

CCCLXXXIX.—*A Phase Rule Investigation of Cupric Bromide in Aqueous and Hydrobromic Acid Solutions.*

By SYDNEY RAYMOND CARTER and NORMAN JOSEPH LANE  
MEGSON.

APART from the desirability of acquiring accurate data for the solubility of copper bromide, a number of interesting problems arise concerning its hydrates and hydrobromides, as well as the remarkable colour effects which are observed in hydrobromic acid solutions containing cupric salts. From its heat of formation, Bodländer (*Z. physikal. Chem.*, 1898, **27**, 61) has calculated the solubility of cupric bromide in water as 1.3 equivs. per litre, but this value, which presumably refers to ordinary temperatures, is necessarily only approximate and has not yet been verified.

The salt is known in the anhydrous form and as a tetrahydrate,

the former being obtained by evaporation of solutions on the water-bath, and the latter crystallising as green needles from solutions at about  $0^{\circ}$ ; Kurnakow and Sementschenko (*Z. anorg. Chem.*, 1899, **19**, 337) give  $29.0$ — $30.5^{\circ}$  as the transition temperature of the system. The tetrahydrate has no analogue in cupric chloride, the stable variety of which is  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . Löwig ("Das Brom und seine chemischen Verhältnisse," 1829) is said to have obtained  $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$  by evaporation of solutions of cupric bromide, but Berthémot (*Ann. Chim. Phys.*, 1830, **44**, 386), although usually credited with preparing greenish-yellow needles of the same salt, gives no analyses.

Cupric bromide gives a deep violet coloration with hydrogen bromide, which is attributed by Sabatier (*Compt. rend.*, 1894, **118**, 1260) to a hydrated hydrobromide; he prepared this salt in an unstable condition by passing hydrogen bromide into saturated cupric bromide solution, and although analysis gave  $3\text{CuBr}_2 \cdot 2\text{HBr} \cdot 6\text{H}_2\text{O}$ , he considered that, owing to instability, it was really represented by  $\text{CuBr}_2 \cdot \text{HBr} \cdot 2\text{H}_2\text{O}$ . Dilution tended to destroy the colour, but if the dilution had not been carried too far heating restored it.

Other bromides (*e.g.*, those of potassium, sodium, calcium, and especially lithium) also give this colour with cupric bromide, and Kurnakow and Sementschenko (*loc. cit.*) have isolated a compound  $\text{CuBr}_2 \cdot 2\text{LiBr} \cdot 6\text{H}_2\text{O}$ . Moreover, cupric chloride and sulphate give a similar colour reaction with hydrobromic acid.

Weinland and Knöll (*Z. anorg. Chem.*, 1905, **44**, 116) prepared black, hygroscopic needles, to which they assigned the formula  $\text{CuBr}_2 \cdot \text{HBr} \cdot 10\text{H}_2\text{O}$ , by leaving a solution of cupric bromide in 40% hydrobromic acid in contact with the product of the action of hydrogen bromide on molybdenum trioxide; if the molybdenum compound was omitted, cupric bromide was the sole product.

Since Foote (*J. Amer. Chem. Soc.*, 1923, **45**, 663), from a study of the system cupric chloride–hydrogen chloride–water, had found  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  to be the only stable solid phase at  $25^{\circ}$ , whereas at  $0^{\circ}$ , in high concentrations of acid, the compound  $\text{CuCl}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$  existed in addition, we undertook a similar study of the bromine analogues in order to gain information on the various points raised in the foregoing discussion.

#### EXPERIMENTAL.

*Materials.*—Cupric bromide was used in the anhydrous form, but since it was liable to contain a small percentage of cuprous bromide, it was purified by oxidation with hydrogen peroxide, or by recrystallisation.

The hydrobromic acid for the weaker solutions was approximately

6*N*; frequently, however, higher concentrations were required, in which case the gas was prepared by the action of bromine on a solution of naphthalene in xylene (Kastle and Bullock, *Amer. Chem. J.*, 1896, **18**, 105) and purified by red phosphorus suspended in concentrated hydrobromic acid. The purity of the gas was tested by repetition with it of several solubility determinations already obtained by the use of the aqueous hydrobromic acid, and in all cases identical results were obtained.

