Discussion

The spectrophotometric results show beyond question that the $PbNO_3^+$ ion is actually present in these solutions. The formation constant so obtained, although differing by a factor of two from the results of the electrical methods is actually not in bad agreement when it is considered that the lead-to-nitrate ratio differs by a factor of 20,000. Furthermore, it would be surprising indeed if the specific effects on individual activity coefficients of lead, nitrate and lead mononitrate ions were the same in 2.0 *M* sodium perchlorate as in 0.67 *M* lead perchlorate, even though the ionic strengths of the two are the same.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF ETHYL CORPORATION]

Phase Study of the $PbO–PbBr_2$ System by X-Ray Diffraction

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The binary system $PbO–PbBr_2$ has been investigated by X-ray diffraction. The results confirm the existence of the four intermediate compounds, $PbO·PbBr_2$, $2PbO·PbBr_2$, $3PbO·PbBr_2$ and $7PbO·PbBr_2$, previously demonstrated by thermal analyses, all except the dibasic compound exhibit polymorphism. The monobasic compound exists in four polymorphic forms, each of which reacts with water to produce the same hydrate, $PbO·PbBr_2·H_2O$. Thermal relationships are given for these four forms and for the hydrate. The significance of the preferential production of one of the crystalline modifications of $PbO·PbBr_2$ by a low temperature solid state reaction is discussed. The tribasic compound exists in two crystalline forms, each of which combines with one molecule of water to produce a different crystalline modification of the hydrate $3PbO·PbBr_2·H_2O$. The thermal relationships of the two forms of $3PbO·PbBr_2$ and of the hydrate are given. The heptabasic compound exists in two forms, a high temperature and a low temperature form. The latter combines with water to produce two hydrates, $7PbO·PbBr_2·5H_2O$ and $7PbO·PbBr_2·7H_2O$. On dehydration by heating, each of these undergoes successive phase changes and finally, at 500°, reverts to the original low temperature form of the heptabasic compound. Heating either of the heptabasic compounds above 600° in the presence of SiO_2 results in formation of a basic bromosilicate. The interplanar spacing values are given for the major reflections of the four intermediate compounds (including their various polymorphic forms), the hydrates and the silicate.

Introduction

During the course of an extensive investigation in these laboratories[1] of the formation and composition of engine-deposit compounds, it has become necessary to make a phase study of the binary systems of several lead compounds. The present paper gives the results of the X-ray diffraction study of the $PbO–PbBr_2$ system, the thermal analysis data for which are given in a preceding paper.[2] The X-ray diffraction data previously reported for this system are very limited. Although Baroni[3] supplemented his thermal analysis of the $PbO–PbBr_2$ system by crystallographic and X-ray diffraction observations of the various compounds formed, he stated that the photographs were complicated and difficult to interpret, and no data[1] were included in his publication. The only published X-ray data found, aside from those for the two components, PbO and $PbBr_2$, were the interplanar spacing values given in the ASTM Index File[4] for the compound, $PbO·PbBr_2$. The results from the present study show that these data are in error, since they were found to correspond to the values obtained for $3PbO·PbBr_2·H_2O$ and not for $PbO·PbBr_2$.

Experimental Method

Powder patterns were obtained for the various preparations by means of a Norelco Geiger Counter X-ray Spectrometer using CuKα radiation. The methods used for mounting the specimen and for angular calibration of the goniometer are described in an earlier publication.[5] The so-called "thermal analysis preparations" used in this study were the samples resulting from the thermal measurements previously described.[2] The fused and quenched preparations were obtained by melting mechanical mixtures of appropriate amounts of the two components, PbO and $PbBr_2$, in magnesium oxide crucibles, mixing well, and quenching by pouring on the flat surface of a large block of copper.

The method for preparing the monobasic hydrate $PbO·PbBr_2·H_2O$ has been described previously.[1] The tribasic hydrate, $3PbO·PbBr_2·H_2O$, was prepared by slowly adding with mechanical stirring 10 g. of 200-mesh PbO (yellow orthorhombic) to 250 ml. of CO_2-free, 80° distilled water containing 39 g. of NaBr. The yellow precipitate formed was filtered, washed with 95% ethyl alcohol and dried in an oven at 70° for 24 hours. Chemical analyses and X-ray diffraction examination indicated a purity of 98% or better for various preparations of the two hydrates.

Results and Discussion

Thermal Analysis Preparations.—An X-ray diffraction study was made of the numerous preparations resulting from the thermal measurements. Each of these preparations had been fused and then allowed to cool very slowly through the primary crystallization point and, also, through its peritectic and eutectic temperatures before removing it from the furnace and allowing to cool to room temperature. The X-ray diffraction data obtained from the powder patterns of these preparations confirmed the results obtained by thermal analyses. They showed the existence of intermediate compounds corresponding to the compositions: $PbO·PbBr_2$, $2PbO·PbBr_2$, $3PbO·PbBr_2$ and $7PbO·PbBr_2$. The phase diagram obtained from the thermal analysis

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[1] F. W. Lamb and L. M. Niebylski, *Anal. Chem.*, **23**, 1388 (1951).

[2] L. M. Knowles, *J. Chem. Phys.*, **19**, 1128 (1951).

[3] A. Baroni, *Atti accad. Lincei*, **20**, 384 (1934).

[4] ASTM X-Ray Diffraction Index Card No. II, 1399.

[5] G. Calingaert, F. W. Lamb and F. Meyer, THIS JOURNAL, **71**, 3709 (1949).

measurements by Knowles[2] is reproduced here as Fig. 1 for reference.

