72. *Bromine Hydrate.*

By IVAN WALTER HENRY HARRIS.

LÖWIG (*Pogg. Ann.*, 1829, **16**, 376) first showed that bromine hydrate separated from aqueous solutions of bromine below a temperature of 4°, and gave one analysis of it, leaving its composition doubtful. Attempts to determine this were made by Alexejeff (*Ber.*, 1876, **9**, 1025) and Roozeboom (*Rec. trav. chim.*, 1884, **3**, 84). The former concluded that the substance was the decahydrate, but adduced no analytical data, admitting that the lack of a definite result was due to the loss of bromine from the material even at — 5°. Roozeboom's analyses, made on crystals dried between filter-paper at 4—5°, range from 45·0 to 46·8% of bromine, corresponding to 10·1—10·9 molecules of water (Calc. for $Br_2,10H_2O$: Br, 47·0%).

Giran (*Compt. rend.*, 1914, **159**, 246) examined the melting points in the system bromine–water, and from those data, together with some analyses of crystals separated from mother-liquor in a centrifuge, decided in favour of an octahydrate.

The uncertainty of the composition of the hydrate is due to the difficulty of obtaining dry material without considerable loss of bromine by volatilisation. In the present experiments, a third component, potassium bromide, was added. It was found that bromine hydrate could then exist in stable equilibrium with solutions of bromine and potassium bromide up to concentrations of about 15% of the latter, and its composition could be accurately determined by Schreinemakers's construction method from analyses of solution and wet crystals.

EXPERIMENTAL.

The system potassium bromide–bromine–water was studied at 0°, since the hydrate is not stable above 6·8°. Mixtures of suitable composition were stirred in a closed system. The stirrer was operated by means of a solenoid, controlled by an electrically maintained pendulum, and the vessel containing the mixture was immersed in ice in a Dewar vessel. For comparison, some mixtures were kept in stoppered bottles in an ice-box, and shaken at intervals. The attainment of equilibrium was followed by titration of the iodine liberated from aqueous potassium iodide by weighed portions of solution. It was found that, in the stoppered bottles, about 15 days were required before constancy was established, but in the stirred material only some 5 days were needed. It was necessary to cool the mixtures to about − 15° when first prepared, in order to initiate the separation of the hydrate, as otherwise they remained supercooled for indefinite periods at 0°.

Sampling of the liquids was carried out by means of a pipette with a fine jet which was pre-cooled in a tube immersed in ice. Consistent results showed that a filtering device was unnecessary, owing to the readiness with which the hydrate settled. Samples of wet crystals were taken out on a small glass fork similarly pre-cooled.

Analysis.—Analyses were carried out by a modification of the method devised by Grace (J., 1931, 594) for analysis of polyiodides. Owing to the volatility of bromine at room temperature, it was impracticable to weigh samples of material, for, even when leakage was avoided, the displacement of air by bromine vapour when the material was first put into the apparatus introduced errors of several milligrams. Since, however, all the components of the mixture were determined, it was not necessary to know the weight of the sample independently. In the case of the liquids, a check was obtained by weighing a sample into potassium iodide solution in a weighing bottle (there being no liberation of bromine vapour in this case) and titrating the liberated iodine with *N*/10-thiosulphate.

The apparatus used is illustrated in Fig. 1: *A* is a bent tube with a ground-glass stopper at one end and fitted at the other by a ground joint to the tube *B*, which was packed with fine strips of silver foil and heated to about 340° by an electric furnace *E*. At the other end *B* was connected by short pieces of pressure tubing to two tubes, *F* and *G*, containing phosphoric oxide. In carrying out an analysis, the lower part of *A* was surrounded with ice and water. Samples of liquid or wet solid were quickly placed in *A*, the stopper at *H* was immediately replaced, and a stream of air, dried by passage through concentrated sulphuric acid and a series of phosphoric oxide tubes, was passed *via* the side tube at *H* through the apparatus. *A* was heated, gently at first, to drive off the volatile constituents, leaving the potassium bromide, which was weighed as such. The bromine was weighed as silver bromide in *B*, and the water in *F*. The method gave quantitative results on known mixtures. The potassium bromide showed no tendency to retain traces of bromine. The tendency for moisture to diffuse back against the air stream was overcome by inserting a pear-shaped glass bulb into *A*. This rested on three small glass prongs projecting from the side of the tube and caused the air to pass through a narrow annular space. This also decreased the time taken to carry out an analysis. An accidental increase in the temperature of the furnace surrounding the tube containing the silver foil showed the necessity for keeping the temperature below 420° owing to the volatility of silver bromide at that temperature. There is a possibility of hydrogen bromide being formed, which, on passing over hot silver, would evolve hydrogen, thus leading to low values for the water content. A small quantity of platinised asbestos was therefore placed in *B* to

