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A Comparative Study of the Kinetics and Mechanism of Reactions between Copper(I) Iodide and Mercury(II) Halides in Solid State

Mirza Aijaz BEG* and Afaq AHMAD

Department of Chemistry, The Aligarh Muslim University, Aligarh-202001, India

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Kinetics and mechanisms of reactions of HgI_2, HgBrI, or $HgBr_2$ with CuI were studied in the solid state. Mercury(II) halides react *via* vapor phase, and reactions proceed through counter diffusion of Cu^+ and Hg^{2+}. X-Ray and chemical analyses indicate that powdered CuI gives Cu_2HgI_4 when mixed with HgI_2 and a mixture of Cu_2HgI_4 and CuBr when mixed with HgBrI. CuI and $HgBr_2$ react differently in different molar ratios. In a 1:2 molar ratio mixture of CuI and $HgBr_2$, a new product $CuHgBr_3$ and HgBrI are obtained. Data for lateral diffusion best fit the equation $X^n=kt$ where X is the thickness of product layer at time t, and n and k are const. Formation of solid solutions among reactant and product phases is also noted.

AgI reacts with HgI_2[1] in solid state yielding highly conducting Ag_2HgI_4. Its reactions with $HgBr_2$ or $HgCl_2$ are complex and altogether different.[2,3] Formation of Cu_2HgI_4 from HgI_2 and CuI in solid state is long known,[4] but no effort seems to have been made to understand the mechanism of the interaction of CuI with Mercury(II) halides in solid state.

This paper presents a study on Kinetics and mechanisms of the reaction of CuI with HgI_2, HgBrI, or $HgBr_2$ in solid state. It was observed that while the first halide is involved in a simple addition reaction, the last two are involved in multi-step reactions. But in each of these, Cu_2HgI_4 and HgI_2 were formed as intermediates. Mixtures of different molar ratios gave rise to different products, including $CuHgBr_3$ which does not seem to have been reported so far either in solid or in solution. Formation of solid solutions among the products were also noted.

Experimental

Materials. $HgBr_2$ and HgI_2 (E. Merck) were used without further purification. Copper(I) halides, being photosensitive, were prepared fresh for each set of experiments.

CuI was prepared according to Berthemot[5] and Guichard.[6] Its X-Ray diffraction patterns showed it to be single phase. CuI was stored in a dark bottle, and experiments were carried out in dark.

Cu_2HgI_4 was prepared by precipitation from solution containing stoichiometric amounts of CuI and HgI_2.[7] Mercury bromideiodide was prepared by Oppenheim's method.[8] X-Ray diffraction patterns showed them to be β-Cu_2HgI_4,[9] and HgBrI.[10]

Rate Measurements. Kinetics of reactions were studied by placing Mercury(II) halides over CuI (each above 300 mesh size) in a vertically held Pyrex glass tube about 0.5 cm in diameter as reported earlier.[11] Each experiment was run in triplicate and the average values were used to calculate rate constants (the readability of the microscope was 0.001 cm and the average deviation of measured values ranged between ± 0.00038 cm) as reported in Tables 1—3.

Soon after the placement of Mercury(II) halide (HgBrI, HgI_2, or $HgBr_2$) over CuI in the reaction tube, a dark brown boundary was formed at the interface and this grew with time on the CuI side. A light yellow layer appeared between HgBrI and a brown dark product layer in the case of HgBrI, and a yellow layer between $HgBr_2$ and brown product layer in the case of $HgBr_2$. On cooling to room temperature, the dark brown product turned scarlet red (Cu_2HgI_4 is dark brown above 70 °C and scarlet below this temperature).[12]

TABLE 1. DEPENDENCE OF PARAMETERS OF EQUATION $X^n=kt$ ON TEMPERATURE FOR CuI-HgI_2 REACTION

T/°C[a)]	k/cm h^{-1}	n
70	1.42×10^{-4}	2.48
82	3.70×10^{-4}	
93	1.25×10^{-3}	
103	3.54×10^{-3}	
112	5.55×10^{-3}	

a) Accurate within ± 0.5 °C.

TABLE 2. DEPENDENCE OF PARAMETERS OF EQUATION $X^n=kt$ ON TEMPERATURE FOR CuI-HgBrI REACTION

T/°C[a)]	k/cm h^{-1}	n
64	1.06×10^{-6}	2.53
75	2.56×10^{-6}	
87	7.08×10^{-6}	
95	14.96×10^{-6}	
104	39.81×10^{-6}	

a) Accurate within ± 0.5 °C.

