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CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE EFFICIENCY OF CALCIUM BROMIDE, ZINC BROMIDE AND ZINC CHLORIDE AS DRYING AGENTS.

BY G. P. BAXTER AND R. D. WARREN.

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The problem of the drying of hydrobromic acid gas is one which has frequently been met in this laboratory in the preparation of anhydrous metallic bromides for analysis. Until recently phosphorus pentoxide was used as the final drying agent, but experiments by Baxter and Hines[1] in the drying of hydrochloric acid gas with phosphorus pentoxide have shown that the pentoxide is attacked by the acid gas with the formation of volatil phosphorus compounds, and that therefore there is danger in using this drying agent for hydrobromic acid also. Since hydrobromic acid gas is decomposed by concentrated sulfuric acid, fused metallic bromides seemed to be the most suitable substances for the desiccation of this gas. Hence experiments were carried out with two anhydrous bromides which can easily be prepared in a state of sufficient purity, with the purpose of determining their efficiency as drying agents.

Since phosphorus pentoxide was used to absorb the residual moisture in the gas which had been exposed to the anhydrous bromides, it was not possible to employ hydrobromic acid as the gas to be dried. Instead air was used for this purpose, since the nature of the gas is of no consequence, provided the gas does not combine with the drying agent.

The method was as follows: A measured amount of moist air was passed through a tube containing a layer of crushed fused bromide, and then through a weighed phosphorus pentoxide tube. From the gain in weight of the pentoxide tube and the volume of air passed through the system, the pressure of the aqueous vapor in the air which was in equilibrium with the fused bromide could be determined.

The calcium bromide was made from very pure calcium carbonate which had been precipitated from a solution of the nitrate, and a solution of hydrobromic acid which had been synthesized from pure bromine and hydrogen. The bromine had been twice distilled from a bromide so that it must have been free from chlorine. The slightly acid solution of the bromide was evaporated in a platinum dish, and the residue was

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[1] THIS JOURNAL, 28, 779 (1906).

fused. The mass was next broken into small pieces, and transferred to the drying tube.

The drying tube consisted of a U-tube with arms about 25 cm. in length and about 15 mm. in diameter. About 30 mm. of this tube was filled with the anhydrous bromide. The air was purified and partially dried by passing through a tower filled with beads moistened with a concentrated potassium hydroxide solution. After passing through the tube containing calcium bromide, the air was conducted into a weighed glass-stoppered U-tube containing phosphorus pentoxide which had been resublimed in a current of oxygen. Beyond the weighed phosphorus pentoxide tube was placed a second pentoxide tube to prevent back diffusion of moisture. The current of air was produced by means of an 8-liter aspirator bottle, provided with a thermometer for determining the temperature of the air at the end of the experiment, an open-tube manometer filled with water, and a siphon tube. Fused or ground glass joints were used in the system as far as the weighed phosphorus pentoxide tube.

During an experiment the portion of the tube containing the calcium bromide was immersed in a water thermostat, the temperature of which was kept constant within 0.1°. The pentoxide tube was weighed by comparison with a counterpoise of very nearly equal size, shape, and weight, one stopcock of each tube being open during the weighing. The volume of air passed through the system was determined by measuring the water delivered by the siphon tube from the aspirator bottle.

In each experiment the weighed phosphorus pentoxide tube was attached in place by short, tightly fitting rubber connections and about 8 liters of air were passed through the system. The phosphorus pentoxide tube was then reweighed. From the weight of water was calculated its volume under standard conditions. The volume of air passed through the system was corrected to standard conditions, dry, and the proportion of water vapor by volume was found by dividing the volume of the water vapor by the sum of the volumes of the water and dry air. The pressure of the water vapor was found by multiplying the internal pressure of the system, as determined from the barometric reading and the reading of the manometer in the aspirator bottle, by the proportion of water by volume.

The experiments were varied by passing air which had been previously dried with phosphorus pentoxide through the calcium bromide tube, after the first portions of the calcium bromide had been allowed to take up moisture in the experiments carried out as described above. In this way equilibrium was approached from the opposit direction.

Furthermore, in order to determin whether the drying or saturation of the gas was efficient and whether the absorption of the water in the pentoxide tube was complete, the rate at which the air was passed through the calcium bromide tube was varied from 1 liter per hour to 1 liter per quarter hour. These variations were without very marked effects upon the observed aqueous pressure, although the maximum rate employed gave somewhat lower results, especially when the gas was dried before passing it into the calcium bromide tube.

Morley[1] has shown that phosphorus pentoxide leaves not more than 1 mg. water in 40,000 liters of air. Blank experiments with our apparatus showed a gain in weight of the phosphorus pentoxide tube averaging 0.3 mg., so that the values recorded below represent maxima.

TABLE I.—$CaBr_2$.