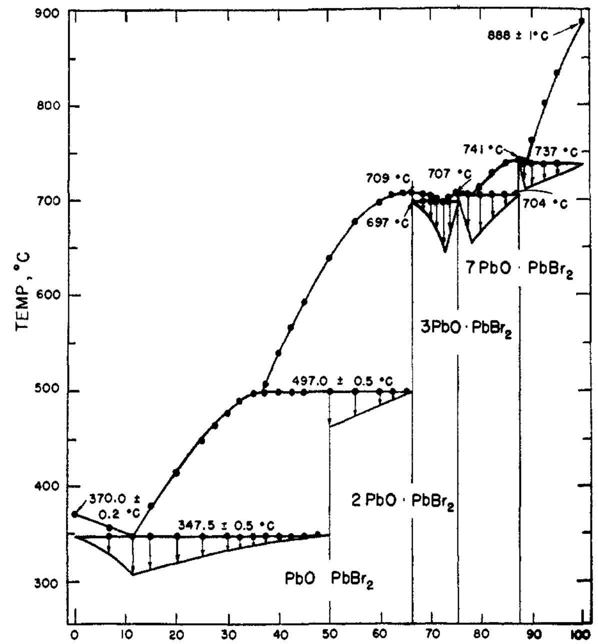

Fig. 1.—Phase diagram of the PbO–PbBr$_2$ system.

The monobasic lead bromide was found to exist in one crystalline form for the composition range of 0 to 40 mole % PbO and in a second crystalline form from 40 to 66.7 mole % PbO. These two polymorphic modifications of the monobasic lead bromide have been designated as R and N, respectively. The reflections characteristic of the R form increased in intensity up to a composition of 40 mole % PbO and were entirely absent in compositions containing more than 45.0 mole % PbO. The reflections characteristic of the N form predominated in compositions of 42.50 to 55 mole % PbO, showing a maximum intensity in the 45 to 50 mole % range. Further relationships of these two forms as well as those of two other crystalline forms of the monobasic lead bromide are discussed in a later section. The other three intermediate compounds, 2PbO·PbBr$_2$, 3PbO·PbBr$_2$ and 7PbO·PbBr$_2$, existed in one crystalline form only in the thermal analysis preparations. The tribasic and heptabasic compounds, however, each were found to exist in a second crystalline form in the fused and quenched preparations. The polymorphism of these two compounds is discussed under separate headings.

Fused and Quenched Preparations.—Previous to the study of the thermal analysis preparations, a series of fused and quenched preparations covering the complete composition range in 1 to 2 mole % increments of PbO was examined. The results from these preparations were found to be more complex than those obtained from the thermal analysis preparations. They are reported here since they constitute a part of a complete phase study of the system and also since they may explain the conflicting results obtained by previous and current workers in the field.

The powder patterns obtained of the fused and quenched preparations indicated eight phases between the two primary compounds, PbBr$_2$ and PbO. The reflections characteristic of these different phases showed a maximum intensity in the powder patterns at compositions of 20, 35, 40, 66.7, 72.5, 78, 84 and 88 mole % PbO. The composition ranges and positions of maximum intensity for the eight phases are shown graphically in Fig. 2 where the relative amounts of the phases are indicated on an arbitrary intensity scale. Except for the results obtained by thermal analysis and a subsequent clarification of the various polymorphic modifications through heat treatment and chemical studies, each of the eight phases identified in the powder patterns could well have been mistaken for an individual compound.

A comparison of the patterns characterizing each of the above eight phases with those obtained from the thermal preparations revealed the following: (1) There is no evidence of the so-called 20 mole % PbO phase in the thermal analysis preparations. Supplemental chemical and heat treatment studies have shown that it is a polymorphic form of PbO·PbBr$_2$. It has been arbitrarily designated as the X form. (2) The phase showing a

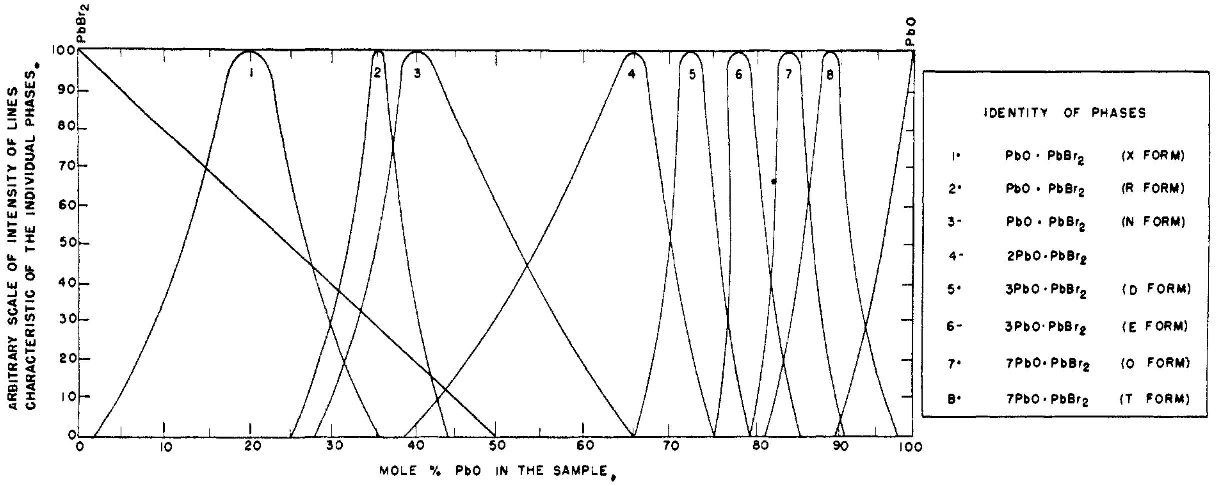

Fig. 2.—Summary of X-ray diffraction results on fused and quenched preparations.

TABLE I

INTERPLANAR SPACING VALUES

Copper K_α Radiation, $\lambda_{W.M.} = 1.5418$ Å.