*Analytical Methods.*—Copper was estimated volumetrically by titanous chloride, standard ferric alum and a large excess of 10% potassium thiocyanate being used as indicator. The latter contained hydrochloric acid (about 1*N*) to stabilise the cupric and ferric thiocyanates formed, as recommended by Emmett (J., 1927, 2059). Bromide was estimated by Volhard's method. Estimations of the radicals in trustworthy specimens of cupric bromide were quite concordant, and showed that these methods were accurate to within 1 part in 300 or 400 parts.

*Solubility Apparatus.*—In view of the high solubility of cupric bromide in water, it was desirable to use fairly small quantities of solution. Accordingly, a solubility vessel was devised in which the lower portion was narrow (2.5 cm. diameter; capacity 40 c.c.), whilst the neck was wide enough to take a rubber bung carrying a mercury-sealed stirrer and a sliding glass stopper. A small glass cup was sealed on to the shaft of the stirrer to prevent ground glass and vaseline lubricant falling into the mixtures.

The sliding stopper was used for inserting a tube for the removal of the liquid-phase samples through small sintered-glass filters, into either a pipette or a weighing bottle. The collecting apparatus was suitably water-jacketed at the appropriate temperature when necessary. An approximate density determination of the liquid was obtained at this stage by collecting a further sample in a small pycnometer having a capacity of about 1.0 c.c. The solid phase was finally examined by draining away the remaining liquid and removing a specimen of the moist solid by a flattened glass spatula. The solubility mixtures were usually stirred for 7—8 hours, and this period was shown to be ample for the attainment of equilibrium.

#### *The System CuBr<sub>2</sub>-H<sub>2</sub>O.*

Solubility determinations (Table I) were made at a series of temperatures ranging from 0° to 50°, the solid phase being examined in each experiment. The results are stated as g. of anhydrous CuBr<sub>2</sub> per 100 g. of solution, and are shown graphically in Fig. 1.

Examination of these figures in conjunction with the graph shows two features of interest. (1) First, the solubility of cupric

TABLE I.

Temp.	CuBr <sub>2</sub> , %.	Appearance of solid phase.	Temp.	CuBr <sub>2</sub> , %.	Appearance of solid phase.
0.0°	51.8	Green needles in deep brown liquid.	20.0°	55.9	Black rhomboids in deep brown liquid.
5.75	52.8		25.0	55.8	
9.9	53.7		30.1	56.1	
15.0	55.0		34.8	56.0	
		(Metastable state)	50.0	56.8	
			0.0	*55.7	

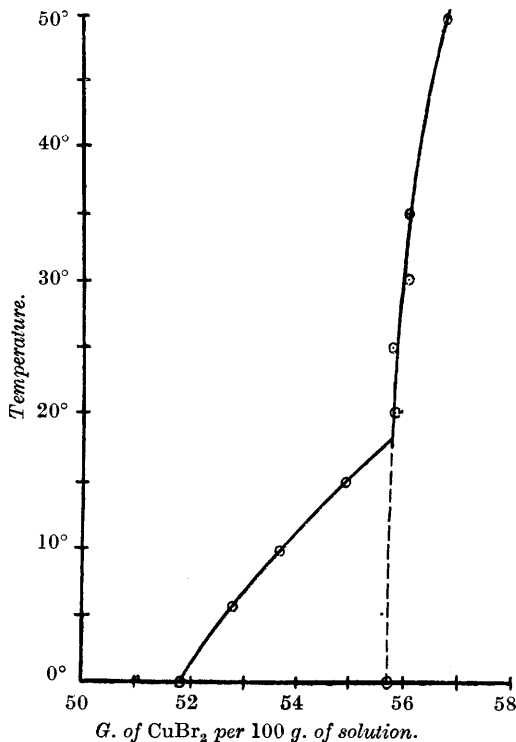
\* This value was obtained by stirring only a slight excess of cupric bromide with water for 5½ hours at 0°, a supersaturated solution being produced.

bromide is considerably greater than the value given by Bodländer (*loc. cit.*): the saturated solution has  $d_{4}^{20}$  1.84 (see below), giving the solubility of the anhydrous salt as 1030 g. or 9.2 g.-equivs. per litre. (2) Secondly, there is a distinct break in the curve between 15° and 20°, indicating some change in the solid phase present, and corresponding with the difference in crystalline form noticed under the microscope (see Table I).

