---- | ½ | 80° |
| | Air | ·1381 | ·0000 | 00·00 | ---- | ---- | ---- | ---- | | |
| 3 | HBr | ·1344 | ·0000 | 00·00 | ---- | ---- | ---- | ---- | ½ | 90° |
| | Air | ·1360 | ·0000 | 00·00 | ---- | ---- | ---- | ---- | | |
| 4 | HBr | ·1317 | ·0008 | 00·60 | ·0831 | 63·13 | 00·83 | 00·23 | ½ | 100° |
| | Air | ·1316 | ·0014 | 01·06 | ·0842 | 64·05 | 00·10 | 01·16 | | |
| 5 | HBr | ·1364 | ·0008 | 00·58 | ·0861 | 63·60 | 00·35 | 00·23 | ½ | 110° |
| | Air | ·1378 | ·0024 | 01·74 | ·0865 | 62·83 | 01·13 | 00·61 | | |
| 6 | HBr | ·1381 | ·0008 | 00·57 | ·0878 | 63·62 | 00·33 | 00·24 | ½ | 120° |
| | Air | ·1367 | ·0054 | 03·95 | ·0834 | 61·07 | 02·91 | 01·04 | | |
| 7 | HBr | ·1297 | ·0006 | 00·46 | ·0825 | 63·64 | 00·31 | 00·15 | ½ | 130° |
| | Air | ·1318 | ·0106 | 08·04 | ·0767 | 58·24 | 05·78 | 02·26 | | |
| 8 | HBr | ·1379 | ·0011 | 00·79 | ·0831 | 60·32 | 03·67 | 02·89 | ½ | 140° |
| | Air | ·1357 | ·0127 | 09·35 | ·0771 | 56·85 | 07·18 | 02·17 | | |
| 9 | HBr | ·1366 | ·0113 | 08·27 | ·0730 | 53·46 | 10·62 | 02·35 | ½ | 150° |
| | Air | ·1355 | ·0549 | 40·51 | ·0485 | 35·84 | 28·46 | 12·05 | | |
| 10 | HBr | ·1308 | ·0121 | 09·25 | ·0740 | 56·57 | 07·43 | 01·82 | ½ | 160° |
| | Air | ·1348 | ·0668 | 49·55 | ·0413 | 30·66 | 33·71 | 15·84 | | |
| 11 | HBr | ·1380 | ·0270 | 19·56 | ·0703 | 50·94 | 13·17 | 06·39 | ½ | 170° |
| | Air | ·1390 | ·0919 | 66·11 | ·0281 | 20·72 | 43·77 | 22·34 | | |
| 12 | HBr | ·1378 | ·0561 | 40·71 | ·0477 | 34·65 | 29·67 | 11·04 | ½ | 180° |
| | Air | ·1346 | ·0949 | 70·50 | ·0232 | 17·28 | 47·26 | 23·24 | | |
| 13 | HBr | ·1331 | ·0850 | 63·86 | ·0280 | 21·09 | 43·40 | 20·46 | ½ | 190° |
| | Air | ·1307 | ·0976 | 74·67 | ·0193 | 14·80 | 49·72 | 24·95 | | |
| 14 | HBr | ·1362 | ·0938 | 68·87 | .0232 | 17·08 | 47·46 | 21·41 | ½ | 200° |
| | Air | ·1377 | ·1090 | 79·15 | ·0197 | 14·33 | 50·24 | 28·91 | | |
| 15 | HBr | ·1355 | ·0958 | 70·70 | ·0246 | 18·04 | 46·49 | 24·21 | ½ | 210° |
| | Air | ·1345 | ·1040 | 77·32 | ·0158 | 11·76 | 52·85 | 24·47 | | |