$PbO\cdot PbBr_2$ X form[a]		$PbO\cdot PbBr_2$ R form		$PbO\cdot PbBr_2$ N form		$2PbO\cdot PbBr_2$		$3PbO\cdot PbBr_2$ D form		$3PbO\cdot PbBr_2$ E form		$7PbO\cdot PbBr_2$ T form		$7PbO\cdot PbBr_2$ Q form	
d, Å[b]	I/I_1[c]	d, Å.	I/I_1	d, Å.	I/I_1	d, Å.	I/I_1	d, Å	I/I_1	d, Å.	I/I_1	d, Å.	I/I_1	d, Å.	I/I_1
5.88	0.15	8.61	0.10	7.65	0.20	7.55	0.59	6.63	0.41	6.54	0.16	10.63	0.06	8.87	0.09
3.93	0.35	6.20	.30	6.12	.20	5.15	.30	3.84	.18	4.50	.14	10.35	.07	6.21	.07
2.87	1.00	6.00	.30	4.05	.14	4.88	.12	3.77	.12	3.73	.30	10.15	.08	4.06	.08
2.80	0.15	4.58	.30	3.83	.16	3.87	.11	3.33	.10	3.61	.21	6.08	.06	3.95	.06
2.32	.25	4.16	.25	3.60	.15	3.58	.17	3.26	.06	3.36	.30	5.97	.06	3.84	.10
2.09	.15	3.88	.35	3.41	.11	3.14	1.00	2.98	1.00	3.31	.20	3.91	.17	3.33	.06
1.68	.15	3.67	.26	3.33	.13	2.93	0.16	2.83	0.38	3.06	.60	3.06	.17	3.21	.09
		3.32	1.00	3.18	.15	2.85	.45	2.78	.19	3.02	.46	2.99	.22	3.05	.12
		3.15	0.95	3.13	.20	2.78	.24	2.22	.13	2.92	1.00	2.87	1.00	2.99	1.00
		2.91	.87	3.06	.10	2.72	.35	2.19	.07	2.91	0.90	2.37	0.06	2.94	0.40
		2.89	.55	2.97	.40	2.59	.10	2.16	.14	2.90	.50	2.07	.24	2.90	.54
		2.84	.65	2.91	.55	2.56	.29	2.14	.08	2.86	.56	1.99	.24	2.80	.11
		2.80	.31	2.86	1.00	2.45	.10	2.05	.06	2.78	.51	1.96	.03	2.54	.05
		2.74	.68	2.83	0.43	2.37	.06	2.01	.18	2.77	.45	1.86	.02	2.52	.05
		2.64	.38	2.79	.18	2.27	.14	1.99	.08	2.37	.30	1.73	.03	2.18	.15
		2.60	.42	2.72	.25	2.25	.47	1.96	.09	2.16	.33	1.71	.15	2.15	.30
		2.47	.30	2.55	.10	2.14	.11	1.74	.19	2.14	.18	1.67	.13	2.08	.15
		2.41	.46	2.51	.15	2.04	.09	1.72	.15	2.12	.16	1.58	.04	2.03	.09
		2.35	.29	2.24	.25	2.00	.08	1.66	.19	2.09	.17	1.44	.20	1.99	.05
		2.05	.22	2.20	.20	1.96	.12	1.49	.10	1.98	.40	1.31	.10	1.73	.14
		1.95	.56	2.15	.13	1.94	.15	1.48	.07	1.93	.10	1.27	.15	1.72	.14
		1.89	.10	2.09	.13			1.44	.06	1.90	.13			1.70	.14
		1.87	.24	1.84	.12			1.42	.06	1.84	.15			1.68	.12
		1.84	.15					1.39	.10	1.78	.12	$3PbO\cdot PbBr_2$ E Form Contd.		1.67	.10
										1.74	.48			1.65	.06
										1.73	.35	1.67	0.32	1.50	.07
										1.72	.22	1.64	.18	1.36	.06
										1.71	.19	1.62	.16	1.31	.05
										1.69	.19	1.59	.15	1.29	.05

[a] It is possible to give only a few of the interplanar spacing (*d*) values for the X form of $PbO\cdot PbBr_2$ since it has not been prepared free from $PbBr_2$. [b] The interplanar spacing (*d*) values are accurate to ±0.05 Å. for values of 4 Å. or greater, to ±0.02 Å. for values of 2 to 4 Å., and to ±0.01 Å. for values less than 2 Å. [c] The relative intensity I/I_1 values were obtained by dividing the heights of the various reflections by the height of the strongest reflection.

maximum intensity at the 35 mole % PbO composition is the same as the above mentioned R form of $PbO\cdot PbBr_2$ which also occurs in the thermal analysis preparations. (3) The 40 mole % PbO phase is the same as the N form of $PbO\cdot PbBr_2$ observed in the thermal analysis preparations. (4) The 66.7 mole % PbO composition gives the same pattern as obtained for the thermal analysis preparation of $2PbO\cdot PbBr_2$. (5) The phase showing a maximum at 72.5 mole % PbO does not appear in the thermal analysis preparations. Supplemental results obtained from chemical and heat treatment studies have shown that this phase is a polymorphic form of $3PbO\cdot PbBr_2$. It has been designated the D form. (6) The phase showing a maximum at 78 mole % PbO is the same as the thermal analysis preparation of $3PbO\cdot PbBr_2$. This phase has been designated the E form. (7) The 84 mole % PbO phase does not appear in the thermal analysis preparations. However, heat treatment studies indicate that it is a polymorphic form of $7PbO\cdot PbBr_2$ and it has been designated as the Q form. (8) The phase showing a maximum at 88 mole % PbO is the same as the crystalline form of $7PbO\cdot PbBr_2$ which occurs in the thermal analysis preparations. This phase has been designated the T form.

The interplanar spacing values for the major reflections of these eight phases are given in Table I.

Polymorphism of $PbO\cdot PbBr_2$. Dehydration of the Hydrate, $PbO\cdot PbBr_2\cdot H_2O$.—A study involving the dehydration and subsequent heat treatment of the hydrate, $PbO\cdot PbBr_2\cdot H_2O$, showed that monobasic lead bromide exists in more than one crystalline form. The thermal relationships of the several forms are indicated in equation 1 in which the letters L, N and R are used to designate the individual forms.

$$PbO\cdot PbBr_2\cdot H_2O \xrightarrow[125\text{–}210^\circ]{-H_2O} PbO\cdot PbBr_2\text{ (L form)} \xrightarrow[210\text{–}260^\circ]{} \underset{\text{(N form)}}{PbO\cdot PbBr_2}$$
$$\xrightarrow[260\text{–}450^\circ]{} PbO\cdot PbBr_2\text{ (R form)} \xrightarrow[450^\circ]{} \underset{\text{(N form)}}{PbO\cdot PbBr_2} \qquad (1)$$

Chemical analyses and material balance experiments showed that each of the indicated polymorphic forms is anhydrous. For the material balance experiments a 1- to 2-g. sample of the hydrate was heated in a closed system flushed with a stream of dry nitrogen. The liberated water was conducted to an absorption bulb containing magnesium perchlorate. The weight per cent. of water liberated by various heat treatments was determined both by loss of weight of the sample and by gain of weight of the absorption tube. The values obtained by the two methods checked closely, as shown by the results given in Table II.

