4. Lead metarsenate has been made and its physical and chemical properties described.

5. Dilead pyroarsenate has been prepared in crystalline form, and certain of its physical and chemical properties determined.

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THE EFFICIENCY OF CALCIUM CHLORIDE, SODIUM HYDROXIDE AND POTASSIUM HYDROXIDE AS DRYING AGENTS.

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In a recent paper upon the efficiency of certain drying agents, Baxter and Warren[1] make the statement that Dibbits[2] found the aqueous vapor pressures 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. Our attention has been called by Dr. W. F. Hillebrand to the fact that these figures refer to a hydrate containing 26% of water. As we have been unable to discover reliable data upon the drying efficiency of anhydrous calcium chloride,[3] the matter has been investigated experimentally. We have found the efficiency of this salt to be far greater than the above values indicate. In addition we seized the opportunity to test two other common drying agents, fused sodium and potassium hydroxides.

The air current method was employed, the details of the apparatus and procedure being essentially identical with those described by Baxter and Warren. Calcium chloride was prepared in an anhydrous condition by fusion in an open platinum dish.[4] While still warm it was crushed to pieces the size of a small pea and packed in a glass stoppered U-tube about 15 mm. in diameter, the column of salt being about 30 cm. long.[5] In most of the experiments the air was passed over a 20% solution of sodium hydroxide to ensure an excess of moisture before being conducted through the calcium chloride tube. After a considerable amount of moisture had been absorbed by the calcium chloride, in a few experiments the air was first dried by means of concentrated sulfuric acid in order that the equilibrium might be approached from the reverse side. The

[1] THIS JOURNAL, 33, 340 (1911).

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

[3] See however, Marden and Elliott, *J. Ind. Eng. Chem.*, 7, 320 (1915).

[4] The calcium chloride was undoubtedly basic after fusion. It is, however, unlikely that the basic impurity was present in quantity sufficient to affect the results even if of a greater efficiency than the neutral salt.

[5] In the paper by Baxter and Warren it is erroneously stated that the column of salt was 30 mm. long, as in reality it was ten times this length.

results with calcium chloride at 0° and 25° were very consistent and satisfactory, but the first experiments at 50° showed gradually higher values for succeeding experiments. Fearing that the chloride had by this time absorbed so much water that its efficiency had been impaired, the salt was again fused. While the results then became more nearly concordant, irregularities still persisted, until the layer of active salt was doubled to about 70 cm. by inserting a second U-tube containing the fused salt. The results then showed the most satisfactory agreement. In order to find out whether the layer of chloride had been sufficiently long at the lower temperatures, additional experiments, Nos. 4, 5, 13, 14, were carried out at the lower temperatures with the longer layer, with results identical with the earlier ones.

TABLE I.—$CaCl_2$ AS DRYING AGENT.

Number of experiment.	Temperature.	Conditions of experiment.	Liters per hour.	Liters of air. (0°; 760 mm.)	Mg of water.	Cc. of water vapor. (0°; 760 mm.)	Internal pressure of system. Mm.	Pressure of water vapor. Mm.
1	0°	Moist	1.1	5.8	0.41	0.51	770	0.07
2		Moist	1.0	5.8	0.45	0.56	763	0.07
3		Moist	1.2	5.8	0.50	0.62	764	0.08
4		Moist	2.3	5.7	0.50	0.62	750	0.08
5		Dry	1.5	5.8	0.40	0.50	761	0.07
							Average,	0.07
6	25°	Moist	1.3	6.38	1.85	2.30	758	0.27
7		Moist	0.8	5.71	1.93	2.40	761	0.32
8		Moist	0.8	5.82	2.43	3.02	768	0.40
9		Moist	1.0	5.73	2.15	2.67	761	0.35
10		Moist	1.2	5.84	1.97	2.45	770	0.32
11		Moist	2.3	5.78	2.00	2.49	768	0.33
12		Moist	1.0	5.66	2.40	2.99	752	0.39
13		Moist	1.0	5.63	1.90	2.36	746	0.31
14		Dry	2.0	5.67	2.01	2.50	750	0.33
							Average,	0.34
15	50°	Dry	1.2	5.72	8.18	10.17	758	1.35
16		Moist	2.3	5.66	7.96	9.90	752	1.32
17		Dry	1.3	5.76	7.80	9.70	765	1.28
18		Moist	1.3	5.63	8.17	10.16	749	1.35
19		Dry	2.9	5.69	8.60	10.70	751	1.41
20		Moist	0.9	5.59	8.08	10.05	738	1.33
							Average,	1.34

The attempt was made to weigh the phosphorus pentoxide tube in which the water was absorbed to hundredths of a milligram, by using a No. 10 Troemner balance and gold plated weights carefully standardized by the Richards method. No claim is made, however, that the accuracy

is greater than a tenth of a milligram. It was repeatedly shown that the tube remained constant in weight within this amount for periods of fourteen to sixteen hours.