TABLE 3. DEPENDENCE OF PARAMETERS OF EQUATION $X^n=kt$ ON TEMPERATURE FOR CuI-$HgBr_2$ REACTION

T/°C[a)]	k/cm h^{-1}	n
75	1.13×10^{-6}	2.22
85	7.58×10^{-6}	
98	2.18×10^{-5}	
108	6.60×10^{-5}	
118	8.31×10^{-5}	
128	9.33×10^{-5}	
140	10.50×10^{-5}	

a) Accurate within ± 0.5 °C.

Later, when the reactants were placed in a tube with some air gap, the product layers were formed, but with a much slower rate, which decreased with increase in the length of the air gap. This clearly indicates that these reactions proceed *via* surface migration of Mercury(II) halides.

Analysis of the Product Layers. Sufficient amounts of different product layers of reactions CuI–HgI_2(A), CuI–HgBrI(B), and CuI–$HgBr_2$(C) were separately collected carefully by breaking the reaction tubes. Cu^+, Hg^{2+}, and I^- in the case of reaction A, and Cu^+ and Br^- and Cu^+, Hg^{2+}

Table 4. Compounds present in different molar mixtures of CuI and HgI_2

Molar ratio CuI : HgI_2	Compounds present in mixture heated to 120 °C and then cooled to 30 °C
3 : 1	Cu_2HgI_4, CuI
2 : 1	Cu_2HgI_4
1 : 1	Cu_2HgI_4, HgI_2

and I^- in layers of reaction B and C, respectively, were detected by spot tests.[13] X-Ray diffraction analyses showed them to be Cu_2HgI_4, CuBr, and Cu_2HgI_4, respectively.

X-Ray Studies. The reactants (each above 300 mesh) were mixed thoroughly in an agate mortar in different molar ratios. One part of each mixture was heated in an air thermostat at (120±0.5) °C, and another part was maintained at 30 °C. Mixtures were analysed after 48 h using a Norelco Geiger counter X-Ray diffractometer by Cu $K\alpha$ radiations with a Ni filter, applying 32 kV at 12 mA. The compounds thus identified are given in Tables 4—6.

Thermal amd Conductance Measurements. CuI and Mercury(II) halides (HgI_2, HgBrI, or $HgBr_2$) in different molar ratios ranging from 4:1 to 1:2 were weighed separately and mixed thoroughly in a Dewar flask calorimeter. The rise in temperature was noted against time. The electrical conductance of the same molar-ratio mixtures were measured with a current ratio I. C. bridge:[14] as reported elsewhere.[2,3]

Results and Discussion

X-Ray diffraction analyses (Tables 4—6) reveal that while CuI reacts with HgI_2 or HgBrI in 2:1 or 3:1 molar ratios, respectively, it reacts differently with different molar mixtures of $HgBr_2$.

CuI–HgI_2 Reaction. X-Ray analysis (Table 6) of the products obtained with different molar mixtures of CuI and HgI_2 showed that only Cu_2HgI_4 is formed:

$$2CuI + HgI_2 \longrightarrow Cu_2HgI_4. \quad (1a)$$

Thermal and conductance curves are also indicative of only a single step reaction.

CuI–HgBrI Reaction. A 3:1 molar mixture of CuI and HgBrI, maintained at 120 °C for about 48 h after mixing, showed presence of only Cu_2HgI_4 and CuBr:

$$3CuI + HgBrI \longrightarrow Cu_2HgI_4 + CuBr. \quad (1)$$

Thermal (Fig. 1) as well as conductance (Fig. 2) measurements made with different molar mixtures of CuI and HgBrI provide no evidence for any additional step in reaction (1). However, the presence of HgI_2 in the mixture maintained at 30 °C but the absence in the one kept at a higher temperature (Table 5) suggests that the reaction goes through formation of HgI_2, which is rapidly consumed by CuI giving the addition product Cu_2HgI_4. The reaction sequence, therefore, may be written as:

$$CuI + HgBrI \longrightarrow HgI_2 + CuBr, \quad (i)$$

$$2CuI + HgI_2 \longrightarrow Cu_2HgI_4, \quad (ii)$$

$$3CuI + HgBrI \longrightarrow Cu_2HgI_4 + CuBr.$$

The failure of thermal and conductance measurements to provide evidence for the substep (ii) (Fig. 5(i)) is because it is faster than step (i).[1] However, it is not