TABLE II

DEHYDRATION OF $PbO \cdot PbBr_2 \cdot H_2O$

Heating time, 24 hours

np., °C.	Compound formed	Water loss in wt. % By absorption	Water loss in wt. % By loss of wt.
260	$PbO \cdot PbBr_2$ (R + N form)	2.98	2.96
		2.91	2.93
180	$PbO \cdot PbBr_2$ (L form)	2.64	2.64
		2.60	2.61
		2.66	2.66

The theoretical value for the weight per cent. of H_2O in $PbO \cdot PbBr_2 \cdot H_2O$ is 2.960 and in $PbO \cdot PbBr_2 \cdot {}^1/_2\,H_2O$ it is 1.503. The data of Table II show that the R and N forms are completely dehydrated and that the material heated at 180° for 24 hours contains about 0.33% H_2O. It is not considered likely that the L form is a low hydrate containing approximately 0.1 mole of H_2O, but rather that it is also anhydrous and that the 0.33% H_2O may be accounted for by the presence of about 11% of $PbO \cdot PbBr_2 \cdot H_2O$. This amount of hydrate might not be detectable in the patterns since it probably is in a more or less amorphous form due to the solid state dehydration process. On hydration all three forms of $PbO \cdot PbBr_2$ produce the same hydrate. The thermal relationships of the three crystalline forms (L, N and R) of $PbO \cdot PbBr_2$ and the hydrate are shown in Fig. 3.

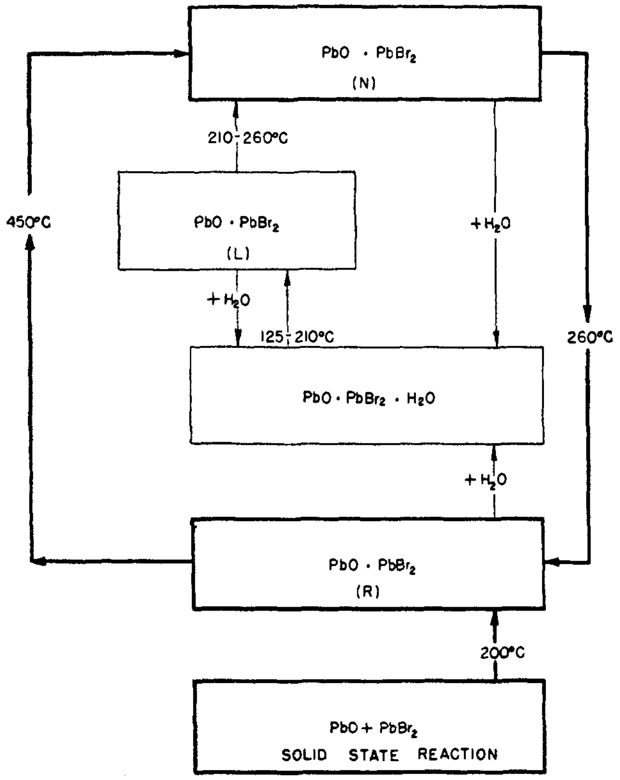

Fig. 3.—Diagram of thermal relationships of the polymorphic forms of $PbO \cdot PbBr_2$ and the hydrate, $PbO \cdot PbBr_2 \cdot H_2O$. All data based on a heating time of 24 hours.

The interplanar spacing values for the major reflections of the hydrate, $PbO \cdot PbBr_2 \cdot H_2O$, and the L form of $PbO \cdot PbBr_2$ are given in Table III.

TABLE III

INTERPLANAR SPACING VALUES

Copper Kα radiation, $\lambda_{W.M.}$ = 1.5418 Å.

$PbO \cdot PbBr_2 \cdot H_2O$		$PbO \cdot PbBr_2$ L form		$3PbO \cdot PbBr_2 \cdot H_2O$ A form[c]		$3PbO \cdot PbBr_2 \cdot H_2O$ B form	
d, Å.[a]	I/I_1[b]	d, Å.	I/I_1	d, Å.	I/I_1	d, Å.	I/I_1
5.96	0.25	7.80	0.55	6.50	0.05	7.00	0.09
5.03	.16	7.08	.60	3.93	.20	6.33	.12
4.16	1.00	5.27	.22	3.25	.13	4.20	.18
3.76	0.10	4.34	.20	3.06	.11	3.95	.06
3.71	.22	4.00	.18	2.98	1.00	3.80	.18
3.48	.61	3.90	.24	2.95	0.25	3.35	.06
3.38	.85	3.80	.18	2.88	.28	3.18	.15
3.05	.19	3.51	.35	2.20	.06	3.11	.13
2.98	.55	3.27	.29	2.17	.17	3.06	.85
2.92	.50	3.22	.61	2.06	.17	3.00	.59
2.75	.06	3.10	.33	1.96	.03	2.94	.55
2.72	.06	3.04	.57	1.85	.03	2.90	1.00
2.65	.50	2.94	.71	1.81	.03	2.74	0.18
2.60	.55	2.80	1.00	1.80	.04	2.67	.12
2.51	.14	2.75	0.59	1.75	.14	2.42	.06
2.49	.19	2.67	.20	1.73	.16	2.37	.06
2.40	.63	2.64	.40	1.71	.16	2.23	.14
2.22	.20	2.60	.59	1.70	.21	2.18	.18
2.13	.18	2.50	.35	1.69	.24	2.16	.19
2.07	.12	2.46	.35	1.63	.05	2.12	.13
2.05	.14	2.42	.12	1.50	.09	1.99	.19
1.95	.18	2.37	.27	1.44	.04	1.86	.08
1.84	.08	2.27	.22	1.43	.04	1.80	.10
1.80	.08	2.17	.22	1.37	.06	1.78	.10
1.76	.11	1.96	.20	1.31	.06	1.76	.14
1.69	.26	1.94	.20	1.30	.06	1.74	.22
1.62	.31	1.90	.18			1.72	.22
1.58	.06	1.87	.22			1.68	.23
1.56	.15	1.73	.20			1.67	.24
1.53	.09					1.65	.08
1.51	.04					1.54	.10
1.47	.08					1.47	.09
1.43	.07					1.45	.09
						1.27	.10

