

ON THE HYDRATION OF CALCIUM BROMIDE AND IODIDE.¹

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THE official calcium bromide of the U. S. P. is intended to be substantially anhydrous, and to contain 99.7 per cent. of pure calcium bromide. Such a salt may be obtained by saturating a solution of hydrobromic acid with pure calcium carbonate, filtering, and evaporating the solution to dryness at a temperature considerably below a red heat (about 360° C.). A solid salt may at first be obtained, containing considerable water, which melts at about 80°-81° C., and in composition closely approximates the formula $\text{CaBr}_2 + 3\text{H}_2\text{O}$. This fused salt continues to lose a small amount of water, even a few degrees above that temperature, so that it is difficult to obtain a fused salt of a definite composition.

When the heat is raised to about 180°-181° C. a greater activity appears to take place in the separation of water, and if the fused mass be cooled at that point, a salt is obtained whose formula would somewhat approximate $2\text{CaBr}_2 + 5\text{H}_2\text{O}$. At a higher temperature the water separates with a kind of effervescence, leaving a spongy, anhydrous mass.

It appears to be probable that a hydration corresponding to $\text{CaBr}_2 + 3\text{H}_2\text{O}$ exists, and may be obtained by very careful fusion at 80° C., while the intermediate one, at about 180° C., may be a mere coincidence, though closely approached by two of the commercial specimens examined.

A similar behavior was observed with *calcium iodide*, made by saturation of hydriodic acid with calcium carbonate. The salt, which fuses below the temperature of boiling water, closely approaches the formula $\text{CaI}_2 + 3\text{H}_2\text{O}$, but cannot well be isolated by fusion, on account of a gradual loss of water, even below 100° C. With a rising temperature the water escapes very slowly and gradually, and towards the end with a slight effervescence, leaving a spongy, anhydrous mass. There was no

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appearance of any definite intermediate stage of hydration, as was observed with the bromide.

Six specimens of calcium bromide, manufactured by different firms, were obtained in the market. They all contain water, but by no means in uniform proportions, and but little calcium bromide can be found which conforms to the directions of the U. S. P. for anhydrous salt. The following is a short résumé of the analysis of the six specimens:

No. 1. (M.)—Dry white powder. When 1.9109 grams were heated for half an hour to 80° C., neither fusion nor loss of weight occurred. When heated till the preparation became spongy and anhydrous, it lost 0.3250 gram, corresponding to 17.007 per cent. of water, and 82.993 per cent. of calcium bromide. When titrated with silver nitrate and potassium chromate as indicator, it showed 82.98 per cent. of calcium bromide.

No. 2. (M. "Dry.")—Dry white powder. 1.032 grams were heated to 86° C. without loss of weight or fusion. When heated to perfect dryness the loss was 0.164 gram = 15.9 per cent. of water, and 84.1 per cent. of calcium bromide. Titration with silver nitrate yielded eighty-four per cent. of calcium bromide.

No. 3. (M. C. W.)—White granules, which melt between 80° and 81° C. When heated to 86° C. for half an hour one gram lost 0.0032 gram = 0.32 per cent. of moisture. When heated to perfect dryness, one gram lost 0.1816 gram = 18.16 per cent. of water and 81.84 per cent. of calcium bromide. In titration with silver nitrate, 0.44 gram of the salt required 36.1 cc. of decinormal silver nitrate = 81.81 per cent. of calcium bromide.

This closely approaches the proportion of $2\text{CaBr}_2 + 5\text{H}_2\text{O}$, which requires 18.34 per cent. of water and 81.66 per cent. of calcium bromide.

No. 4. (R.)—White semi-fused lumps which melt between 80° and 81° C. When heated to dryness, 1.1036 grams lost 0.2349 gram, corresponding to 21.28 per cent. of water and 78.72 per cent. of dry substance. In titration, 0.2493 gram required 19.65 cc. of decinormal silver nitrate, corresponding to 78.6 per cent. of calcium bromide. The composition closely approaches the formula $\text{CaBr}_2 + 3\text{H}_2\text{O}$, requiring 21.27 per cent. of water.

