778. *The Ternary System* $BaBr_2$–$HgBr_2$–H_2O *at* 25°, 10·4°, *and* 4·5°.

By H. J. V. TYRRELL and J. RICHARDS.

Analysis of saturated solutions of mercuric bromide and barium bromide in water, and of the solid phases in equilibrium with such solutions, has shown that at 25° no solid phase other than mercuric bromide and barium bromide dihydrate appears. At 10·4° a solid phase of undetermined composition, containing all three components, appeared, stable in contact with a very narrow range of solutions. At 4·5°, the new phase was more stable, and consisted then of a solid solution of, probably, $BaBr_2,2HgBr_2,7H_2O$ in $BaBr_2,3HgBr_2,8H_2O$.

THE ease with which mercuric bromide, iodide, and chloride dissolve in aqueous solutions of other halides is well known, and the phenomenon has been much investigated. The more concentrated solutions are dense and have a high refractive index and a high dispersion. They have, therefore, attracted some attention as possible materials for use in liquid prisms, mercuric bromide dissolved in a concentrated solution of barium bromide being especially suitable for this purpose (Duclaux and Jeantet, *Rév. d'Optique*, 1938, **17**, 417; Tyrrell and Conn, *J. Opt. Soc. America*, 1952, **42**, 106). The solubility relations in the system barium bromide–mercuric bromide–water have previously been studied only over a limited range of compositions (Herz and Paul, *Z. anorg. Chem.*, 1913, **82**, 431). The present paper describes a more detailed study carried out at 25°, 10·4°, and 4·5°.

TABLE 1. *System at* 25°.

Supernatant liquid		Wet residue		
$HgBr_2$	$BaBr_2$	$HgBr_2$	$BaBr_2$	Solid phase
0·609	0·00	—	—	$HgBr_2$
15·2	8·64	63·2	8·54	
34·5	19·1	66·0	10·1	
44·7	26·0	49·3	22·9	
50·5	25·4	67·4	17·6	
55·1	29·3	62·2	26·5	
55·0	29·9	69·8	20·2	

Supernatant liquid		Wet residue		
$HgBr_2$	$BaBr_2$	$HgBr_2$	$BaBr_2$	Solid phase
55·1	29·5	45·2	39·9	$BaBr_2,2H_2O$
36·0	35·5	15·4	67·1	
16·0	42·7	10·2	60·0	
5·25	47·8	0·00	87·6	
0·00	50·1	—	—	

Other values for the solubility of mercuric bromide in water at this temperature are 0·609 g. per 100 g. of solution (Garrett, see below) and 0·61 g. per 100 c.c. of solution (Herz and Paul, see below). Figures given for the solubility of mercuric bromide in barium bromide by Herz and Paul are expressed in terms of a volume of solution and are not therefore directly comparable with those tabulated.

TABLE 2. *System at* 10·4°.

Supernatant liquid		Wet residue		
$HgBr_2$	$BaBr_2$	$HgBr_2$	$BaBr_2$	Solid phase
0·427	0·00	—	—	$HgBr_2$
20·0	10·1	89·6	1·87	
35·4	19·0	84·6	4·62	
48·8	26·1	61·2	19·7	
53·2	28·7	80·4	12·2	
53·0	29·7	60·0	27·5	Intermediate phase of undetermined and variable composition
53·0	29·6	59·6	27·1	
52·0	30·5	60·5	28·7	
52·0	30·0	58·1	28·8	
52·0	30·5	57·5	29·2	
51·9	30·8	56·6	30·2	
51·8	30·6	58·5	29·5	

Supernatant liquid		Wet residue		
$HgBr_2$	$BaBr_2$	$HgBr_2$	$BaBr_2$	Solid phase
51·8	31·0	6·75	81·4	$BaBr_2,2H_2O$
32·3	35·8	4·12	82·1	
11·6	44·6	5·09	66·9	
0·00	50·2	—	—	

