404. *Cæsium Polybromides.*

By I. W. H. Harris.

Cremer and Duncan (J., 1931, 1857) found no evidence of the existence of any anhydrous polybromide of cæsium other than the tribromide. Rae (*ibid.*, p. 1578) reported the discovery of the tetrabromide, but made only one indirect analysis. Wells and Wheeler (*Amer. J. Sci.*, 1892, **44**, 43) prepared a cæsium pentabromide; the cæsium content, however, is more in agreement with a tetra- than a penta-bromide.

An investigation of the system cæsium bromide–bromine–water has now been made : it fails to reveal any solid higher polybromide and indicates that Wells and Wheeler's pentabromide was probably a mixture of the tribromide and bromine hydrate.

Experimental.

CsCl, extracted from pollucite by Harned and Schupp's method (*J. Amer. Chem. Soc.*, 1930, **52**, 3886), was converted into $CsHSO_4$ by evaporating it with conc. H_2SO_4 in a Pt dish until the excess of acid was removed and the

Table I.

The system $CsBr–Br_2–H_2O$ *at* 25°.

	Composition of liquid phase.				Composition of moist solid phase.				
No.	CsBr, %.	Br_2, %.	H_2O, %.			CsBr, %.	Br_2, %.	H_2O, %.	
1	0·00	3·48	96·52			—	—	—	(*e*)
2	13·53	11·70	74·77		(2′)	32·25	63·28	4·46	(*f*)
3	14·55	12·13	73·32	(*a*)	(3′)	48·17	40·53	11·30	(*g*)
4	14·57	12·12	73·31			—	—	—	
4′	34·77	59·20	6·03	(*b*)		26·20	30·00	43·80	
5	20·14	4·26	75·60			29·30	14·00	56·70	(*h*)
6	55·51	2·15	42·34	(*c*)		60·01	10·05	29·94	(*i*)
*7	55·23	—	44·77			—	—	—	(*j*)
8	32·08	64·42	3·50			46·91	51·70	1·39	(*k*)
9	18·94	81·06	—			—	—	—	
10	18·90	16·35	64·75	(*d*)					

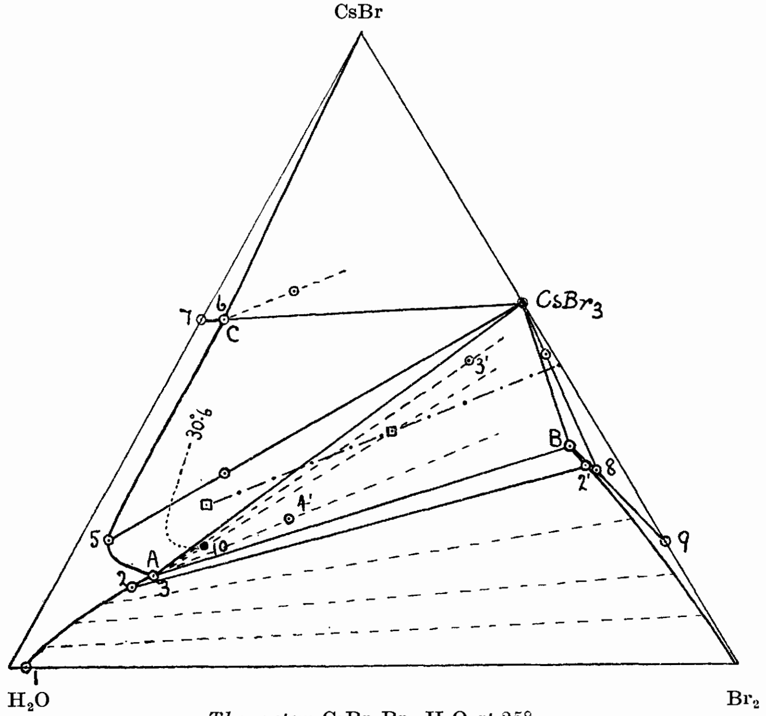
* Determination by Foote (*Amer. Chem. J.*, 1907, **37**, 125).