FIG. 1.

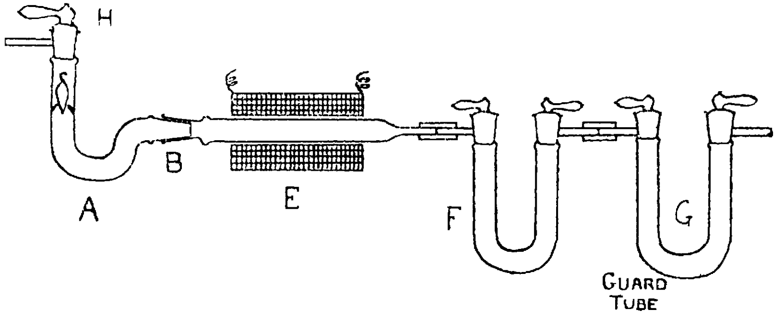
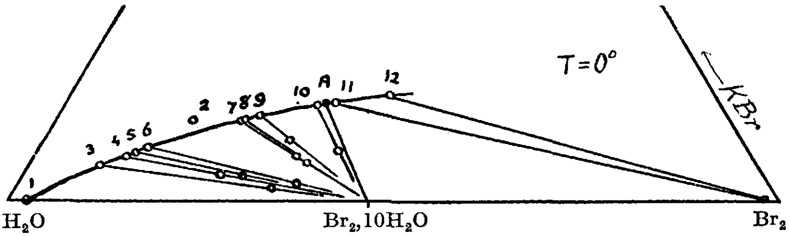


FIG. 2.



ensure that any such hydrogen would be re-oxidised to water. Tests were also made to show that no hydrogen bromide was passing unchanged through the apparatus.

The results obtained are given in the table and shown graphically in Fig. 2, from which the hydrate is clearly indicated as $Br_2,10H_2O$.

The system KBr–Br_2–H_2O *at* 0° *for low concentrations of* KBr.

	Composition of liquid phase.				Composition of moist solid phase.		
No.	KBr, %.	Br_2, %.	H_2O, %.		KBr, %.	Br_2, %.	H_2O, %.
*1	0·00	2·31	97·69		0·00	31·20	68·80
2	12·25	18·00	69·75		No solid present		
3	5·39	9·73	84·88		1·90	33·75	64·35
*4	6·85	12·15	81·00		4·04	26·30	69·66
5	7·25	13·22	79·53		3·85	29·14	67·01
*6	8·20	14·54	77·26		2·62	36·60	60·78
7	12·23	24·77	63·00		5·88	36·40	57·72
*8	12·39	24·97	62·64		7·00	34·55	58·45
9	13·07	26·71	60·22		9·33	32·55	58·12
*10	14·70	32·76	52·54		7·87	39·36	52·77
*11	15·09	35·36	49·55	2 liquid layers	—	—	—
12	16·14	41·95	41·91	,, ,,	0·20	98·00	1·80
13	14·78	34·10	51·12	Invariant *A*; 3 phases present			
14	14·80	34·15	51·05				

* Stirred material.

The invariant *A* corresponds with the separation of liquid bromine. The decahydrate is thus the only hydrate appearing in the system at 0°. The rapid increase in the bromine concentration in the solution with addition of potassium bromide may be due to the formation of polybromide ions (see Boericke, *Z. Elektrochem.*, 1905, **11**, 57).

Summary.

1. The system potassium bromide–bromine–water has been studied at 0°, where bromine hydrate forms the solid phase.

2. It is shown that only one hydrate exists at this temperature, and its composition is $Br_2,10H_2O$.

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