It was considered that the green needles represented the tetrahydrate described by several workers (*e.g.*, Sabatier, *Bull. Soc. chim.*, 1894, **11**, 677). This was confirmed by draining and drying a sample as rapidly as possible at a low temperature. It was a bright olive-green solid (Found: CuBr<sub>2</sub>, 75.85. Calc. for CuBr<sub>2</sub>.4H<sub>2</sub>O: 75.63%), darkening on keeping for a few days at room temperature.

On drying a sample of the black rhomboidal crystals on a porous tile and filter paper at room temperature, a solid was obtained

FIG. 1.



apparently identical with the anhydrous cupric bromide (Found :  $\text{CuBr}_2$ , 99.9%). The lower portion of the curve therefore represents the solubility of  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$  in water, whilst the upper portion gives the solubility of anhydrous  $\text{CuBr}_2$ . The latter is peculiar in that it has little or no temperature coefficient over the ranges  $0-18-25^\circ$ , and only a slight positive one from  $35^\circ$  to  $50^\circ$ .

The break in the curve at  $18.0^\circ$  obviously corresponds to the transition temperature of the hydrated salt; since this value is about  $12^\circ$  below that given by Kurnakow and Sementschenko (*loc. cit.*), various methods were adopted to substantiate it.

*The Transition Temperature of  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O} \rightleftharpoons \text{CuBr}_2 + 4\text{H}_2\text{O}$ .*

Experiments with the dilatometer indicated that the transition temperature lay between  $21^\circ$  and  $14^\circ$ , but owing to considerable supercooling, the method was unsuitable for more exact values.

A thermometric method gave more information, since the heating and cooling curves exhibited breaks at  $19.8^\circ$  and  $16.2^\circ$ , respectively, indicating a transition temperature of approximately  $18^\circ$ . Several difficulties prevented this determination from being completely successful, however, the chief being the consistency of the solid, which rendered efficient stirring almost impossible.

A more accurate value was obtained by using a modification of the thermometric method, due to Richards (*Z. physikal. Chem.*, 1898, **26**, 690). A specimen of the tetrahydrate was prepared by intimately mixing 12 g. of the recrystallised salt with the theoretical amount of water (4 g.) and cooling the mass in ice with continuous stirring until it became nearly solid. The mixture was drained on porous plate, and allowed to dry in a closed vessel below  $10^\circ$ . The hard green cake so produced showed the characteristic green needles of the tetrahydrate under the microscope, and since analysis indicated almost 100% of that salt, it was used without further purification.

About 12 g. of this salt were introduced into a test-tube fitted with thermometer and glass stirrer, and contained in a wider tube, leaving an annular air space of about 3 mm. The whole was placed in a water-bath at  $19.5^\circ$ , and the inner tube removed and dipped in the warm water until partial melting of the contents occurred; it was then wiped dry, replaced in the jacket, and allowed to stand in the bath. On stirring, the temperature of the mixture fell from  $18.5^\circ$  to  $17.97^\circ$ , where it remained constant for 45 minutes. It then rose slowly to  $18.08^\circ$  after falling to  $17.90^\circ$ , and finally fell with the temperature of the outer bath. The value  $17.97^\circ$  was therefore taken as the transition temperature of the system.

No evidence was found to support the existence of  $\text{CuBr}_2 \cdot 2\text{H}_2\text{O}$  either microscopically or from an examination of the solubility curve. The published analyses of this substance by previous authors were possibly carried out on samples of  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$  which had effloresced.

*The System  $\text{CuBr}_2\text{-HBr-H}_2\text{O}$  at  $25^\circ$ .*

This system was investigated in the hope of elucidating the constitution of the compound prepared by Sabatier (*Compt. rend.*, 1894, **118**, 1260), and also of obtaining some evidence as to the cause of the violet colour produced by strong hydrobromic acid solutions and copper salts.

Various mixtures of hydrogen bromide in water were stirred with cupric bromide for 7—8 hours in the solubility bottle at  $25^\circ$ , and samples of the liquid phase and of the moist solid were then collected and analysed, the results being given in Table II and plotted

TABLE II.