(*a*) Invariant A. (*b*) Invariant B : heavy liquid. (*c*) Invariant C. (*d*) Invariant A at 30·6°. (*e*) Liquid Br present. (*f*) Two liquids. (*g*) Solid + heavy liquid + aq. liquid. (*h*) $CsBr_3$. (*i*) $CsBr_3$ + CsBr. (*j*) CsBr. (*k*) $CsBr_3$.

product slightly decomposed. All the sulphate was pptd. by a very slight excess of $BaBr_2$ aq., the filtrate concentrated, Br added to the ice-cold solution, and the pptd. $CsBr_3$ filtered off, washed with a little cold H_2O, and heated gently to give pure CsBr (0·2682 G. gave AgBr, 0·2371 g. Calc.: AgBr, 0·2369 g.).

Br of A.R. quality was redistilled from KBr. Mixtures of the required compositions were kept in small well-stoppered bottles immersed to the neck in a thermostat at 25°, and shaken at intervals until equil. was attained (3—4 days). Solids were analysed by the method previously described (Harris, this vol., p. 582), with the modification that samples of solutions were filtered through asbestos. There was no difficulty in analysing solutions rich in Br at this temp. For the dil. solutions, it was more satisfactory to drop a sample of the liquid on to solid CsBr in a weighing bottle. The stable tribromide was formed immediately, thus sufficiently reducing the conc. of Br in the vapour above the solution to eliminate any error in weighing the sample due to displacement of air by Br. H_2O was removed by embedding the bottle in asbestos inside a Ni crucible heated on a sand-bath. The Br in the solution was determined separately by weighing the latter into NH_4I aq.

FIG. 1.



The system $CsBr–Br_2–H_2O$ *at* 25°.

● *Position of invariant liquid at* 30·6°.

⊡ —·— *Rae's result.*

and titrating the liberated I with $(NH_4)_2S_2O_3$, ammonium salts being used to facilitate recovery of the Cs salt. The results are in Table I and shown graphically in Fig. 1. In order to secure comparison with Rae's results, one invariant was also determined at 30° (see Fig. 1).

The results fail to confirm Rae's observation, and repeated analyses of the aq. liquid in a mixture of the same total composition as used by him have failed to agree with his result. The solid stated to be $CsBr_4$ is a paste of $CsBr_3$ and Br.

Repetition of Rae's loss experiment did not reveal any break in the curve corresponding to the comp. of $CsBr_4$, the only break corresponding to $CsBr_3$.

Since Wells and Wheeler (*loc. cit.*) considered that a polybromide other than the tribromide existed at 0°, the system was examined at this temp. Mixtures were stored in ice, and successive titrations of the solutions showed equilibrium to be attained in 15 days. The results are in Table II and Fig. 2.

TABLE II.

The system $CsBr–Br_2–H_2O$ *at* 0°.

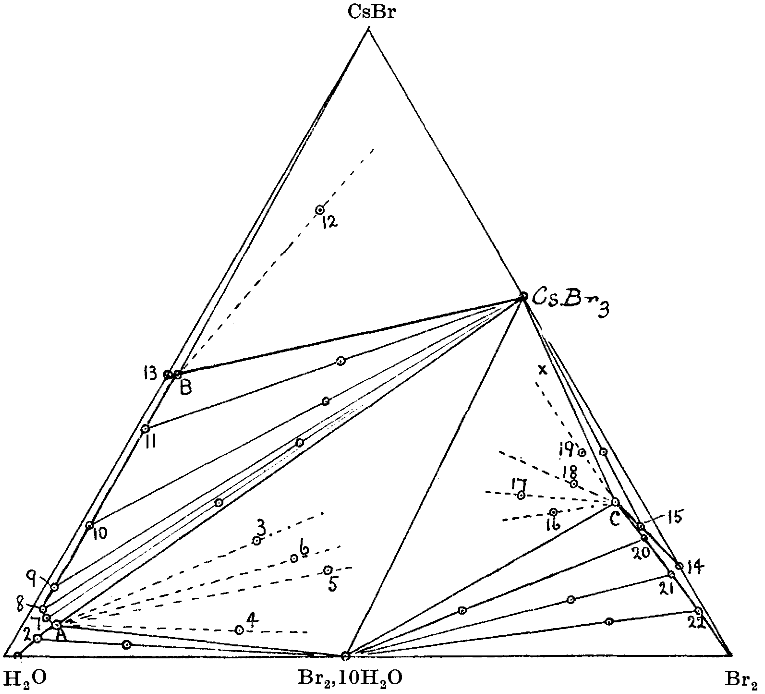
	Composition of liquid phase.				Composition of moist solid phase.			
No.	CsBr, %.	Br_2, %.	H_2O, %.		CsBr, %.	Br_2, %.	H_2O, %.	
1	—	2·31	97·69		—	—	—	
2	2·73	4·25	93·02		1·75	17·1	81·15	(*d*)
3	4·46	5·69	89·85	(*a*)	18·60	24·50	56·90	(*e*)
4	4·46	5·74	89·80		3·63	31·17	65·22	
5	4·48	5·75	89·77		14·11	40·14	45·75	
6	4·46	5·70	89·84		17·11	31·44	51·45	
7	5·07	4·80	90·13		22·74	17·80	59·46	(*f*)
8	6·55	2·97	90·48		34·31	24·94	40·75	
9	10·40	1·66	87·94		—	—	—	
10	20·80	1·12	78·06		40·23	23·35	36·42	
11	38·50	0·83	60·67		47·52	21·45	31·03	
12	45·35	0·81	53·84	(*b*)	71·25	8·41	20·34	(*g*)
13	45·00	—	55·00		—	—	—	(*h*)
14	13·80	86·20	—		—	—	—	(*i*)
15	20·75	77·43	1·85		31·58	67·42	1·00	
16	23·55	73·80	2·65	(*c*)	22·47	65·07	12·46	(*j*)
17	23·45	73·75	2·80		24·01	59·60	16·39	
18	23·60	73·68	2·75		27·50	66·50	6·00	
19	23·55	73·60	2·85		32·33	64·50	3·17	
20	19·14	78·91	1·95		7·70	59·74	32·56	(*k*)
21	13·18	85·61	1·21		8·18	71·32	20·50	
22	6·71	92·63	0·66		4·76	76·45	18·79	