No. 5. (P.)—White granules, melting below 100° C. 0.702

gram heated to dryness lost 0.1325 gram = 18.88 per cent. of water, and 81.12 per cent. of dry substance. Titration showed eighty-one per cent. of calcium bromide. (An approximation to the formula $2\text{CaBr}_2 + 5\text{H}_2\text{O}$, requiring 18.34 per cent. of water.)

No. 6. (P. W.)—White granules and semi-fused lumps. 1.32 grams heated to dryness lost 0.2323 gram = 17.6 per cent. of water, and 82.4 per cent. of dry substance. Titration showed eighty-two per cent. of calcium bromide.

A series of analyses of commercial specimens of calcium iodide gave similar results. The hydration in most cases made a close approach to the formula $\text{CaI}_2 + 3\text{H}_2\text{O}$, which requires 84.465 per cent. of calcium iodide, and 15.535 per cent. of water. No preparation came into my hands showing an intermediate hydration between three molecules of water and the anhydrous state.

The result of the examination is summarized as follows:

No. 1. (M. C. W.)—White, fused lumps. Contain 84.29 per cent. of calcium iodide, and 15.71 per cent. of water.

No. 2. (M.)—Yellowish-brown granules. Contain 83.92 per cent. of calcium iodide, and 16.08 per cent. of water.

No. 3. (R.)—White fused mass. Contains 84.1 per cent. of calcium iodide, and 15.9 per cent. of water.

No. 4. (P.)—Yellowish-brown granules. Contain 85.37 per cent. of calcium iodide, and 14.63 per cent. of water.

No. 5. (P. W.)—White, fused lumps. Contain 84.3 per cent. of calcium iodide, and 15.7 per cent. of water.

Specimens 1, 3, and 5, show a trace of nitrate

From the foregoing it is very probable that a definite hydrate of calcium iodide exists, having three molecules of water, for the deviations from such a formula in all of the commercial specimens examined are not very large.

To reach more conclusive evidence it would be necessary to obtain the salt in definite crystals. Hence, solutions of calcium bromide and calcium iodide were made in water saturated at a temperature of 80°C ., also in alcohol of various degrees of dilution (for a high per cent. alcohol would most likely furnish an anhydrous product). The temperature of the atmosphere being high (30° – 36°C .) artificial refrigeration had to be resorted to.

The result was rather disappointing. The alcoholic solutions remained clear for many hours. From the aqueous solutions crystals of both bromide and iodide were obtained, but of such small size that it was difficult to make out their forms. Those of the iodide were slightly larger and less deliquescent and under the microscope showed rhombic needles and prisms, somewhat rounded, so as to resemble some forms of uric acid.

But they were so difficult to separate from the solution without adhering liquid, that weighing could only be approximate, and most likely would include some liquid as well as the dry substance.

The bromide, on titration, yielded 62.3 per cent. of calcium bromide, which would approximate the formula $\text{CaBr}_2 + 6\text{H}_2\text{O}$, which requires 64.92 per cent. of calcium bromide, and 35.08 per cent. of water.

The iodide yielded 69.9 per cent. of calcium iodide; the formula $\text{CaI}_2 + 6\text{H}_2\text{O}$ would demand 73.11 per cent.

In both salts the adhering liquid would render the result somewhat uncertain, and the yield of dry substance too low.

The evidence thus far is certainly not sufficient to draw definite conclusions, but I believe that the existence of hydrates of the formula $\text{CaBr}_2 + 6\text{H}_2\text{O}$ and $\text{CaBr}_2 + 3\text{H}_2\text{O}$, as well as of the corresponding hydrates of calcium iodide, is very probable.

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A STUDY OF THE CHEMICAL BEHAVIOR OF ARSENOPYRITE.

BY THOMAS MONTGOMERY LIGHTFOOT.

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THE variation in the weathering of pyrite, marcasite, and pyrrhotite, so often to be observed in nature, has already furnished material for several papers on the subject. The consideration of these differences in behavior leads to the question involving the chemical difference between these and allied mineral species. The effect of the electric current on these naturally occurring sulphides and sulpharsenides has already been investigated in this laboratory, but, so far as I am aware, no series of experiments with various oxidants has been recorded. Investigations as to the effect of potassium permanganate on