225. *A Solid Polybromide of Potassium.*

By IVAN WALTER HENRY HARRIS.

POLYHALIDES of the alkali metals have been the subject of numerous investigations, and solid polyhalides of cæsium, rubidium, and ammonium, stable at the ordinary temperature, have long been known. Only recently, however, has the existence of solid polyiodides of potassium at 25° been demonstrated (Grace, J., 1931, 594).

The existence of one or more potassium polybromides in solution has been suspected since it was observed that aqueous potassium bromide readily dissolved large quantities of bromine (Löwig, *Pogg. Ann.*, 1828, **14**, 485); and that potassium bromide diminished the colour of aqueous solutions of bromine (Joseph and Jinendradasa, J., 1911, **99**, 274). This was supported by partition and conductivity experiments. A summary of the work already carried out is given by Griffith, McKeown, and Winn (*Trans. Faraday Soc.*, 1932, **28**, 101).

The present research revealed the existence of the solid *compound* $2KBr_6,3H_2O$ from a phase-rule study of the more concentrated solutions in the system potassium bromide–bromine–water at 0°. This may throw some doubt on the validity of the assumption, always made previously, that the Br_3', Br_5', etc., ions are present in greatest proportion in solution.

EXPERIMENTAL.

Mixtures of the desired compositions were kept in well-stoppered bottles in ice and shaken at intervals until equilibrium was attained (approx. 15 days). The chemicals used were of A.R. quality and the potassium bromide was always very finely powdered.

The supercooling effect already briefly discussed for the dilute solutions in this system (Harris, this vol., p. 582) was even more pronounced in the concentrated solutions. In one case, a mixture was cooled in an ice–salt mixture for 2 hours and was shaken vigorously at intervals. It was concluded that a mixture of this composition was completely liquid over a considerable range of temperature. The mixture was stored in ice for 3 weeks, and was then still liquid. On further shaking, however, crystallisation occurred immediately. This can be induced by "seeding" mixtures with a crystal of the polybromide when available, but the difficulty of bringing about the initial separation may account for this polybromide not having been reported previously.

The only modification necessary in the method of sampling and analysing solution and wet crystals already described (Harris, *loc.*

cit.) was a correction for a trace of bromine retained by the potassium bromide even after strong heating. This was determined by washing the residue into aqueous potassium iodide and titrating the liberated iodine with thiosulphate. The correction was always less than 0·05%.

The results are in the following table and the complete system is shown graphically in the diagram.

The system KBr–Br_2–H_2O *at* 0°.

	Composition of liquid phase, %.				Composition of moist solid phase, %.		
No.	KBr.	Br_2.	H_2O.		KBr.	Br_2.	H_2O.
1	14·78	34·10	51·12	Invariant A, 3 phases present.			
2	16·14	41·95	41·91	Two liquid phases.	Almost pure bromine (99·8%) in each case.		
3	17·13	53·84	29·03				
4	16·77	61·60	21·63				
5	15·54	68·87	15·59				
6	13·77	76·28	9·95	Invariant B, 3 phases.	19·68	73·82	6·50
7	13·85	76·25	9·90		17·33	75·02	7·65
8	14·43	75·28	10·29		17·61	74·37	8·02
9	14·60	74·20	11·20		17·73	74·09	8·28
10	16·25	71·06	12·69		19·91	72·33	7·76
11	18·18	67·61	14·21		20·46	70·57	8·97
12	18·63	66·46	14·91		20·87	70·00	9·13
13	22·87	58·51	18·62		22·47	66·86	10·67
14	26·01	54·87	19·12		23·38	66·83	9·79
15	28·17	53·32	18·51		24·99	64·39	10·62
16	29·02	52·85	18·13	Invariant C.	36·43	54·21	9·36
17	29·50	50·30	20·20		62·41	26·59	11·00
18	31·54	34·46	34·00		63·10	18·50	18·40
*19	34·50	0·00	65·50				

Composition of solid from the diagram is Br_2, 73·0; KBr, 22·0; H_2O, 5·0%; *i.e.*, 4·93 Br : 1KBr : 1·5H_2O or $2KBr_6,3H_2O$.

