LXXII.—*The Ternary System Mercuric Chloride–Mercuric Iodide–Water.*

By Ruth Sugden.

Boullay (*Ann. Chim. Phys.*, 1827, **34**, 340) and Larocque (*J. Pharm. Chim.*, 1843, **4**, 15) describe the formation of a compound $HgCl_2,HgI_2$, which Köhler (*Ber.*, 1879, **12**, 1188) considered he had obtained as a yellow solid after boiling the iodide in water with excess of chloride for 12 hours. From a study of the melting-point curves of the binary system, Padoa and Tibaldi (*Atti R. Accad. Lincei*, 1903, [v], **12**, ii, 158) concluded that there existed a discontinuous series of mixed crystals but no chloroiodide. There has evidently been some difficulty in interpreting results, and this appears to be due partly to the fact that, as with the pure iodide, the stability of the solids obtained changes with temperature. An indication of the nature of the binary system may, however, be gained from the

following observations on the ternary system at 30° and 70°, which have been made at the suggestion of Professor A. C. D. Rivett. The two salts have been found to be mutually soluble but, at the iodide end, two series of mixed crystals, yellow and red, respectively, are obtainable, their relative stabilities depending upon temperature and chloride content. They correspond to the yellow and the red form of the simple iodide stable above and below 129° (Reinders, *Z. physikal. Chem.*, 1900, **32**, 507). As chloride progressively dissolves in the yellow iodide, products are obtained which are stable at temperatures below this transition point.

Experimental.

The system was examined at 30° and 70°. The procedure adopted in preparing complexes was to heat suitable mixtures of the components to 100° and then rapidly to filter the solution from any excess solid. The filtrate was rotated for many hours (in some cases up to 11 days) in a closed glass tube in a thermostat at the required temperature, solid separating out. Unless one starts thus from a homogeneous system, trustworthy results cannot be obtained, since equilibrium throughout solids present from the beginning is established far too slowly. As, however, the solubility of the iodide is not much affected by temperature, the amount of solid obtained at the iodide end of the system by the practice adopted was usually very small, especially at 70°, and the accuracy of analysis was correspondingly diminished. After equilibrium had been attained, wet solid was separated as rapidly as possible on a heated Gooch crucible, transferred to a stoppered weighing bottle, and weighed. Both this and the saturated solution were then analysed.

For purposes of analysis, the solid was brought into solution by addition of the minimum amount of potassium iodide. Ammonium sulphate, in amount equal to at least 1% of the weight of the solution, was added to ensure coagulation of mercuric sulphide, which was then precipitated by hydrogen sulphide under pressure. The sulphide was filtered off and washed on a Gooch crucible, dried at 105—110°, and weighed. From the filtrate, the excess gas was removed by boiling, and iodine set free by addition of sodium nitrite and sulphuric acid. The iodine was removed by boiling, and the chloride in the solution determined gravimetrically as silver chloride. The iodide was thus determined by difference, an unsatisfactory procedure when its amount was relatively small. In such cases it was found better to determine it gravimetrically as silver iodide in a solution which was just sufficiently ammoniacal to prevent the precipitation of the chloride. In a system of such

small solubilities and with these obvious limitations in analytical accuracy, the results have qualitative rather than quantitative significance.

Table I(a) gives the results at 30°, compositions being expressed as percentages by weight. Water (not recorded) is obtainable by difference. The colours of the mixed crystals are denoted by letters.

There are two solution curves, as may be seen in Fig. 1. The white solids corresponding to the shorter curve (see large-scale portion) are mercuric chloride containing a few parts of iodide per

FIG. 1.
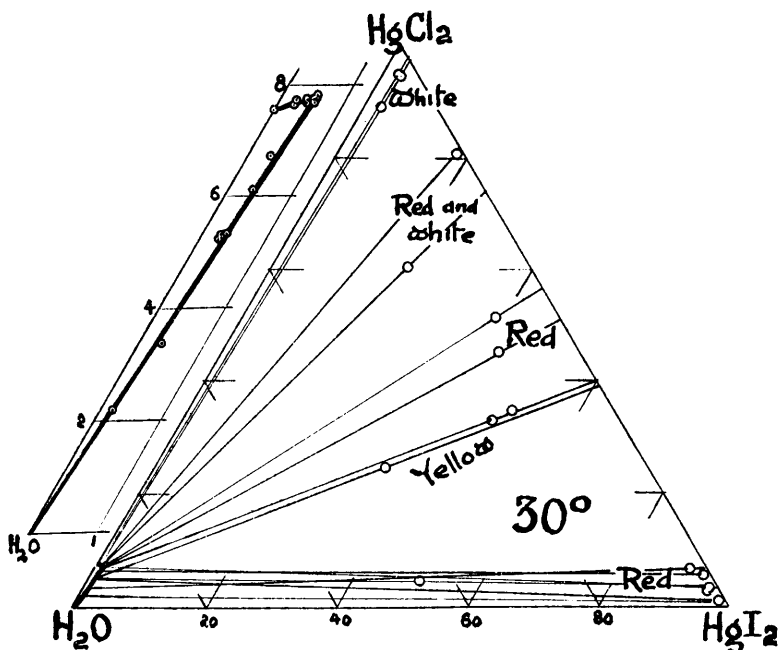
cent. The points shown on the second curve probably belong to two distinct curves which lie very closely together, the corresponding solids being red and yellow mixed crystals of iodide containing chloride. The accuracy obtainable by the present method of working does not permit one to separate these curves. As judged by the time for which yellow crystals may be kept, it seems probable that at 30° the yellow solid is unstable throughout relatively to the red, but at 70° (Table Ib) the former becomes the stable phase in those solutions in which the concentration of mercuric chloride is greatest.

There is no evidence of compound formation.

TABLE I.

Percentages, by weight.					Percentages, by weight.				
Solutions.		Wet solids.			Solutions.		Wet solids.		
$HgCl_2$.	HgI_2.	$HgCl_2$.	HgI_2.		$HgCl_2$.	HgI_2.	$HgCl_2$.	HgI_2.	
(a) *System at* 30°.									
7·55	—	—	—	W	6·75	0·31	5·8	93·6	R
7·67	0·41	89·0	2·5	,,	6·14	0·37	2·81	95·7	,,
7·67	0·25	94·7	2·5	,,	5·32	0·28	4·5	50·4	,,
7·75	0·21	94·2	2·7	,,	5·26	0·28	1·23	98·0	,,
7·76	0·38	80·6	18·3	W & R	3·39	0·33	7·0	90·6	,,
7·78	0·49	60·5	21·0	,,	2·20	0·18	—	97·7	,,
7·78	0·52	45·5	42·1	R	7·82	0·52	33·3	47·4	Y
7·72	0·54	51·9	38·4	,,	7·85	0·57	34·9	49·8	,,
7·69	0·46	3·5	95·2	,,	5·36	0·37	24·7	34·6	,,
(b) *System at* 70°.									
19·12	—	—	—	W	12·8	0·99	—	—	Y
19·5	0·44	82·8	1·62	,,	12·6	0·94	12·1	84·6	,,
20·5	1·10	30·9	64·7	Y	10·2	0·91	11·2	62·0	Y & R
19·8	1·02	—	—	,,	9·9	0·84	9·7	87·0	,,
17·4	0·99	20·2	76·0	,,	7·35	0·75	17·2	74·7	R
16·7	1·00	—	—	,,	3·94	0·52	—	—	,,

W = White; R = red; Y = yellow.