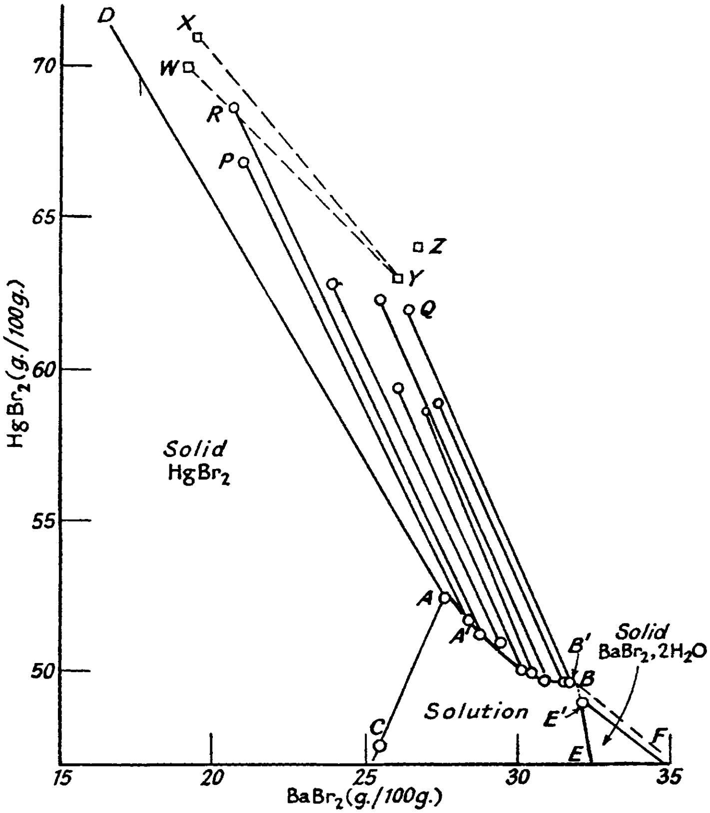
The results are shown in Tables 1, 2, and 3. At 25° no solid phases other than mercuric bromide and barium bromide dihydrate appeared. The solubility of mercuric bromide at this temperature (0·609 g. per 100 g. of solution) agrees with earlier values recorded by Herz and Paul (*loc. cit.*) and Garrett (*J. Amer. Chem Soc.*, 1939, **61**, 2744), while the present figure for the solubility of barium bromide dihydrate is almost identical with that obtained by Kremers (50·14 g. of $BaBr_2$ per 100 g. of solution) (Kremers, *Pogg. Ann.*, 1856, **99**, 47). At 10·4° there was clear evidence of the existence of a fresh solid phase containing all three components, but the range of solution compositions in contact with which this phase was stable was too limited for any real estimate of its composition to be obtained. However, at 4·5° a solid phase containing all three components was found to be stable in contact with a much wider range of solutions. A portion of the isotherm at this temperature is shown in the Figure. The line *A*—*B* represents the compositions of solutions in equilibrium with the new solid phase, the open circles being the experimental points. *A*—*D*, *A*—*C* represent the limits of composition within which solid mercuric bromide is stable, and *B*—*F*, *B*—*E* those within which barium bromide dihydrate is stable. *B* is the intersection of the extended experimental solubility curve *E*—*E'* for barium bromide dihydrate with *A'*—*B'*, the experimental solubility curve for the new phase. *A*—*C* is the solubility curve for mercuric bromide in barium bromide solution. The experimental tie lines running from points on *A'*—*B'* are almost parallel, and it is clear that the new phase consisted of a series of solid solutions. These were decomposed by water, mercuric bromide being formed.

TABLE 3. *System at* 4·5°.

Supernatant liquid		Wet residue		Solid phase
$HgBr_2$	$BaBr_2$	$HgBr_2$	$BaBr_2$	
0·270	0·00	—	—	$HgBr_2$
14·3	8·00	85·4	1·56	
30·1	16·9	79·5	4·97	
45·3	24·2	83·4	7·27	
47·6	25·5	89·2	5·23	
52·4	27·6	82·6	10·0	
51·7	28·3	66·8	21·0	Solid solution of (probably) $BaBr_2,2HgBr_2,7H_2O$ in $BaBr_2,3HgBr_2,8H_2O$
51·2	28·7	68·7	20·7	
51·0	29·4	62·8	23·9	
50·0	30·4	58·6	27·0	
50·0	30·1	59·4	26·0	
49·7	31·7	62·0	26·4	
49·7	30·8	62·3	25·4	
49·7	31·6	58·9	27·3	
49·0	32·1	20·9	64·98	$BaBr_2,2H_2O$
35·9	35·4	10·9	73·0	
21·9	39·7	9·45	67·9	
10·0	45·0	1·64	82·4	
0·00	49·9	—	—	