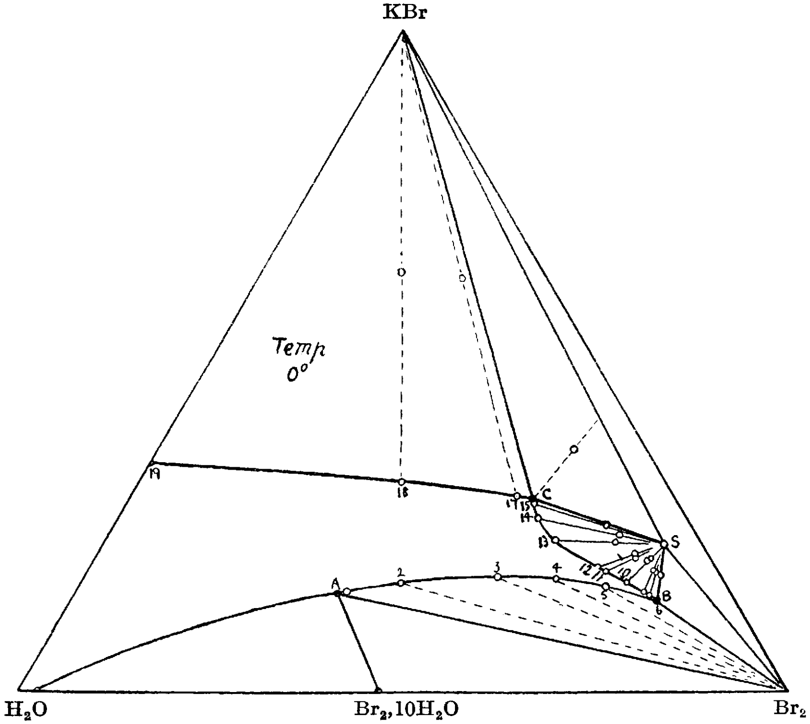
* Determination of Étard (*Compt. rend.*, 1884, **98**, 1432).

The invariant liquid *C* was shown to be in equilibrium with solid potassium bromide and polybromide, for its composition was not altered by addition of either solid. In a similar way, the composition of the liquid *B* was not affected by addition of bromine or polybromide.

The large solubility arc of the material allows of accurate application of Schreinemakers's method of determining the composition of the dry solid, and in this manner its composition is well established. The pure solid was isolated by keeping some of the moist material over a mixture of finely divided potassium bromide and bromine in a stoppered bottle. The method of drying to constant weight was uncertain in this case, owing to the readiness with which the material evolved bromine vapour. It was therefore dried until analysis showed that constant composition was attained. The difficulty of transferring the material without loss of bromine is shown by the low results for it (Found: Br_2, 72·72; KBr, 22·10; H_2O, 5·18.

$2KBr_6,3H_2O$ requires Br_2, 73·26; KBr, 21·80; H_2O, 4·94%). Experience showed that it was far easier to handle the wet crystals without appreciable loss. The *compound* formed long red needles, m. p. (in a sealed tube) 25°.

Several early analyses gave indications of a higher hydrated polybromide corresponding closely to the composition $KBr_7,2H_2O$. Further results showed that this solid did not normally exist at 0°, and these analyses may have been due to the persistence of such a solid which separated at a lower temperature during the initial cooling of the mixtures. This has not been investigated further, owing to difficulties involved in working at a still lower temperature.



The possible existence of an anhydrous polybromide which would be decomposed by water was considered. It was found, however, that dry potassium bromide exhibits no tendency to take up bromine, apart from a preliminary effect due to adsorption and displacement of air by the vapour (1 g. of dry salt exposed for 3 days at 0° gained 0·1 g.; no change after a further 3 days). This confirms the observation of Cremer and Duncan (J., 1931, 1865) that no anhydrous polybromides of potassium exist. This is in marked contrast to the behaviour of the moist material (1 g. of moist salt gained 1·5 g. under similar conditions).

Non-existence of Sodium Polybromide at 0°.—A mixture of finely divided sodium bromide, bromine, and water was prepared from chemicals of the same purity as described above, so that liquid bromine, an aqueous solution, and a solid co-existed. The aqueous solution was thus the highest invariant solution in the system. Analysis of the wet solid showed that it was hydrated sodium bromide. Successful sampling of the liquid for analysis was only achieved by using an asbestos filter, owing to the feathery nature of the solid. Addition of bromine and hydrated sodium bromide did not alter the composition of the aqueous solution.

Summary.

1. The solubility curves in the system potassium bromide–bromine–water have been determined at 0° for the more concentrated solutions.
2. It is shown that a solid potassium polybromide, $2KBr_6,3H_2O$, exists.
3. No anhydrous polybromide exists.
4. Sodium gives no polybromide at 0°.

Thanks are due to Professor H. B. Baker, C.B.E., F.R.S., for his interest in this work; also to the Department of Scientific and Industrial Research for a grant.

ROYAL COLLEGE OF SCIENCE,
LONDON, S.W. 7.

[*Received, March* 17*th*, 1932.]