Mixture.	$d_4^{25}$ *	Liquid phase.		Moist solid phase.	
		$\text{CuBr}_2$ , %.	HBr, %.	$\text{CuBr}_2$ , %.	HBr, %.
1	1.84	55.8	—	100	—
2	1.82	52.3	2.9	80.8	1.4
3	1.78	48.3	6.3	—	—
4	1.73	43.2	10.6	81.8	3.8
5	1.69	37.6	15.4	—	—
5a	1.68	37.0	15.8	81.5	5.0
6	1.65	32.9	19.4	82.2	5.1
6a	—	32.8	19.7	—	—
7	1.63	26.9	26.0	69.1	10.9
8	1.64	25.9	26.9	76.7	8.4 †
9	1.65	23.1	31.9	73.6	11.3
10	1.68	22.2	34.6	—	—
10a	1.68	21.8	35.0	75.1	11.6
11	1.72	20.4	39.1	78.4	10.6
12	1.74	19.2	42.1	75.4	12.6
13	—	18.5	43.6	62.3	19.8
14	1.79	15.8	48.0	79.4	11.1 ‡
15	—	15.1	48.8	—	—
16	—	11.8	53.5	58.9	25.1
17	—	10.8	54.7	—	—
18	1.83	7.7	59.3	51.4	30.7

Mixtures 1—7 have  $\alpha\text{-CuBr}_2$  as the stable solid phase.

Mixtures 8—18 have  $\beta\text{-CuBr}_2$  as the stable solid phase.

\* Under the microscope the solid phase appeared as black rhomboids.

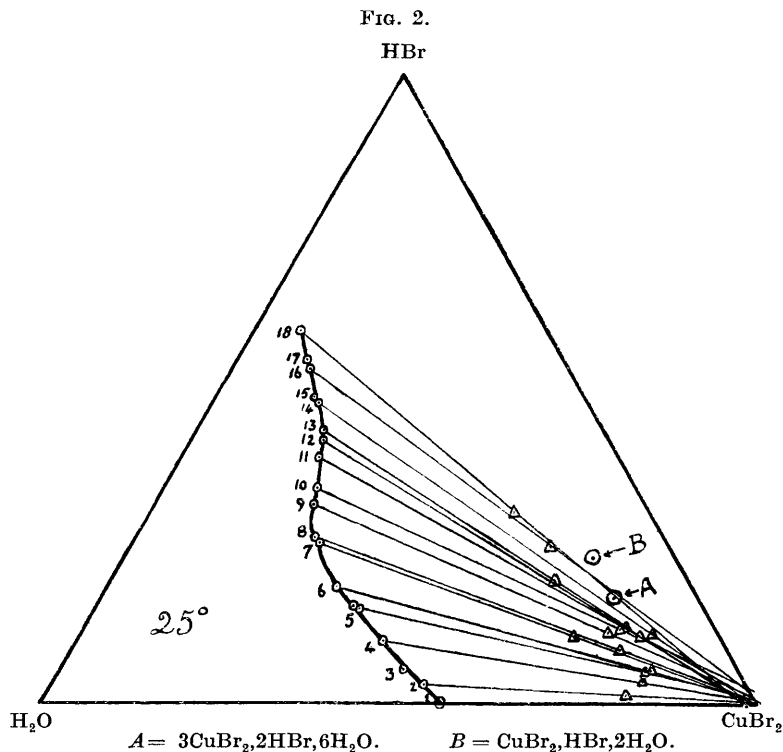
† Under the microscope the solid phase appeared as rhomboids mixed with much amorphous solid.

‡ Under the microscope the solid phase appeared as small, black, non-crystalline particles.

graphically in Fig. 2. From the compositions of the moist residues, those of the pure solid phases were deduced by Schreinemaker's

method (*Z. physikal. Chem.*, 1893, **11**, 76), and the experimental values all pointed consistently to anhydrous cupric bromide as the solid in equilibrium throughout the whole range of acid solutions.

In order to obtain solubilities in high concentrations of acid, a saturated solution of hydrogen bromide at 25° was prepared by the method previously described. Attempts were made to move still further along the curve by passing hydrogen bromide into various



solutions of aqueous cupric bromide, but these were only successful in special circumstances. When these high concentrations of acid were being dealt with, much fuming took place, and as a precaution, water was initially placed in both weighing bottles to prevent loss of the gas from the samples of phases extracted.

The solubility of the cupric bromide is seen to diminish with increasing concentrations of hydrobromic acid, falling from 55.8% to 7.7% with increase of acid from 0% to 59.3%. The solubility curve shows only one break (at Mixture 7), and the solid phase in equilibrium with the solution is in every case pure cupric bromide.

The latter fact had already been foreshadowed for low concentrations of acid by the results from the two-component system.