[a] See footnote *b*, Table I. [b] See footnote *c*, Table I. [c] Note agreement with interplanar spacing (*d*) values reported for $PbO \cdot PbBr_2$ in A.S.T.M. Index Card II, 1399.

Thermal Relationships of N and R Forms.—It has been found that $PbO \cdot PbBr_2$ (N form) is regularly produced from melts cooled rapidly below the peritectic temperature of 497°. The R form may be produced by holding a 50 mole % PbO melt at the peritectic temperature for several hours and then cooling slowly to 300° or less before quenching. If quenched at higher temperatures, the N form is produced. Thus, the N form is the high temperature form, and the R form is the low temperature form, the transition temperature being approximately 300°. More specifically, it was observed that by holding a 50 mole % PbO sample at 500° for 16 hours and then cooling slowly to 250° before removing from the furnace and quenching with an air blast, the N form was entirely converted to the R form. The R form was also produced in melts cooled slowly to 150° before quenching. Cooling to 300° before quenching produced a mixture of the two forms as well as some $2PbO \cdot Br_2$.

A comparison of the results obtained on the fused and quenched preparations with those on the thermal analysis preparations shows that in the thermal analysis preparations the R form of $PbO \cdot PbBr_2$ is produced at all compositions up to and including 45 mole % PbO; whereas, in the fused and quenched preparations the X, R and N forms appear successively (Fig. 2) as the concentration of PbO is increased through this same composition range. The R form of $PbO \cdot PbBr_2$ is produced in a composition range of 30 to 40 mole % of PbO in both the fused and quenched and the thermal analysis preparations. This may indicate that in the presence of certain amounts of $PbBr_2$ the $PbO \cdot PbBr_2$ preferentially crystallizes in the R form regardless of the cooling rate.

At concentrations of 40 to 66.7 mole % PbO, the N form is produced in both the rapidly and slowly cooled preparations. In studying the thermal analysis preparations, however, an occasional sample containing as high as 45 mole % PbO was observed to be predominately the R form, indicating that this particular preparation had been allowed to cool slowly through the transition temperature. Heat treating experiments have shown that the N form occurring in a 42.5 mole % PbO preparation may be readily converted to the R form if heated for 30 min. at 250° and that the heating time required for this transition increases with the PbO concentration. For example, a 50 mole % preparation whose powder pattern showed it to be chiefly the N form with a small amount of $2PbO \cdot PbBr_2$ required a heating time of at least one week at 250° to convert a portion of the N form to the R form. In preparations containing appreciable amounts of $2PbO \cdot PbBr_2$ it has not been possible to convert the N form to the R form. These results indicate that the transition of the N form of $PbO \cdot PbBr_2$ to the R form is influenced by the presence of a second component. In the presence of $PbBr_2$ the transition occurs more readily, and in the presence of $2PbO \cdot PbBr_2$ the transition is very much retarded if not completely prevented. This is considered to be an example of a special type of solid state reaction and is discussed in detail in a later section.

Thermal Relationships of the X and R Forms.—As shown in Fig. 2, the X form of $PbO \cdot PbBr_2$ is regularly produced in the fused and quenched preparations for compositions of 5 to 30 mole % PbO, the maximum intensity occurring at approximately 20 mole % PbO. The thermal analysis preparations show simply a mixture of $PbBr_2$ and the R form of $PbO \cdot PbBr_2$ for the same composition range, indicating that the X form is readily converted to the R form when the preparations are cooled slowly through the eutectic temperature of 347° before removing from the furnace. Hydration of both series of preparations gave mixtures of $PbBr_2$ and $PbO \cdot PbBr_2 \cdot H_2O$ only, indicating that the X phase is also a crystalline form of $PbO \cdot PbBr_2$. On dehydration, both series of preparations gave $PbBr_2$ and the R form of $PbO \cdot PbBr_2$ with no evidence of the X form.

Several experiments were performed to determine the conditions for conversion of the X to the R form and *vice versa*. Knowing that in the thermal analysis preparations the samples were cooled slowly through the eutectic temperature, it was reasoned that the X phase might be produced if the preparations were quenched at any temperature above the eutectic temperature. Three thermal analysis preparations having 11.43, 11.85 and 12.26 mole % PbO by chemical analysis (close to the eutectic composition of 12.5 mole % PbO) were heated to 400° and quenched on a copper block. Patterns of these quenched preparations all showed the X form of $PbO \cdot PbBr_2$ and $PbBr_2$, showing that under these conditions the monobasic lead bromide preferentially crystallizes in the X form. A 15 mole % PbO thermal analysis preparation was heated at 360 ± 2.5° (intermediate between the eutectic and primary crystallization temperature) for 72 hours and then quenched in air. The patterns showed a mixture of $PbBr_2$ and the X phase. A series of experiments was performed on a 20 mole % PbO thermal analysis preparation. The sample was first fused and quenched. The X-ray diffraction patterns showed a mixture of $PbBr_2$ and the X form of $PbO \cdot PbBr_2$; however, the reflections for the X form were quite broad and diffuse. Following this a portion of the fused and quenched sample was again melted and then held at 370° for 24 hours before quenching. The patterns of this preparation showed sharp and intense reflections for the X form. Next, a portion of the original fused and quenched preparation was heated to 370° and held at this temperature for 24 hours before quenching. Again, the pattern obtained for the X form was very sharp. Finally, a portion of the fused and quenched preparation was heated in a Pyrex test-tube to the eutectic temperature of 347° and held at this temperature for 24 hours before removing from the furnace. The resulting sample had separated in two distinct layers. The upper, buff-colored layer was found to be a mixture of $PbBr_2$ and the R form of $PbO \cdot PbBr_2$, and the lower, gray-colored layer a mixture of $PbBr_2$ and the X form. These experiments show that for a composition range of 5 to 30 mole % PbO the monobasic lead bromide preferentially crystallizes in the X form above the eutectic temperature of 347°, and that the X form is converted to the R form near the eutectic temperature. The X form has not been prepared in a pure state and has only been produced in a mixture with $PbBr_2$ as in the fused and quenched preparations described here.