(*a*) Invariant A. (*b*) Invariant B. (*c*) Invariant C. (*d*) $Br_2,10H_2O$ (*e*) $CsBr + Br_2,10H_2O$. (*f*) $CsBr_3$. (*g*) $CsBr_3 + CsBr$. (*h*) CsBr. (*i*) $CsBr_3$. (*j*) $CsBr_3 + Br_2,10H_2O$. (*k*) $Br_2,10H_2O$.

It was suspected that two invariant solutions existed in the vicinity of *A* (Fig. 2), since analyses of different mixtures showed the existence of two solutions differing by about 0·5% in Br content. This difference is outside the range of experimental error, and was eventually traced to incomplete reaction in several mixtures. Temporary cooling to below 0° was carried out in order to initiate the separation of $Br_2,10H_2O$. Even with the hydrate present, however, it was difficult to cause all the Br to react without vigorous shaking. This was probably due to globules of Br being intermixed with a mass of fine crystals of $CsBr_3$. The presence of liquid Br would account for the increased concn. of it in the liquid phase in several cases.

The possibility of the existence of a polybromide which would be decomp. by excess H_2O was examined, but a study of the solutions rich in Br did not indicate the existence of any other compound. However, the results provided fresh evidence in favour of $Br_2,10H_2O$ as the comp. of bromine hydrate, since the solubility of CsBr in Br leads to the existence of a solubility arc with the hydrate as the solid phase.

FIG. 2.



The system $CsBr–Br_2–H_2O$ *at* 0°.

× *Composition of solid isolated by Wells and Wheeler.*

The dark red solid prep. by Wells and Wheeler (*loc. cit.*) and thought to be $CsBr_5$ must have been a mixture of $CsBr_3$ and $Br_2,10H_2O$: it was analysed for Cs only and the presence of H_2O was not suspected. A repetition of their expt. gave a solid with almost the same Cs content as theirs, but analysis by the complete method showed the presence of H_2O (CsBr, 46·07; Br_2, 50·91; H_2O, 3·02%). The presence of $Br_2,10H_2O$ accounts for the rapid loss of Br after removal of adhering solution.

A further indication that $CsBr_3$ is the only polybromide of Cs existing at 0° was obtained by placing a mixture of the tribromide and Br in an isoteniscope immersed in ice-cold H_2O and proceeding as described by Grace (J., 1931, 594). As long as the solid was dark red, the press. recorded was very close to that of Br itself; immediately after the stage at which it appeared quite dry, the solid turned yellow and the v. p. fell rapidly to a press. too small to be measured by this means. No intermediate range of const. press. due to another compound was found.

SUMMARY.

1. The system CsBr–Br–H_2O has been examined at 25° and 0°.

2. The only polybromide of cæsium which exists at both temperatures is the tribromide.

3. The study at 0° confirms the composition of bromine hydrate as $Br_2,10H_2O$.

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