

### 73. *Potassium Dibromiodide Hydrate.*

By GEOFFREY HERBERT CHEESMAN and JOHN HENRY MARTIN.

As has been pointed out by Cremer and Duncan (J., 1931, 2246), the dissociation pressures given by Ephraim (*Ber.*, 1917, 50, 1069) for potassium dibromiodide are very considerably higher than those measured for the compound prepared in the dry way from potassium iodide and bromine. On the basis of Grace's comment (J., 1931, 594) that Ephraim's high dissociation pressures of potassium triiodide were due to hydration, Cremer and Duncan suggested that potassium dibromiodide also might be hydrated, and quoted an analysis in support of the suggestion.

The only other published analyses are those of Wells, Wheeler, and Penfield (*Z. anorg. Chem.*, 1893, 1, 442), who crystallised their material from water and determined potassium as bromide by heating, and halogens as silver salts, with subsequent conversion into chloride in a stream of chlorine. Their analyses show a considerable amount of free potassium bromide and bromine, and a deficiency in the total amounting to 6.2% which may be attributed to water (1 mol. corresponds to 5.24%).

This has now been confirmed by a complete analysis of the material, showing that potassium dibromiodide crystallises from aqueous solution with one molecule of water; and it has also been shown that the dissociation pressure of this hydrate lies near to the value given by Ephraim.

The analytical method due to Grace (*loc. cit.*), whereby the halogen evolved from the sample heated in a stream of dry air is taken up in hot silver, has been extended by the addition of a tube containing silver iodide, in front of that containing the silver. Both of these tubes are surrounded by small tube furnaces maintaining a temperature of 360°, and are connected by a ground joint. The powdered silver iodide is lightly filled into the tube between several plugs of loose woolly asbestos. The bromine from the sample reacts quite readily and completely with the iodide, and from the loss of mass in this tube the proportion of bromine is readily calculated. The gain in the silver tube represents the iodine in the sample plus the iodine displaced in the iodide tube, which is also calculable. Water is taken up in phosphoric oxide as in Grace's analysis. Care must be taken that the temperature of 360° is not greatly exceeded, as losses are occasioned by the volatility of the silver halides.

This method was tested first by decomposing weighed amounts of potassium bromide with sulphuric acid and manganese dioxide, and

then with potassium dibromiodide prepared by dry methods, and was found to give satisfactory results (Table I).

TABLE I.

No.	KBr, %.	Br, %.	I, %.	H <sub>2</sub> O, %.	Total	
1	37.3	23.8	37.7	1.1	99.9	
2	37.8	23.5	37.7	1.0	100.0	Material taken from stock bottle, no dry- ing precautions.
3	37.7	23.4	37.5	1.2	99.8	
4	37.9	23.4	37.7	1.2	100.2	
5	38.1	23.5	37.6	1.1	100.3	
Calc. for KIBr <sub>2</sub> : KBr, 36.5; Br, 24.5; I, 39.0%.						

The above analyses show how readily the compound tends to pick up water, particularly when it is remembered that 1H<sub>2</sub>O corresponds to only 5%.

A saturated solution of the anhydrous dibromiodide in water was prepared and crystallised by slow evaporation over syrupy phosphoric acid (phosphoric oxide acts too rapidly and good crystals cannot be obtained). By seeding the solution, fine clear crystals up to 7 mm. in length and similar to those sketched by Penfield (*loc. cit.*) were obtained. It was found to be important to keep the enclosure in which the crystallisation was made as small as possible to avoid loss of halogens. In these experiments, in which about 15 g. of dibromiodide were used, a four-ounce, wide-mouthed, stoppered bottle was employed, the phosphoric acid and material being placed in weighing bottles stood inside.

The crystals were drained and left for 3 weeks in a small tube inside a weighing bottle containing the anhydrous compound to remove surplus water, and the analyses shown in Table II were obtained. An analysis of a sample (kindly supplied by Mr. Duncan) which had been dried for several months over the anhydrous compound is also given.

TABLE II.

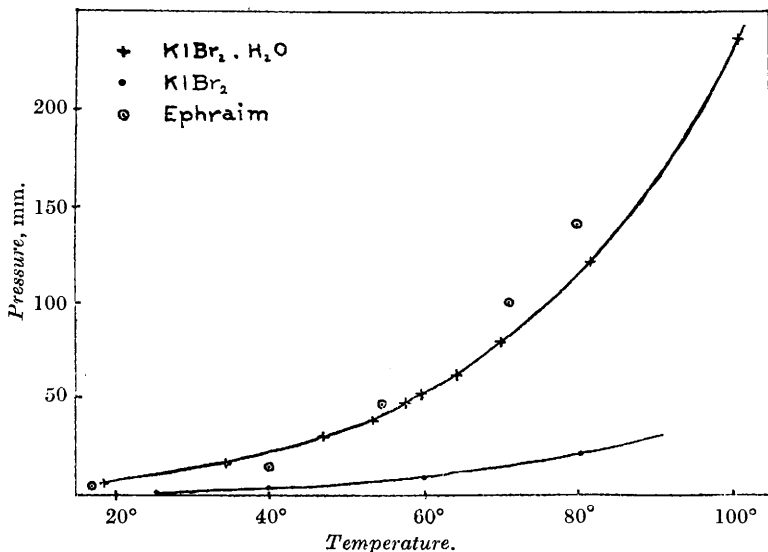
No.	KBr, %.	Br, %.	I, %.	H <sub>2</sub> O, %.	Total	
1	35.5	22.9	36.0	5.4	99.8	Crystal crushed and left over anhydrous com- pound.
2	35.5	22.6	36.1	5.5	99.7	Crystal analysed whole.
3	35.4	23.0	36.5	5.3	100.2	Duncan's sample, small crystals.

Calc. for KIBr<sub>2</sub>.H<sub>2</sub>O: KBr, 34.6; Br, 23.3; I, 36.9; H<sub>2</sub>O, 5.2%.

To confirm the suggestion that Ephraim's high dissociation pressures were in fact due to his use of the hydrate, a sample of the above crystallised material was sealed up in an evacuated glass spring manometer, and a dissociation pressure-temperature curve drawn. This curve is given in the figure, together with Ephraim's

points, and also a curve obtained for the anhydrous compound. Ephraim's points lie near to the former curve, and there seems little doubt that his figures do indeed refer to the hydrated compound, while the dissociation pressure of the anhydrous compound is much lower. The sample in the spring melted quite sharply at  $59^\circ$  to a deep red liquid, solidifying at the same temperature: the dissociation pressure curve shows a break at this point—Ephraim's data are too scanty to reveal this. Recombination appears to occur

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almost instantaneously on cooling, in striking contrast to the case of the anhydrous material, where several days have been found necessary for equilibrium to be reached.

The above study was made in the laboratory of Prof. H. B. Baker, to whom our best thanks are due, and one of us (G. H. C.) is grateful for a Beit Fellowship during the tenure of which this work was carried out.

ROYAL COLLEGE OF SCIENCE,  
SOUTH KENSINGTON.

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