The density of the solution shows no marked break, but on the other hand has a definite minimum. It descends smoothly from 1.84 to 1.63, then rises regularly again to 1.83. Mixture 7, where the break in the curve occurs, in addition to possessing the minimum density of 1.63, has other important features of interest, first, in relation to the colour of the solution, and, secondly, in connexion with the form of the solid phase.

(1) When hydrogen bromide was introduced in small quantities into the deep brown saturated solution of the copper salt, a violet tinge was imparted to the solution, gradually increasing in intensity with rise in concentration and masking the brown colour. When the concentration of the acid indicated by Mixture 7 was reached, all traces of brown disappeared, and the solution assumed a bright violet colour, which persisted in an intensified degree with increase of acid. In thick layers, these solutions were almost opaque.

(2) Microscopic examination of the solid phase at low concentrations of hydrogen bromide showed black, rhomboidal crystals in a brown or violet-brown solution. These persisted in concentrations of acid up to 26% (Mixture 7) and to a small extent to Mixture 8, after which no definite crystalline form for the solid could be obtained, in spite of many attempts.

Since, throughout the curve, the stable solid phase is anhydrous cupric bromide, it seems probable that the break at Mixture 7 must correspond to a change in the form of that salt. For convenience, these two forms may be designated  $\alpha$ -CuBr<sub>2</sub> and  $\beta$ -CuBr<sub>2</sub>, the former being crystalline, and the latter existing in a non-crystalline form in high concentrations of hydrobromic acid.

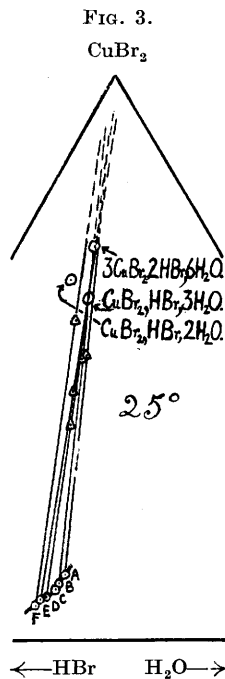
*The Different Forms of Cupric Bromide and the Colours of their Solutions.*—It will be noted that the ranges of existence of the brown and of the violet-coloured solutions coincide approximately with the ranges of existence of the  $\alpha$ - and  $\beta$ -salts respectively, and it might be thought that the violet coloration is associated in some way with the  $\beta$ -form. The coincidence may be merely accidental, but, on the other hand, it is well known that a change in the solid phase leads to a distinct change in the physical properties of the saturated solution in equilibrium with it. There are very few data in other systems to test whether this principle holds in the case of modifications of the same substance with regard to the colour of their solutions, but it may be mentioned that the various acid ferric phosphates are associated with solutions having different colours (J., 1923, 123, 2231).

The changes in colour which salt solutions undergo as the result



of alteration of temperature or the addition of acids or other salts have been extensively studied by Donnan, Sidgwick, Ostwald, and others (for references, see J., 1910, 97, 957), and they can usually be explained by considerations of hydration, ionisation, or complex formation.

*The Possibility of Complexes of Cupric Bromide and Hydrogen Bromide.*—Since one of our main objects was the investigation of



of the possible solid phases, we thought it of interest to seek evidence of complex acid salts which might exist in the solid state. Examination of the solubility curve shows no indication of a stable solid phase having either of the formulæ put forward by Sabatier to represent the composition of the compound prepared by him (see points A and B, Fig. 2). An attempt was made to repeat his experiment of passing hydrogen bromide into a saturated solution of cupric bromide, and the mixture was allowed to cool before being stirred in the thermostat. A modification was also introduced by cooling the solution during the actual passage of the gas. In each case, after stirring for 7—8 hours, the points obtained lay on the solubility curves (14, 16, and 17) and had anhydrous cupric bromide as their stable solid phase.

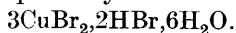
Attempts were also made to obtain analyses before stirring, by draining samples of the solid immediately after preparation by the above method, in a closed vessel, until apparently dry. Very inconsistent results were obtained, varying from practically pure CuBr<sub>2</sub> to a compound having the formula CuBr<sub>2</sub>.HBr.3H<sub>2</sub>O. The substance seemed, therefore, both from its appearance while draining (during which it apparently lost water) and from the analysis, to be extremely unstable.

*Metastable Portion of System CuBr<sub>2</sub>-HBr-H<sub>2</sub>O at 25°.*—Some determinations were carried out by stirring mixtures obtained as above for short periods of from 1—4 hours at 25° in the hope of gaining evidence of a complex solid phase before the latter had time to break up. Table III and Fig. 3 illustrate the results obtained in these circumstances, the solid phase appearing under the microscope as very irregular particles having slight and indefinite crystalline form.