Temperature centigrade.	Conditions of experiment.	Time. Hours.	Volume of air under standard conditions. Liters.	Weight of water. Gram.	Volume of water vapor under standard conditions. Cc.	Pressure of water vapor. Mm.
0°	Moist	4	7.1	0.0007	0.9	0.10
	Moist	8	7.1	0.0009	1.1	0.12
	Dry	4	7.3	0.0005	0.6	0.06
	Dry	8	7.0	0.0010	1.2	0.13
	Dry	8	7.2	0.0005	0.6	0.06
					Average,	0.09
25°	Moist	4	7.0	0.0015	1.9	0.20
	Moist	4	7.2	0.0015	1.9	0.20
	Moist	2	7.3	0.0011	1.4	0.14
	Moist	2	7.2	0.0007	0.9	0.10
	Moist	2	7.0	0.0007	0.9	0.10
	Moist	8	7.1	0.0013	1.6	0.17
	Dry	4	6.9	0.0012	1.5	0.16
	Dry	4	7.0	0.0013	1.6	0.17
	Dry	3	7.2	0.0015	1.9	0.21
	Dry	2.5	7.2	0.0005	0.6	0.06
	Dry	2.5	7.0	0.0008	1.0	0.11
	Dry	2	7.0	0.0003	0.4	0.04
	Dry	7	6.9	0.0011	1.4	0.15
	Dry	8	7.0	0.0011	1.4	0.15
			Average, rejecting 2-hour determinations,			0.18
50°	Moist	4	7.1	0.0011	1.4	0.15
	Moist	4	7.1	0.0012	1.5	0.16
	Moist	2	7.1	0.0013	1.6	0.17
	Moist	8	7.1	0.0012	1.5	0.16
	Dry	4	7.2	0.0019	2.4	0.25
	Dry	4	7.1	0.0015	1.9	0.20
	Dry	2	7.1	0.0014	1.7	0.18
	Dry	8	7.1	0.0019	2.4	0.25
					Average,	0.19

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[1] *Am. J. Sci.*, 34, 199 (1881); THIS JOURNAL, 26, 1171 (1904).

A second series of experiments was carried out with zinc bromide, which was prepared by allowing bromine which had been distilled from a bromide to act upon commercial C. P. zinc under water. The solution of the bromide was evaporated and fused in a platinum dish. The experiments with zinc bromide were carried out in the same fashion as in the case of calcium bromide, variations of the same sort being introduced.

TABLE II.—$ZnBr_2$.

Temperature centigrade.	Conditions.	Time. Hours.	Volume of air under standard conditions. Liters.	Weight of water. Gram.	Volume of water vapor under standard conditions. Cc.	Pressure of water. vapor. Mm.
0°	Moist	4	7.2	0.0023	2.9	0.30
	Moist	8	7.4	0.0018	2.2	0.23
	Dry	4	7.1	0.0022	2.7	0.29
	Dry	8	7.2	0.0023	2.9	0.31
					Average,	0.28
25°	Moist	4	7.14	0.0090	11.2	1.23
	Moist	8	7.04	0.0084	10.5	1.12
	Dry	8	6.96	0.0083	10.3	1.12
					Average,	1.16
50°	Moist	8	7.38	0.0484	60.7	6.36
	Moist	8	7.36	0.0476	59.3	6.23
	Dry	8	7.35	0.0357	44.5	4.66*
	Dry	8	7.08	0.0490	61.0	6.42
			Average, rejecting the starred experiment,			6.34

The preceding table indicates that the first hydrate of zinc bromide has an aqueous vapor pressure six times as great as that of calcium bromide at ordinary temperatures, and that the increase in this aqueous vapor pressure with the temperature is very much more rapid than with calcium bromide. Evidently calcium bromide is very much better suited as a drying agent than zinc bromide.

Finally, in order to compare zinc chloride with sulfuric acid and calcium chloride for drying hydrochloric acid gas, similar experiments were made with zinc chloride.

Morley[1] found that sulfuric acid leaves only 0.25 mg. of water in 100 liters of air, while Dibbits[2] found the aqueous vapor pressure of the lowest hydrate of calcium chloride to be 0.29 mm., 2.17 mm., and 3.50 mm. at 0°, 24°, and 30° respectively. Evidently zinc chloride is less well suited for drying hydrochloric acid gas than sulfuric acid, but more so than calcium chloride.

[1] *Am. J. Sci.*, **30**, 141 (1885).

[2] *Z. anal. Chem.*, **15**, 159 (1876).

TABLE III.—$ZnCl_2$.

Temperature centigrade.	Conditions.	Time. Hours.	Volume of air under standard conditions. Liters.	Weight of water. Gram.	Volume of water vapor under standard conditions. Cc.	Pressure of water vapor. Mm.
25°	Dry	4	7.1	0.0066	8.2	0.88
	Moist	4	6.9	0.0063	7.8	0.84
	Dry	8	7.0	0.0064	8.0	0.85
	Moist	8	7.0	0.0063	7.8	0.83
					Average,	0.85
50°	Dry	4	7.05	0.0164	20.4	2.16
	Moist	4	6.90	0.0243	30.2	3.25*
	Dry	8	7.05	0.0115	14.3	1.51*
	Moist	8	6.92	0.0167	20.8	2.24
	Moist	8	6.97	0.0163	20.3	2.18
			Average, rejecting starred experiments			2.19

To summarize the results of this research, the aqueous vapor pressures of the lowest hydrates of the three salts examined are found to have the following maximum values:

	0° Mm.	25° Mm.	50° Mm.
$CaBr_2$	0.09	0.18	0.19
$ZnBr_2$	0.28	1.16	6.34
$ZnCl_2$	..	0.85	2.19

The weights of residual water in one liter of a gas dried at 25° by these salts and by calcium chloride and sulfuric acid are:

	Gram.
$CaBr_2$	0.0002
$ZnBr_2$	0.0011
$ZnCl_2$	0.0008
$CaCl_2$	0.0021
H_2SO_4	0.000003

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 184.]

A SIMPLE CONSTANT-TEMPERATURE BATH FOR USE AT TEMPERATURES BOTH ABOVE AND BELOW THAT OF THE ROOM.

BY J. LIVINGSTON R. MORGAN.

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The apparatus described in this paper is for the purpose of maintaining any desired temperature, from a little above 0° to one in the neighborhood of 90°, with an accuracy of a few hundredths of a degree. The principle of the method of regulating the temperature, in few words, is to deliver to the bath, as it is necessary, water[1] which is either higher or lower in

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[1] Foote (*Z. physik. Chem.*, 33, 740 (1900)) has used this principle in a less con-