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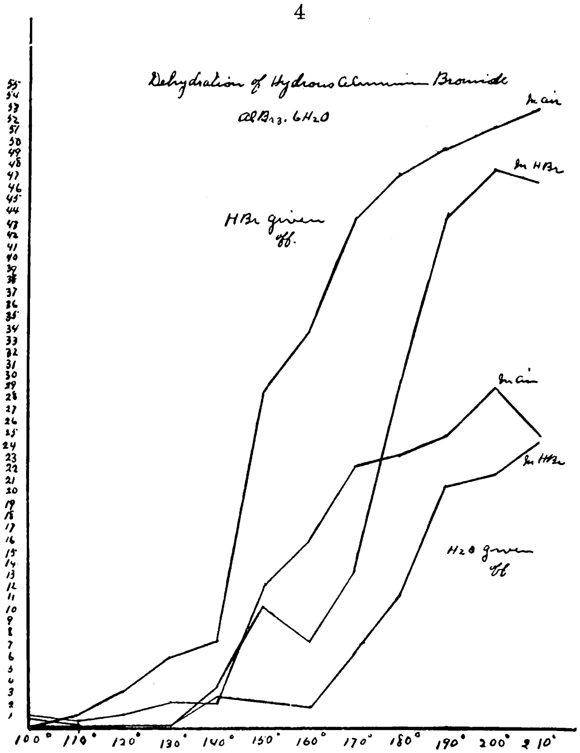
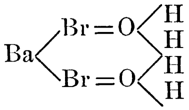


From these results it appears that, at 100° and higher temperatures, hydrous aluminum bromide loses water and hydrogen bromide simultaneously, both in air and in an atmosphere of hydrogen bromide; but that the loss of water, as well as of hydrogen bromide, from the salt is retarded by the atmosphere of hydrogen bromide. At the highest temperature recorded, 210° C. the salt still retained bromine. There is nothing to indicate that any part of the water possesses a different relation to the salt from that possessed by any other part of the water.

### *Discussion of Results.*

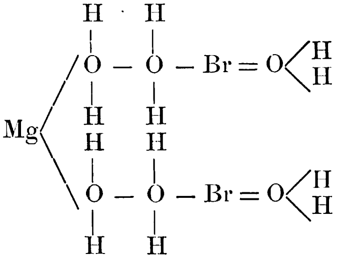
In correlating the phenomena noted, Cushman's hypothesis of inner and outer linkages of water relative to the molecular complex, upon the assumption of quadrivalent oxygen, seems applicable.

Thus the symbol



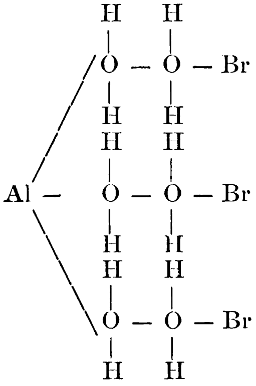
for hydrous barium bromide, showing two molecules of water externally attached, suggests the observed easy removal of all water without simultaneous loss of hydrogen bromide, and indicates, as was observed, that concentration of hydrogen bromide in the system is not likely to affect the course of dehydration.

The symbol



for hydrous magnesium bromide, in which two molecules of water are externally attached and four internally, shows why one-third of the water may be removed at a moderate temperature, without much loss of hydrogen bromide; why the remaining two-thirds of the water require a higher temperature for their removal with simultaneous evolution of hydrogen bromide; and why increase in the concentration of hydrogen bromide in the system retards both the loss of water and hydrogen bromide, after the first third of the water has been expelled.

The symbol



for hydrous aluminum bromide suggests the observed impossibility of evolving water without simultaneous loss of hydrogen bromide, the salt tending on continued heating to go over to the oxide. With a salt showing this constitution the natural effect of the concentration of hydrogen bromide in the system would be to retard the dehydration of the salt, as was observed.

So it appears that the phenomena of dehydration of the hydrous bromides under discussion admit of explanation upon Cushman's hypothesis of the molecular attachment of water within and without the complex.

The author is greatly indebted to Prof. F. A. Gooch for advice and assistance throughout this work.