TABLE III.

Mixture.	$d_{4}^{25^{\circ}}$ .	Liquid phase.		Moist solid phase.	
		CuBr <sub>2</sub> , %.	HBr, %.	CuBr <sub>2</sub> , %.	HBr, %.
A.	1.81	15.3	49.5	52.6	27.9
B.	1.83	14.1	51.1	52.0	28.8
C.	1.83	13.0	52.4	—	—
D.	1.83	11.9	54.3	41.1	36.0
E.	1.83	11.5	55.3	46.7	32.9
F.	1.87	10.4	56.7	58.5	26.6

It will be seen from the figure that the tie-lines through the moist solid phases focus probably on the compound



The complex is certainly not  $\text{CuBr}_2, \text{HBr}, 2\text{H}_2\text{O}$ , as suggested by Sabatier, although it is possibly  $\text{CuBr}_2, \text{HBr}, 3\text{H}_2\text{O}$ ; if this were so, it would correspond to the analogous compound,  $\text{CuCl}_2, \text{HCl}, 3\text{H}_2\text{O}$ , described by Foote (*loc. cit.*). Evidence that one of the above formulæ really represents the composition of the solid phase is afforded by the fact that the moist solid phase gives points much farther from the apex of the triangle than do moist specimens of cupric bromide alone.

The mixtures themselves lie on a smooth curve, of which the relationship to the main curve (Fig. 2) will be seen from Fig. 4, where a portion of the triangular diagram is drawn to a larger scale; being on the right of the main curve, *i.e.*, nearer the solid phase, this curve must represent the more unstable form. In addition, from the position of the curve subsequently obtained at  $0^{\circ}$  (shown in Fig. 4), increase of temperature would appear to favour the stability of the compound, which was always destroyed after continued stirring for 7—8 hours at  $25^{\circ}$ , even in concentrated hydrobromic acid solution.

In this connexion it is of interest to notice that combination between cupric bromide and soluble bromides is already suspected to occur in solution, and the existence of the resulting complex ions has been detected by Denham by migration experiments (*Z. physikal. Chem.*, 1909, **65**, 641; *J.*, 1919, **115**, 1269). The presence of such complex compounds or their resulting ions may be advanced as an alternative explanation of the violet coloration of cupric bromide in hydrobromic acid solutions. If this were the case it would be in agreement with an observation of Sabatier (*loc. cit.*), *viz.*, that the violet colour of a solution which has been just destroyed by dilution may be restored by gentle warming.

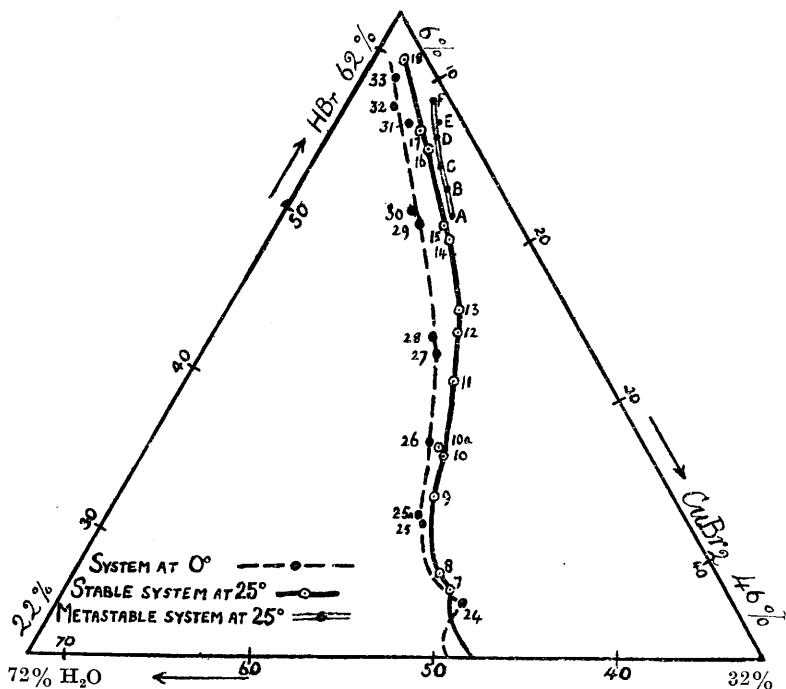
The actual causes of the colour changes in acid solutions of cupric bromide, however, cannot be decided simply by a consideration

of solid phases in equilibrium with them : a study of the solutions themselves would be necessary for a complete explanation.