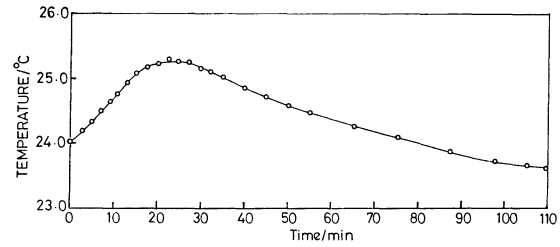

Fig. 1. Temperature rise as a function of time for CuI–HgBrI reaction in 3:1 molar mixture.

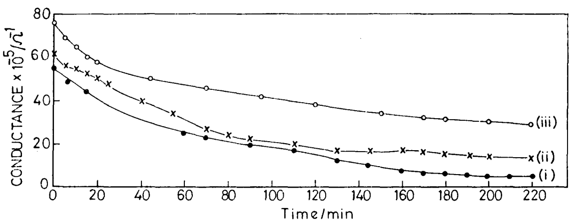

Fig. 2. Change in conductance as a function of time for CuI–HgBrI reaction, molar ratios (i) 3:1, (ii) 2:1, and (iii) 1:2.

Table 5. Compounds present in different molar mixtures of CuI and HgBrI

Molar ratio CuI : HgBrI	Compounds identified at 30 °C	Compounds identified in mixture heated to 120 °C and then cooled to 30 °C
4 : 1	Cu_2HgI_4, CuBr, CuI and HgI_2	Cu_2HgI_4, CuBr, CuI
3 : 1	Cu_2HgI_4, CuBr, HgI_2	Cu_2HgI_4, CuBr
1 : 2	Cu_2HgI_4, CuBr, $HgBr_2$ and HgI_2	Cu_2HgI_4, CuBr and HgBrI

Table 6. Compounds identified in different molar mixtures of CuI and HgBr

Molar ratio CuI : $HgBr_2$	Compounds present at 30 °C	Compounds present in mixture heated to 120 °C and then cooled to 30 °C
4 : 1	Cu_2HgI_4, CuBr, HgI_2	Cu_2HgI_4, CuBr
3 : 1	Cu_2HgI_4, CuBr, HgBrI and HgI_2	Cu_2HgI_4, CuBr, HgBrI
2 : 1	Cu_2HgI_4, CuBr, HgBrI and HgI_2	Cu_2HgI_4, CuBr, HgBrI
1 : 1	Cu_2HgI_4, CuBr, HgBrI	CuBr, HgBrI
1 : 2	Cu_2HgI_4, CuBr, HgBrI and $HgBr_2$	HgBrI and $CuHgBr_3$

so fast as to remove HgI_2, otherwise the latter could not have been detected in the mixture. Reaction (i) is slow because the ionic radii of Cu^+ and Hg^{2+} are very close to each other.

With all other molar mixtures, namely 4:1, 2:1, and 1:2 of CuI and HgBrI, the reaction sequence follows the same pattern and the excess of either reactant remained in the mixtures unreacted.

CuI–HgBr₂ Reaction. While HgBrI reacts with CuI in the molar ratio 1:3, $HgBr_2$ seems to do so primarily in 4:1 molar ratio:

$$4CuI + HgBr_2 \longrightarrow Cu_2HgI_4 + 2CuBr. \tag{2}$$

Thermal (Fig. 3) as well as conductance (Fig. 4) measurements show the reaction to be a simple one-step process. The presence of HgI_2 in the 4:1 molar mixture of CuI and $HgBr_2$, kept at room temperature for about 24 h, and its absence in the mixture maintained at 120 °C suggests that this reaction proceeds *via* the formation of HgI_2, much in the same way as CuI–HgBrI reaction does:

$$2CuI + HgBr_2 \longrightarrow 2CuBr + HgI_2. \tag{iii}$$

However, the absence of HgI_2 in the mixture kept at 120 °C raises two possibilities, First, HgI_2 may react with $HgBr_2$ to give HgBrI, which is stable and is known to be formed in the solid state[10] at high temperatures:

$$HgI_2 + HgBr_2 \longrightarrow 2HgBrI. \tag{iv}$$

Second, HgI_2 may also react with CuI present in the

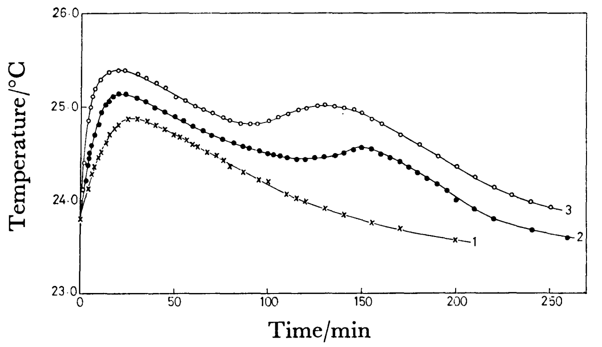

Fig. 3. Temperature rise as a function of time for the reaction between CuI and $HgBr_2$ molar ratios (1) 4:1, (2) 2:1, and (3) 1:2.

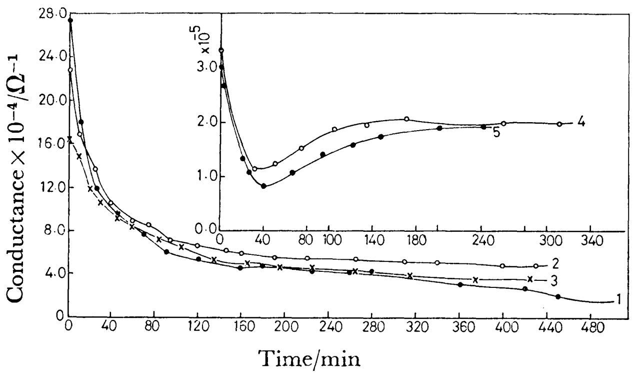

Fig. 4. Conductivity change as a function of time for the reaction between CuI and $HgBr_2$ at 30 °C. Molar ratios of CuI:$HgBr_2$ are (1) 4:1, (2) 3:1, (3) 2:1, (4) 1:1, and (5) 1:2.

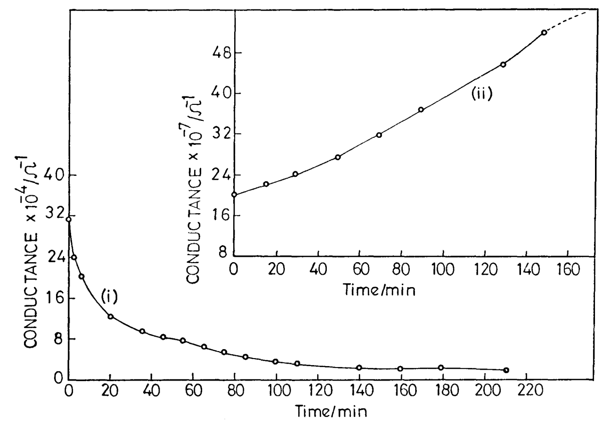

Fig. 5. Change in conductance as a function of time for reactions (i) $2CuI+HgI_2$ and (ii) HgI_2+HgBr_2.

reaction mixture to give Cu_2HgI_4:[4)]

$$2CuI + HgI_2 \longrightarrow Cu_2HgI_4. \tag{v}$$

From the conductance curve for the 4:1 molar mixture of CuI and $HgBr_2$ (Fig. 4), it is evident that most of the reaction is over in about only 25 min, whereas conductance measurements (Fig. 5) made with a 1:1 molar mixture of HgI_2 and $HgBr_2$ clearly show that this reaction continues to proceed uniformly even after 3 h. CuI–HgI_2 reaction is, however, quite fast as is evident from Fig. 5(i). Furthermore, the sudden decrease in the conductance curve for the 4:1 molar mixture (Fig. 4) conforms to the change in the conductance curve obtained for reaction (v) and not to reaction (iv). Moreover, the former is already known[10] to be slow at room temperature whereas the latter is fast.[4] Therefore, HgI_2 produced in reaction (iii) reacts mostly with CuI giving Cu_2HgI_4 and to a little extent, if at all, with $HgBr_2$ yielding HgBrI. Hence, the overall reaction may be described as:

$$\begin{array}{l} 2CuI + HgBr_2 \longrightarrow 2CuBr + HgI_2, \\ 2CuI + HgI_2 \longrightarrow Cu_2HgI_4, \\ \hline 4CuI + HgBr_2 \longrightarrow 2CuBr + Cu_2HgI_4, \end{array}$$

and

$$\begin{array}{l} 2CuI + HgBr_2 \longrightarrow 2CuBr + HgI_2, \\ HgBr_2 + HgI_2 \longrightarrow 2HgBrI, \\ 6CuI + 2HgBrI \longrightarrow 2CuBr + 2Cu_2HgI_4, \\ \hline 8CuI + 2HgBr_2 \longrightarrow 4CuBr + 2Cu_2HgI_4. \end{array}$$

The compounds identified in the 3:1 molar mixture of CuI and $HgBr_2$ maintained at 120 °C were HgBrI, CuBr, and Cu_2HgI_4. At 120 °C, the reaction seems to proceed according to

$$9CuI + 3HgBr_2 \longrightarrow 2Cu_2HgI_4 + HgBrI + 5CuBr. \tag{3}$$

The presence of HgI_2 in this molar mixture (Table 5) at 30 °C shows that this reaction also proceeds through initial formation of HgI_2 which thereafter gives rise to Cu_2HgI_4. The presence of HgBrI may create an impression that this could be formed in the initial stage of reaction (iv), but this is not actually the case as already discussed. Excess $HgBr_2$ combines with Cu_2HgI_4 formed in the reaction giving HgBrI and CuBr. The complete reaction sequence may thus be as follows:

$$6CuI + 3HgBr_2 \longrightarrow 6CuBr + 3HgI_2, \quad (3a)$$

$$6CuI + 3HgI_2 \longrightarrow 3Cu_2HgI_4, \quad (3b)$$

$$Cu_2HgI_4 + 3HgBr_2 \longrightarrow 2CuBr + 4HgBrI, \quad (3c)$$

$$6CuI + 2HgBrI \longrightarrow 2Cu_2HgI_4 + 2CuBr, \quad (3d)$$

$$18CuI + 6HgBr_2 \longrightarrow 4CuHgI_4 + 2HgBrI + 10CuBr.$$

Indeed, when Cu_2HgI_4 and $HgBr_2$ were mixed in 1:3 molar ratio it was found, after keeping it for about 24 h at 120 °C, (by X-Ray diffraction analysis) that it was completely changed into HgBrI and CuBr. Reaction (3d) has already been discussed rearlier. It is perhaps due to the very slow occurrence of Reactions (3c) and (3d) at room temperature that no inflection in the conductance curve (Fig. 4) shows up.

The 1:1 and 1:2 molar mixtures heated to 120 °C showed only the presence of CuBr and HgBrI and of CuBr and $CuHgBr_3$, respectively (Table 6):

$$CuI + HgBr_2 \longrightarrow CuBr + HgBrI, \quad (4)$$

$$CuI + 2HgBr_2 \longrightarrow CuHgBr_3 + HgBrI. \quad (5)$$

It appears as if in the 1:1 mixture, simple exchange took place, which indeed is not the case. When the reactants were mixed at room temperature, they formed a scarlet product turning gradually yellow. The scarlet product turned brown above 70 °C, which incidentally shows that the intermediate could be Cu_2HgI_4. This is also supported by thermal and conductance measurements (Figs. 3 and 4). X-Ray patterns taken about an hour after mixing the two in unimolecular ratio did indicate the presence of Cu_2HgI_4 and HgI_2, which shows that this reaction, too, takes place *via* HgI_2 as the others do.

$$2CuI + HgBr_2 \longrightarrow 2CuBr + HgI_2, \quad (4a)$$

$$2CuI + HgI_2 \longrightarrow Cu_2HgI_4, \quad (4b)$$

$$Cu_2HgI_4 + 3HgBr_2 \longrightarrow 4HgBrI + 2CuBr, \quad (4c)$$

$$4CuI + 4HgBr_2 \longrightarrow 4HgBrI + 4CuBr.$$

The initial fall in the conductance curve (Fig. 4) is due to conversion of highly conducting CuI into Cu_2HgI_4, and the rise thereafter refers to formation of HgBrI.