No blank experiments were considered necessary, since in the runs with potassium hydroxide the gain in weight of the tube was scarcely perceptible.

While three points are obviously insufficient to define a curve exactly, since the plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature is very nearly a straight line it seems worth while to point out that the preceding averages can be represented by the modification of the Antoine[1] formula

$$\log \text{v. p.} = 8.614 - \frac{3234}{T + 58}.$$

The desiccating efficiency of sodium hydroxide was determined in the same manner as that of calcium chloride, using the two tubes (70 cm.) of drying agent. The sodium hydroxide was fused in a silver dish and broken up while still warm. Apparently the greater part of the water was absorbed by the first 5 cm. of the hydroxide.

TABLE II.—NaOH AS DRYING AGENT.

Number of experiment.	Temperature.	Conditions of experiment.	Liters per hour.	Liters of air. (0°; 760 mm.)	Mg. of water.	Cc. of water vapor. (0°; 760 mm.)	Internal pressure of system. Mm.	Pressure of water vapor. Mm.
1	0°	Moist	2.0	11.6	0.60	0.75	765	0.05
2		Dry	2.0	11.4	0.35	0.44	755	0.03
3		Moist	1.6	11.3	0.40	0.50	745	0.03
							Average,	0.04
4	25°	Moist	2.0	11.43	2.00	2.49	756	0.16
5		Moist	1.1	5.69	0.90	1.12	752	0.15
6		Dry	2.0	11.43	1.82	2.26	756	0.15
							Average,	0.15
7	50°	Moist	1.4	5.69	6.82	8.48	756	1.13
8		Dry	1.7	11.42	14.07	17.50	761	1.16
9		Moist	1.7	11.55	13.90	17.30	763	1.15
							Average,	1.15

The experimental values may be computed from the expression

$$\log \text{v. p.} = -4.041 - \frac{373.3}{(T - 414)}.$$

Potassium hydroxide was next investigated in the same way. The potassium hydroxide was fused in a silver dish and while still warm was broken into small pieces and transferred to the drying tubes. Two experiments at 25°, and two more at 50°, each involving nearly twelve

[1] *Compt. rend.*, **110**, 632 (1890); **112**, 284 (1891); **113**, 328 (1892); **116**, 170 (1893).

liters of air, gave changes in the weight of the phosphorus pentoxide tube no greater than the error of weighing. Then two experiments at 50°, each extending over three days, were performed. Air was actually passing through the apparatus only during the day; at night all stopcocks were closed.

TABLE III.—KOH AS DRYING AGENT.

Number of experiment.	Temperature	Conditions of experiment.	Liters per hour.	Liters of air. (0°; 760 mm.)	Mg. of water.	Cc. of water vapor. (0°; 760 mm.)	Internal pressure of system. Mm.	Pressure of water vapor. Mm.
1	50°	Moist	2.0	39.9	0.28	0.35	759	0.007
2		Moist	2.3	45.6	0.34	0.42	759	0.007
								Average, 0.007

As pointed out by Morley[1] there is a possibility, in these long experiments, that water diffused through the rubber connections, or was formed by oxidation of the rubber.[2] In view of this possibility the results are to be considered as maxima. No weighable amount of moisture could have passed the pentoxide, since Morley[3] found that phosphorus pentoxide leaves not more than one milligram of water in 40,000 liters of air.

The noteworthy facts shown by the foregoing results are (1) the very considerable temperature coefficients in the case of calcium chloride and sodium hydroxide,[4] and (2) the remarkable efficiency of potassium hydroxide even at 50°. Judging from the temperature coefficients of the other two salts, potassium hydroxide at 25° is fully as efficient as sulfuric acid.

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

	0°. Mm.	25°. Mm.	50°. Mm.
$CaCl_2$	0.07	0.34	1.34
NaOH	0.04	0.15	1.15
KOH	..	..	0.007

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

Substance	$CaCl_2$	$CaBr_2$	$ZnBr_2$	$ZnCl_2$	NaOH	KOH (50°)	KOH[5]	H_2SO_4
Milligrams	0.36	0.2	1.1	0.8	0.16	0.007	0.002	0.003

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[1] *Am. J. Sci.*, **30**, 441 (1885).

[2] Only one very short rubber connection was used in our apparatus before the air reached the phosphorus pentoxide tube.

[3] *Am. J. Sci.*, **34**, 199 (1887); THIS JOURNAL, **26**, 1171 (1904).

[4] Baxter and Warren found similar increments with rising temperature with the salts examined.

[5] Estimated from the temperature coefficient of the other salts.