*The System  $\text{CuBr}_2\text{-HBr-H}_2\text{O}$  at  $0^\circ$ .*

The system at  $0^\circ$  was investigated in a very similar way to that used at  $25^\circ$ , although some of the experimental details were slightly modified. The temperature of the thermostat was maintained constant by a mixture of water and crushed ice. The liquid phase

FIG. 4.

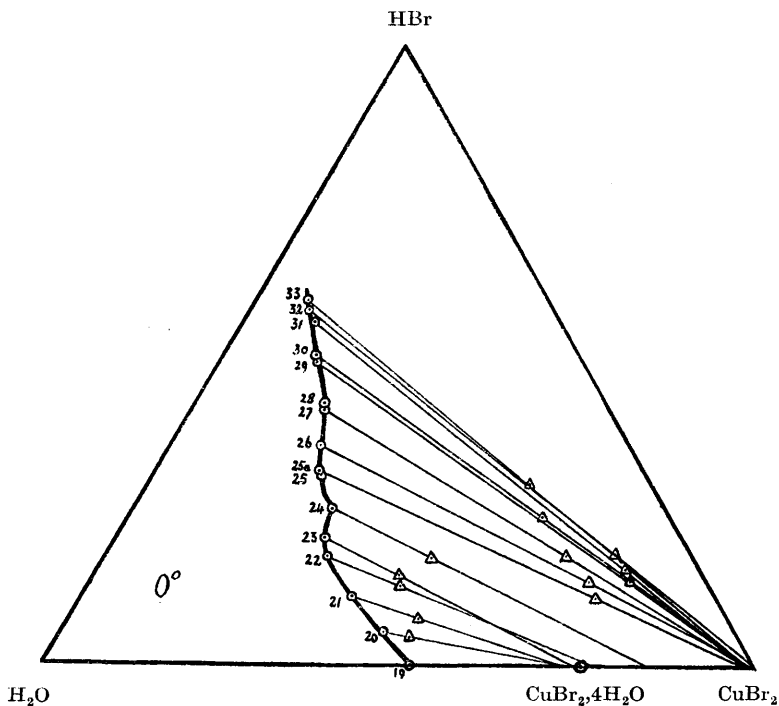


was extracted by means of the apparatus previously employed, but it was necessary to jacket the filter with ice-cold water. The solid phase was removed precisely as before, but it was found impracticable to carry out density determinations at  $0^\circ$ , partly by reason of the viscous nature of the solutions. For low concentrations of acid, it was deemed advisable to inoculate mixtures with a crystal of  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$  after 2—3 hours in the solubility vessel, for otherwise, even after 7—8 hours there was considerable risk of supersaturation occurring, and of anhydrous bromide being left as the stable solid phase. Table IV and Fig. 5 summarise the results obtained for this system.

TABLE IV.

Mixture.	Liquid phase.		Moist solid phase.		Mixture.	Liquid phase.		Moist solid phase.	
	CuBr <sub>2</sub> , %.	HBr, %.	CuBr <sub>2</sub> , %.	HBr, %.		CuBr <sub>2</sub> , %.	HBr, %.	CuBr <sub>2</sub> , %.	HBr, %.
19	51.8	—	75.85	—	26	21.3	35.2	69.8	13.5
20	45.6	5.1	49.4	4.8	27	18.8	41.2	64.5	17.8
21	38.1	10.9	49.3	7.3	28	18.2	42.0	—	—
22	31.3	17.5	43.9	12.9	29	13.8	49.0	75.4	13.8
23	29.4	20.3	43.1	14.5	30	13.2	49.7	58.0	24.0
24	28.0	25.1	45.9	17.4	31	10.1	55.4	73.6	15.5
25	23.6	30.4	—	—	32	8.4	56.9	53.5	29.3
25a	23.2	30.7	71.9	11.2	33	7.7	58.8	71.1	18.2

FIG. 5.