The reaction sequence for the 1:2 molar mixture is the same as that for 1:1. But, unlike 1:1 reaction, CuBr was not found in the end product (Table 6) in this case. This is because CuBr formed during the reaction is consumed up by $HgBr_2$ giving the addition product $CuHgBr_3$. $CuHgBr_3$ does not seem to have been reported so far either in solid or in solution. $KHgBr_3$ is, however, known in nonaqueous media.[15] Later $CuHgBr_3$ was prepared by heating a unimolar mixture of CuBr and $HgBr_2$ (each above 300 mesh) at 70 °C for about five days. The reflectance spectra (Fig. 6) for the 1:2 molar mixture showed that the product formed is different from the one obtained in the 1:1 molar mixture. The product thus obtained is yellow. The X-ray analysis and indexing of $CuHgBr_3$ are given in Table 7.

Mechanism of Lateral Diffusion. In the initial stage, at the reaction zone, the mercury(II) halide vapor surrounds each CuI grain and reacts through counter diffusion of Cu^+ and Hg^{2+} with simultaneous separation of CuBr and Cu_2HgI_4.

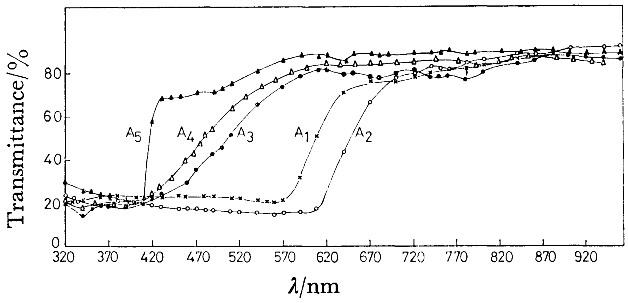

Fig. 6. Reflectance spectra for the CuI+$HgBr_2$ reaction (i) A_2, 4:1 (ii) A_1, 3:1 (iii) A_3, 2:1 (iv) A_4, 1:2 and (v) A_5, 1:2.

TABLE 7. X-RAY DIFFRACTION PATTERNS OF $CuHgBr_3$ TAKEN BY NORELCO, (PHILIPS 1010) DIFFRACTOMETER USING Cu $K\alpha$ RADIATION AND Ni-FILTER

d/Å	I/I_0	$h\,k\,l$	a_0[a)]
5.9986	40	111	10.3899
3.8522	25	220	10.9240
3.1015	45	222	10.7439
2.4918	25	411	10.5718
2.2787	100	332	10.6881
2.1245	62	500, 430	10.6225
2.0336	25	511, 333	10.5669
1.9786	12	520, 432	10.6551
1.7614	14	610	10.7142
1.6851	7	620	10.6575
1.6143	5	622	10.7081
1.5367	25	444	10.6467

a) $a_0 = 10.6575$ Å.

Reactions on the two sides of the product layer proceed as follows:

$$HgX_2 + Cu^+ \longrightarrow 2CuX + Hg^{2+}, \quad (9)$$

$$4CuI + Hg^{2+} \longrightarrow Cu_2HgI_4 + 2Cu^+. \quad (10)$$

As the reaction proceeds, the thickness of the product layers increase and the rate decreases. The increase in thickness slows down the diffusion, and reaction rates thus fall gradually.

The kinetic data best fit the equation

$$X^n = kt,$$

where X is the total thickness of the product layers at time t and k and n are constants. k is related to the diffusion coefficient and follows the Arrhenius equation. The reactions proceed by movement of ions of one kind only, in such a way that the cations move through the product layers in opposite directions and react at phase boundaries with further formation of product layers. The continuous flow of cations from one into the other reactant through the product layer is responsible for the reaction. This is similar to the reaction of AgI and HgI_2 to form Ag_2HgI_4.[1)]

Activation energies calculated by computer for CuI–HgI_2, CuI–HgBrI, and CuI–$HgBr_2$ reactions are, 97.75

± 2.74, 91.74 ± 2.55, and 82.787 ± 6.829 kJ mol^{-1}. respectively. These activation energies suggest that the reactions are diffusion controlled.

X-Ray analysis of the reaction mixture showed a change in *d*-values of the components which indicates formation of solid solutions in the systems CuBr–CuI, Cu_2HgI_4–CuBr, and HgBrI–Cu_2HgI_4. No attempt was, however, made to study the solutions in detail.

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