Production of R Form by Solid State Reaction.—In a discussion of the various crystalline forms of monobasic lead bromide, it is of interest to note that the solid state addition reaction between equimolar amounts of PbO and $PbBr_2$ the R form and only the R form of $PbO \cdot PbBr_2$ is produced on heating an intimate mixture of the two primary compounds at 250°. Details of this investigation are given in an earlier publication.[1] The R form of $PbO \cdot PbBr_2$ resulting from the low temperature solid state reaction may be converted to the N form if heated at 450° or higher for 24 hours, the same as indicated in equation 1 for the R form resulting from the hydrate. The N form thus produced may in turn be converted to the R form by heating at 260 to 300° for 24 hours. This solid state reaction cycle is shown by the heavy lines in Fig. 3.

The strong tendency for production of the R form by solid state reaction is further emphasized by the following two experiments involving a type of solid state replacement reaction: (1) A mechanical mixture of the pure N form of $PbO \cdot PbBr_2$ and of $PbBr_2$, corresponding to a 33.3 mole % PbO composition, was prepared and heated at 200° for two hours. X-Ray diffraction patterns showed that the N form had been completely converted to the R form. As stated above, in the absence of added $PbBr_2$ the transition of the N form to the R form would require heating at 260 to 300° for 24 hours. It is theorized that the added $PbBr_2$ aids the transition by taking part in a type of solid state replacement reaction in which the free $PbBr_2$ reacts with the PbO portion of the N form of $PbO \cdot PbBr_2$ to form the low temperature, solid state R form. Similar solid state reactions between the PbO portion of a basic lead compound and a primary lead compound have been discussed in detail elsewhere by the authors.[1] The first step of the solid state reaction for a mixture of $PbBr_2$ and $PbO{\cdot}PbBr_2$ (N form) in a 1:2 mole ratio may be represented as

$$PbBr_2 + 2(PbO{\cdot}PbBr_2)\ \text{N form} \xrightarrow[2\ \text{hr.}]{200°} \qquad (2)$$
$$PbO{\cdot}PbBr_2\ (\text{R form}) + PbBr_2 + PbO{\cdot}PbBr_2\ (\text{N form})$$

The $PbBr_2$ released in the above replacement reaction will then react in the same manner with the PbO portion of the remaining N form of $PbO{\cdot}PbBr_2$ to complete the transition by producing another mole of the R form. In case the mole ratio of $PbBr_2$ to the N form of $PbO{\cdot}PbBr_2$ is appreciably less than one, this replacement reaction will continue to take place in steps until the conversion to the R form is complete. However, the lower the mole ratio, the longer the time required for complete conversion; for example, it has been found that for a mole ratio of 0.11 or less (45 to 50 mole % PbO) a much longer time is required at the somewhat higher temperature of 250 to 300°.

(2) A similar solid state replacement reaction is believed to take place between $PbBr_2$ and the X form of $PbO{\cdot}PbBr_2$ during its conversion to the R form. For example, a fused and quenched 20 mole % PbO preparation (60:40 mole ratio of $PbBr_2$ to $PbO{\cdot}PbBr_2$ X form) heated at 200° for 3 hours was found to be converted to a mixture of $PbBr_2$ and the R form of $PbO{\cdot}PbBr_2$. Doubtless, this solid state replacement reaction follows the same course as indicated in equation 2 with the exception that in this case the N form is replaced by the X form.

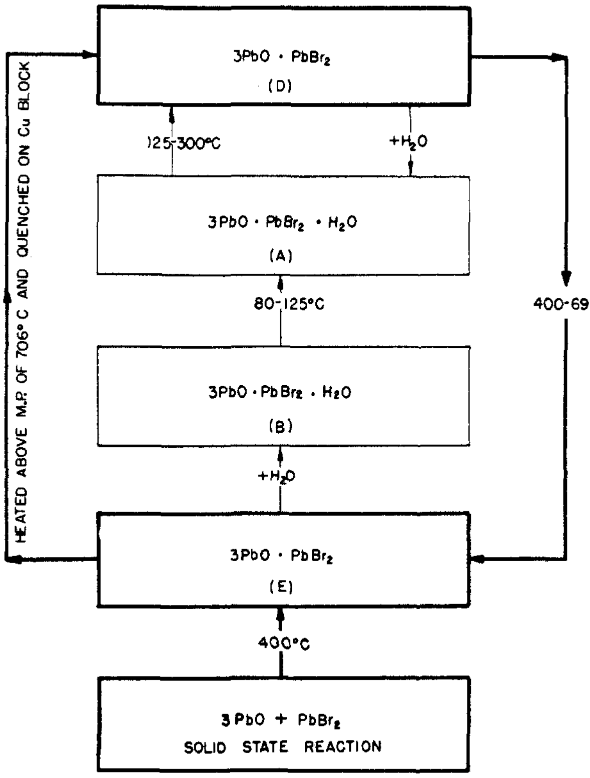

Fig. 4.—Diagram of thermal relationships of the polymorphic forms of $3PbO{\cdot}PbBr_2$ and the hydrate, $3PbO{\cdot}PbBr_2{\cdot}H_2O$. All data based on a heating time of 72 hours.

