154. *Bromine Chloride Hydrate.*

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THE compound BrCl has been discussed in several recent publications, but almost the only reference to a possible hydrate of it is that by Löwig (*Diss.*, Heidelberg, 1829), who isolated an orange-red crystalline compound, $BrCl,5H_2O$, by mixing chlorine, bromine, and water at about 0°. Bornemann (*Annalen*, 1877, **189**, 183) repeated Löwig's work and concluded that the crystals might only be mixed crystals of the simple hydrates, but that if they were to be regarded as a true compound, this must be $BrCl,10H_2O$.

The present experiments arose from the following observation. Chlorine was passed into liquid bromine under a layer of water. After apparent saturation had been reached, the system was kept for some hours at room temperature, and a large crop of orange-red crystals then separated spontaneously.

At atmospheric pressure, the decomposition temperature of chlorine hydrate is 9°, and that of bromine hydrate is 6°. It was therefore certain that these crystals could not be either of these simple hydrates, but must be either the hydrate of bromine chloride, or, less probably, mixed crystals of the two simple hydrates.

Further experiments made it obvious that chlorine and bromine markedly increase one another's solubility in water, so that water saturated with respect to both halogens must contain a considerable concentration of bromine chloride, and hence it again seemed probable that the crystals mentioned above were of the binary hydrate.

It was sought to establish the composition of the crystals by determining (1) the ratio of the two halogens and (2) the proportion of water.

(1) *Chlorine* : *Bromine Ratio.*—Chlorine was passed into bromine under water at 0° until a large crop of hydrate had separated in the aqueous layer. The water and crystals were decanted from the bromine, and warmed to about 20° to dissolve the hydrate. On being cooled to 14° and inoculated with a few crystals from another preparation, the solution afforded a mass of the orange hydrate. This was rapidly collected on a sintered-glass plate, and part of it, on being dropped into dilute aqueous ammonia at 0°, quietly dissolved without effervescence. The ammonia solution was then boiled, and subsequent titration of the total halogen by means of silver nitrate, combined with a weighing of the mixed silver halide precipitated by an excess of the reagent, afforded the requisite data. The following table shows the results of six such determinations, made upon crops of hydrate separating at 14° or above.

Wt. of halide, g.	Ag in ppt., g.-mol.	Cl, g.-mol.	Br, g.-mol.	Ratio Cl : Br.
0·5052	0·00312	0·001545	0·00157	1 : 1·02
0·7428	0·004452	0·00237	0·002079	1 : 0·877
0·3098	0·00201	0·001424	0·001719	1 : 1·20
0·8884	0·005324	0·002745	0·002579	1 : 0·959
0·4662	0·002854	0·001301	0·001553	1 : 1·19
0·4500	0·00273	0·001127	0·001603	1 : 1·42

The average molecular ratio Cl : Br is 1 : 1·08. The individual determinations deviate considerably from this ratio, but a small error in the analytical procedure produces a relatively large effect on the apparent ratio. As a further test of the constancy of the Cl : Br ratio in the hydrate, chlorine was bubbled through a saturated solution of bromine and chlorine at 14° ; the ratio Cl : Br in the resulting crop of crystals was unchanged. On the other hand, crystals grown just above the decomposition temperature of chlorine hydrate (10—12°) gave irregular analyses :

Wt. of halide, g.	Ag in ppt., g.-mol.	Cl, g.-mol.	Br, g.-mol.	Ratio Cl : Br.
0·9550	0·005634	0·001613	0·004021	1 : 2·5
0·9561	0·00581	0·002408	0·0034	1 : 1·4
1·11580	0·006860	0·002137	0·004723	1 : 2·2
1·6104	0·009558	0·003232	0·006326	1 : 2·0
0·3098	0·00201	0·001424	0·000526	1 : 0·41
0·1242	0·00069	0·0002	0·00049	1 : 2·4

It appears, therefore, that crystals containing bromine and chlorine in equimolecular ratio can always be prepared from aqueous solutions of the two halogens by keeping the temperature sufficiently high, but that near the point at which chlorine hydrate becomes stable they contain excess of bromine and may be mixed crystals of the hydrates of bromine chloride and bromine. The proportion of water present in these crystals was not determined.

(2) *Water Content.*—In the preceding paper, several methods of analysis have been described for the determination of water in chlorine hydrate. Of these, only method III*a* is applicable to the present problem. It is not possible to dry crystals containing both bromine and chlorine in the manner used for chlorine hydrate in method III, so the use of an indicator substance to give an estimate of the uncombined water, weighed along with the undried crystals, is essential. Analytical details were as already described (*loc. cit.*). The values tabulated below were all obtained from crops of crystals grown at 14°.

Wt. of wet crystals, g.	Wt. of water, g.	Wt. of halogens, g.	Wt. of combined water, g.	Ratio, halogen : water.
1·6394	0·7814	0·5334	0·3246	1 : 3·9
1·6052	0·5926	0·7433	0·2693	1 : 4·3
0·5844	0·1850	0·2502	0·1489	1 : 3·82
1·9451	1·3560	0·3610	0·2281	1 : 4·052

The mean ratio BrCl : H_2O is 1 : 4·02, indicating the hydrate $BrCl,4H_2O$. This was an unexpected result, in view of measurements on chlorine hydrate, but it is difficult to attribute the low water content to experimental errors, since all the most probable errors lead rather to high values for water, as in the case of chlorine hydrate. Löwig's estimate of the water present was almost certainly too high, as he had no means of drying the crystals or of estimating the uncombined water in his wet crystals, so his alleged pentahydrate may well have been a tetrahydrate. On the other hand, the present work disagrees with that of Bornemann, who, however, used the same unsatisfactory method of analysis.

The evidence in favour of a compound $BrCl,4H_2O$, therefore, is based upon (1) the constancy of the Cl : Br ratio at 1 : 1 ; (2) the fact that the crystals are stable in contact with water saturated with both halogens for some 10° above the decomposition temperature of the separate hydrates; (3) the formation of a tetrahydrate, as compared with a hexahydrate for the individual elements. None of the above facts, taken separately, would suffice to establish the existence of the compound, but together, they suggest the conclusion very strongly.

If the compound be regarded as a definite entity, a phase-rule consideration of the system bromine–chlorine–water leads to some interesting conclusions. In this three-component system, one may expect only one solid phase to be in equilibrium (except at a unique temperature) with a liquid bromine–chlorine layer, with the aqueous layer, and with the vapour. Further, in such an equilibrium system, the composition of the two liquid layers should be constant at a given temperature. It is possible, of course, that these regularities would, in any case, be disturbed by mixed-crystal formation below a certain temperature, but it is hoped to continue the investigation of this system along the lines here indicated.

Summary.

(1) Although bromine and chlorine hydrates both decompose below 10°, yet a crystalline hydrate containing both halogens can be isolated from aqueous solutions up to 18°.

(2) The composition of these crystals approximates to the formula $BrCl,4H_2O$.

(3) The solubility of bromine in water is considerably enhanced by the presence of chlorine.

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