Application of the phase rule shows that, because of the sharp discontinuities at both *A* and *B*, neither anhydrous mercuric bromide nor barium bromide dihydrate took part in solid solution formation. The direction of the tie lines from *A*—*B* suggests strongly that no lower hydrate of barium bromide (or the anhydrous salt) was involved either (cf. system $HgCl_2$–$SrCl_2$–H_2O; Bassett, Barton, Foster, and Pateman, *J.*, 1933, 151). It seems most probable therefore that solid-solution formation occurred between two salts of the form $BaBr_2,xHgBr_2,yH_2O$ and $BaBr_2,x'HgBr_2,y'H_2O$. On the mercuric bromide-rich side a short extrapolation of *A'*—*P*, or any parallel line through *A*, leads close to *W* ($BaBr_2,3HgBr_2,9H_2O$) or *X* ($BaBr_2,3HgBr_2,8H_2O$): either, on the basis of the data available, could represent the composition of the mercury-rich member of the series of solid solutions reasonably well. A similar extrapolation of *B'*—*Q* leads to *Y* ($BaBr_2,2HgBr_2,7H_2O$). *Z* corresponds to $BaBr_2,2HgBr_2,6H_2O$; this point does not lie on a line parallel to *B'*—*Q* through *B*, and is therefore unlikely to represent a terminal composition for the series of solid solutions. The composition of all solid phases in this region thus lies probably on either *X*—*Y* or *W*—*Y*. The point *R*, representing the composition of a wet residue drained as free as possible from mother-liquor, however, falls on *W*—*Y*. Since it is improbable that this residue contained no mother-liquor at all, the line *X*—*Y* is to be preferred as the most plausible representation of the composition of the solid phases formed in this region, that is, solid solution formation occurred between the probable limits of composition $BaBr_2,3HgBr_2,8H_2O$, and $BaBr_2,2HgBr_2,7H_2O$. Some doubt must remain concerning the proportion of water present; the assumption that the composition must correspond to an integral number of molecules of water of crystallisation may not be correct. Some of the water of crystallisation present may be held interstitially since Tourneux (*Ann. Chim. Phys.*, 1919, **11**, 225) observed that hydrated double salts formed in the system potassium chloride–mercuric chloride–water could be reversibly dehydrated to some degree without change in the appearance of the crystals.

The formation of solid solutions in systems of this kind is not unknown. Tourneux (*loc. cit.*), after careful examination of the system potassium chloride–mercuric chloride–water, concluded that many of the double salts which had been reported were probably solid solutions of $2KCl,HgCl_2,H_2O$ and $KCl,2HgCl_2,H_2O$. Bassett and his co-workers (*loc. cit.*) found evidence of mixed crystal formation between $SrCl_2,3HgCl_2,8H_2O$ and $SrCl_2,2H_2O$, though the evidence for the participation of the latter salt is not especially convincing. The appearance of new phases at temperatures below room temperature has also been observed in related systems; for example, Contet (*Compt. rend.*, 1943, **217**, 277) isolated double salts of sodium and mercuric bromides at temperatures below 15°, and Foote and Bristol (*Amer. Chem. J.*, 1904, **32**, 246) showed that the salt $BaCl_2,3HgCl_2,6H_2O$ is not formed above 17·2°. A bewildering variety of hydrated double salts containing mercuric halides is reported in the older literature (Mellor, " Treatise on Theoretical and Inorganic Chemistry," Longmans, Green and Co., London, 1923, Vol. IV), and it seems possible that many of these may also be solid solutions, not more than one or two genuine new phases appearing in each system.



System $BaBr_2$–$HgBr_2$–H_2O.
Portion of isotherm at 4·5°.

There is, at present, little evidence concerning the nature of the new solid phases occurring in these systems containing mercuric halides. Dilute solutions of mercuric halides in aqueous solutions of other halides contain ions of the types HgX_3' and HgX_4'' (X = halogen) as the principal complex anions (Bethge, Jonevall-Westoo, and Sillén, *Acta Chem. Scand.*, 1948, **2**, 828) (Richards, Thesis, Sheffield, 1952), and it is possible that these exist in the solid phases formed from these systems. The whole problem requires further study beyond the scope of the present investigation.

EXPERIMENTAL

Mercuric bromide (B.D.H., Technical) was purified by a single sublimation. Barium bromide dihydrate (B.D.H.) was recrystallised twice from water. Determination of the total bromine content of the purified salts by Friedheim and Meyer's method (see Sutton, "Volumetric Analysis," J. and A. Churchill, London, 12th Edn., 1935, p. 254) showed that they were better than 99·8% pure.

Suitable mixtures of the three components were prepared at temperatures sufficiently above the working temperature to ensure complete solubility. These were then kept at the desired temperature in a thermostat controlled to $\pm 0{\cdot}1°$ In work below room temperature, heat was extracted by means of an Electrolux refrigeration unit (Type 11 A.1) from the thermostat at such a rate that the thermostat-heater could maintain the bath at the desired temperature. The values of T used (other than 25°) were those which proved convenient to maintain in the desired temperature range.

Preliminary experiments showed that 3—4 days were sufficient for equilibrium to be reached. At the end of this period, as much as possible of the supernatant liquid was removed from the solid by suction through a No. 4 filter stick without removal of the specimen from the thermostat. A weighed sample of the wet residue was dissolved in water, or in dilute sodium chloride solution if the mercuric bromide content were high, and both this and the supernatant liquid were analysed gravimetrically. The mercury was first precipitated as sulphide, the solution filtered, and the barium determined as sulphate. This method of analysis was checked against a complete range of mixtures of barium bromide and mercuric bromide and the experimental error found not to exceed $\pm 0{\cdot}3\%$ for either salt.

Results.—All the figures tabulated represent grams of anhydrous salt per 100 g.

THE UNIVERSITY, SHEFFIELD, 10.

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