These postulated solid state replacement reactions account for the mechanism by which added $PbBr_2$ aids in the conversion of the X and N forms of $PbO{\cdot}PbBr_2$ to the low temperature, solid state R form.

Polymorphism of $3PbO{\cdot}PbBr_2$. Dehydration of the Hydrate, $3PbO{\cdot}PbBr_2{\cdot}H_2O$.—A study of the hydration and subsequent heat treatment of the hydrate, $3PbO{\cdot}PbBr_2{\cdot}H_2O$, showed that $3PbO{\cdot}PbBr_2$ exists in two crystalline forms. By heating the tribasic hydrate at 125 to 300° for 72 hours, the so-called D form is produced. The X-ray diffraction pattern for the anhydrous D form is quite similar to that for the original hydrate; however, the two compounds cannot be said to be isomorphous since some reflections appear to be shifted to higher *d* values and others to lower *d* values. By heating either the D form or the original hydrate at 400° for 72 hours a second crystalline form of $3PbO{\cdot}PbBr_2$ designated as the E form is produced. The D form may be readily hydrated to produce the original hydrate as obtained by aqueous preparation, whereas hydration of the E form produces a hydrate having a different crystalline form, designated as the B form. It was found that the B form of the hydrate would yield the original hydrate or A form if heated at 80 to 125° for 72 hours. It was also noted that if the B form were ground in water for a long period of time some of the original hydrate would be produced. In no case was the B form of the hydrate produced by aqueous preparation. The thermal relationships of the hydrates and of the D and E forms of $3PbO{\cdot}PbBr_2$ are shown graphically in Fig. 4. It has been established by material balance experiments that both forms of the tribasic hydrate contain one molecule of water. The weight per cent. water was determined for: (1) $3PbO{\cdot}PbBr_2{\cdot}H_2O$ (A form) as prepared from aqueous solution; (2) the A form after heating for 24 hours at 125°; and (3) the B form of $3PbO{\cdot}PbBr_2{\cdot}H_2O$. The values obtained are given in Table IV.

TABLE IV

DEHYDRATION OF $3PbO{\cdot}PbBr_2{\cdot}H_2O$

Starting material	Heat-treatment Temp., °C.	Heat-treatment Time, hr.	Compound formed	Water loss in wt. % By absorption	Water loss in wt. % By loss of wt.
A form	400	72	$3PbO{\cdot}PbBr_2$	1.65	1.75
A form	400	72	(E form)	1.73	1.68
A form	400	72		1.74	1.74
A form,	260	24	$3PbO{\cdot}PbBr_2$	..	1.23
after 24 hr.	260	24	(D form)	..	1.32
at 125°	260	24		..	1.21
B form[a]	260	24	$3PbO{\cdot}PbBr_2$	1.65	1.59
B form[a]	260	24	(D form)	1.51	1.56
B form[a]	260	24		1.64	1.62

[a] Chemical analysis for lead and bromine confirmed the formula, $3PbO{\cdot}PbBr_2{\cdot}H_2O$, for these preparations of the B form.

The theoretical amount of water in $3PbO{\cdot}PbBr_2{\cdot}H_2O$ is 1.706 weight per cent. The data of Table IV show that both forms of $3PbO{\cdot}PbBr_2{\cdot}H_2O$ lose approximately one molecule of water on heating and that the two forms of $3PbO{\cdot}PbBr_2$ are anhydrous. The sample of $3PbO{\cdot}PbBr_2{\cdot}H_2O$ preheated at 125° for 24 hours was partially converted to the D form of $3PbO\cdot PbBr_2$ so that a determination equivalent to a loss of one molecule of water was not obtained. The interplanar spacing values for the two forms of the tribasic hydrate are given in Table III.

Fused Preparations of $3PbO\cdot PbBr_2$.—The thermal analysis preparations showed only the E form of $3PbO\cdot PbBr_2$, the characteristic reflections showing a maximum intensity in the powder patterns at 75 mole % PbO. The fused and quenched preparations showed the D form at 72.5 mole % PbO and the E form at 78 mole % PbO. It was found that heating the D form to its melting point and then cooling slowly to a temperature of 695° or lower before quenching converted it to the E form. Also, it was possible to produce the D form from the E form by heating above the melting point at 706° and quenching on a copper block.

The E form is believed to be the equilibrium or more stable form since it is produced in the thermal analysis preparations and also on prolonged heat treatment of the hydrate. The D form may be a distorted form of $3PbO\cdot PbBr_2$ since it can be produced by fusing and quenching the E form and also since it is the first form to result on dehydration of the hydrate. It is considered likely that the similarity of the pattern for the original hydrate and the D form is due to the fact that on removal of the water, the lattice structure is only slightly altered and that on heating at temperatures of 400° and higher, the atoms then rearrange themselves to form the more stable E lattice.

Production of E Form by Solid State Reaction.—The E form of $3PbO\cdot PbBr_2$ is produced by a solid state reaction according to the equation

$$3PbO + PbBr_2 \xrightarrow[350-450^\circ]{24\ \text{hr.}} 3PbO\cdot PbBr_2\ \text{(E form)} \qquad (3)$$

The solid state reaction cycle is shown by the heavy lines in Fig. 4. There is no evidence of production of the D form at temperatures below fusion; however, there is usually some $2PbO\cdot PbBr_2$ produced in the above reaction. It was thought that possibly a solid state reaction between $PbBr_2$ and $3PbO\cdot PbBr_2$ (D form) would result in a transition to the solid state E form through a reaction similar to that described for the transition of the X and N forms of $PbO\cdot PbBr_2$ to the R form. It was found, however, that heating a mixture of these two compounds at 350° for four hours produced $2PbO\cdot PbBr_2$ in accordance with the equation

$$PbBr_2 + 2(3PbO\cdot PbBr_2)\ \text{D form} \xrightarrow[4\ \text{hr.}]{350^\circ} 3(2PbO\cdot PbBr_2) \qquad (4)$$

Polymorphism of $7PbO\cdot PbBr_2$.—The fused and quenched preparations show two phases of $7PbO\cdot PbBr_2$, one of which—designated the Q form—is most pronounced in the powder patterns at 84 mole % PbO and extends over the composition range of 80 to 89 mole % PbO, and the other of which—the T form—is most pronounced at 88 mole % PbO and extends over the composition range of 83 to 95 mole % PbO. This second phase is the one which occurs in the thermal analysis preparations, where it shows a maximum intensity at 87.5 mole % PbO. Fusing and quenching on a copper block converts the T form to the Q form. The latter can be reconverted to the T form by fusing and then cooling slowly through the primary crystallization and eutectic temperatures before quenching. The interplanar spacing values for the two forms of $7PbO\cdot PbBr_2$ are given in Table I.