As with the curve at 25°, this system at 0° shows a sharp discontinuity, but in this case it is due to the solid phase changing from the tetrahydrate to the anhydrous salt. Mixture 24 is at the break and all points before that have the hydrated salt as their stable solid phase. It has already been determined for Mixture 19 that CuBr<sub>2</sub>·4H<sub>2</sub>O is the stable phase at 0°. Addition of hydrobromic acid causes a lowering of the melting point of the hydrate,

*i.e.*, it lowers the transition temperature. Hence, when sufficient acid has been added, the transition temperature falls to below  $0^{\circ}$ , and anhydrous cupric bromide becomes the only stable form.

Microscopic examination of the solid phase for Mixtures 19—22 showed green needles in a violet-brown or brown solution. Mixture 23 showed very few needles, for these decomposed with the heat of the room, their transition temperature probably being  $3\text{--}4^{\circ}$  in the prevailing concentration of acid: they could actually be seen decomposing and producing the characteristic black rhomboids of anhydrous bromide. Mixture 24 is peculiar, in that microscopic examination revealed only rhomboidal crystals, whilst the tie-line through its moist solid phase falls between  $\text{CuBr}_2$  and  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$ , indicating that this point is at the junction of the two curves. Both solids are capable of existence here, but owing to temperature difficulties, the hydrate was not sufficiently stable to be seen. From Mixture 25 onwards, the only stable solid phase present was anhydrous cupric bromide; from its appearance under the microscope, it must have been the non-crystalline  $\beta$ -variety.

When the hydrobromic acid concentrations are increased, the cupric bromide solutions at  $0^{\circ}$  exhibit a sequence of colour changes from brown to violet which are similar to those observed at  $25^{\circ}$ . It is noteworthy that at high concentrations of acid (*i.e.*, in the region of the violet solutions) the same solid phase ( $\beta\text{-CuBr}_2$ ) persists at both temperatures, whilst in the low acid concentrations (brown solutions) the solid phases at  $25^{\circ}$  and  $0^{\circ}$  are  $\alpha\text{-CuBr}_2$  and  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$ , respectively. No evidence of the formation of any ternary complex compound at  $0^{\circ}$  was obtained from the curve.

The general temperature relationships of the curves at  $0^{\circ}$  and  $25^{\circ}$  may be judged by an examination of Fig. 4. Over the greater part of the system, cupric bromide evidently possesses a positive temperature coefficient of solubility, and this is still more marked when  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$  becomes the stable phase at  $0^{\circ}$ . In the neighbourhood of Mixture 24, however, on the curve at  $0^{\circ}$ , the curves cross, indicating that in this region the solubility of the salt in hydrobromic acid decreases with rise of temperature. There can be little doubt of the accuracy of the observation, since Mixtures 28, 27, 26, and 25 all tend towards the curve at  $25^{\circ}$ , but the region has not been investigated experimentally in greater detail.

#### *Summary.*

1. The solubility curve of the system  $\text{CuBr}_2\text{-H}_2\text{O}$  has been investigated over the range  $0\text{--}50^{\circ}$ , one of two solid phases,  $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CuBr}_2$ , being found according to the temperature of the solution.

2. The transition temperature has been determined as  $18.00^\circ \pm 0.05^\circ$ .

3. The solubility curve of the system  $\text{CuBr}_2\text{-HBr-H}_2\text{O}$  at  $25^\circ$  shows only a solid phase of anhydrous  $\text{CuBr}_2$ . There are two forms— $\alpha\text{-CuBr}_2$ , which has well-defined rhomboidal crystals, and  $\beta\text{-CuBr}_2$ , which is non-crystalline. The break between the two forms occurs at 26% of HBr.

4. A metastable portion of the system at  $25^\circ$  has been investigated and found to possess as its solid phase a complex compound of the probable formula  $3\text{CuBr}_2, 2\text{HBr}, 6\text{H}_2\text{O}$ , the stability of which is probably favoured by increase of temperature.

5. The system  $\text{CuBr}_2\text{-HBr-H}_2\text{O}$  has been investigated at  $0^\circ$ , and the solubility curve found to exhibit a break corresponding to the two stable phases  $\text{CuBr}_2, 4\text{H}_2\text{O}$  and  $\beta\text{-CuBr}_2$ .

6. The characteristic colour changes of cupric bromide in hydrogen bromide solutions have been discussed in the light of this investigation.

7. No evidence has been obtained of the existence of  $\text{CuBr}_2, 2\text{H}_2\text{O}$  in any of the systems studied.

UNIVERSITY OF BIRMINGHAM,  
EDGBASTON.

[Received, April 5th, 1928.]

---