The low temperature, T form of $7PbO\cdot PbBr_2$ may also be produced by solid state reaction as

$$7PbO + PbBr_2 \xrightarrow[625^\circ\text{—1 hr.}]{} 7PbO\cdot PbBr_2\ \text{(T form)} \qquad (5)$$

The high temperature, Q form is not produced by solid state reaction, but can be produced by fusing and quenching the T form. The Q form may be completely converted to the T form by adding a small amount of $PbBr_2$ and heating at 550° for one hour. This conversion is undoubtedly due to the same type of solid state replacement reaction as was observed for conversion of the X and N forms of $PbO\cdot PbBr_2$ to the R form, equation 2.

Hydration of $7PbO\cdot PbBr_2$.—The Q form of $7PbO\cdot PbBr_2$, which is canary yellow in color, maintains its structure on grinding in air, dry oil, and water. The T form is not altered by grinding in dry oil but is readily hydrated by grinding in air and water. There appear to be two hydrates formed. Grinding the T form in water for 10 to 20 minutes produced a definite change in the appearance of the material from a yellowish-tan

TABLE V

INTERPLANAR SPACING VALUES

Copper K_α radiation, $\lambda_{W.M.}$ = 1.5418 Å.

$7PbO\cdot PbBr_2\cdot 5H_2O$		$7PbO\cdot PbBr_2\cdot 7H_2O$		"$7PbO\cdot PbBr_2\cdot SiO_2$"	
d, Å.[a]	I/I_1[b]	d, Å.	I/I_1	d, Å.	I/I_1
6.00	0.04	6.24	0.24	5.83	0.11
4.48	.11	4.84	.20	3.87	.10
4.39	.11	3.59	.09	3.50	.05
4.27	.22	3.52	.17	3.00	1.00
3.94	.20	3.40	.11	2.90	0.25
3.36	.43	3.36	.30	2.77	.30
3.25	.16	3.33	.42	2.32	.30
3.11	.19	3.24	.73	2.25	.05
2.98	1.00	3.14	.53	2.17	.06
2.88	0.36	3.09	.64	2.00	.08
2.62	.25	3.00	.29	1.96	.02
2.51	.15	2.86	1.00	1.86	.02
2.20	.04	2.66	0.11	1.78	.20
2.17	.10	2.50	.08	1.75	.06
2.07	.11	2.43	.17	1.74	.06
1.75	.05	2.33	.09	1.71	.06
1.70	.09	2.20	.52	1.66	.06
1.68	.07	2.18	.17	1.64	.20
		2.09	.08	1.63	.15
		2.07	.07	1.58	.02
		2.05	.08	1.55	.02
		2.01	.20	1.51	.02
		1.96	.11	1.50	.05
		1.95	.07	1.44	.07
		1.80	.11	1.39	.03
		1.77	.33	1.37	.02
		1.74	.27	1.31	.01
		1.73	.33	1.29	.06

[a] See footnote b, Table I. [b] See footnote c, Table I.

to a dark tan color. Determination of the loss of weight on heating this product at 300° for 24 hours indicated that the starting material was $7PbO{\cdot}PbBr_2{\cdot}5H_2O$. If either this hydrate or the original T form was further ground in water and allowed to remain in contact with water for 12 hours or more, a light tan voluminous material was produced. The same product was formed by boiling $7PbO{\cdot}PbBr_2$ (T form) in water. Determination of the loss of weight on heating this hydrate at 300° for 24 hours indicated that the starting material was $7PbO{\cdot}PbBr_2{\cdot}7H_2O$. The interplanar spacing values of the major reflections for the hydrates are given in Table V.

The two hydrates were heated for 24 hours at various temperatures from 125 to 600°. There were no changes in the pattern for $7PbO{\cdot}PbBr_2{\cdot}5H_2O$ below 250°. At this temperature the material was completely dehydrated and a new phase appeared. The $7PbO{\cdot}PbBr_2{\cdot}7H_2O$ lost two molecules of water on heating at 125° and the remainder at 250°, identical patterns being obtained for both hydrates after heating at this temperature. A second phase change was observed at 350° and a third at 475°. The colors noted for these three phases were light brown, dark brown and reddish-brown, respectively. At 500° the low temperature, T form of $7PbO{\cdot}PbBr_2$ was produced.

Reaction of $7PbO{\cdot}PbBr_2$ with SiO_2.—It was observed that molten $7PbO{\cdot}PbBr_2$ reacts with SiO_2 to form a definite compound. This reaction also occurs to a small degree in the solid state at temperatures as low as 550°. The compound has been prepared by heating a mechanical mixture consisting of equimolar amounts of $7PbO{\cdot}PbBr_2$ (either T or Q forms) and SiO_2 (α quartz) in a magnesia crucible for 30 minutes at 780°. The same compound has been obtained by heating a mechanical mixture of PbO, $PbBr_2$ and SiO_2 in a 7:1:1 mole ratio at the same temperature. This silicate is not produced by heating a mixture of PbO and SiO_2 in a 7:1 mole ratio. From this preliminary study and chemical analysis the compound is considered to be a basic bromosilicate of the formula, $7PbO{\cdot}PbBr_2{\cdot}SiO_2$. Theoretical for the Pb, Br and Si are 83.40, 8.03 and 1.41% respectively. Chemical analyses on two products were: Pb, 83.20, 83.25; Br, 7.95, 7.98; and Si, 1.47 and 1.46%. The silicate is a bright yellow colored compound with a glazed appearance, and is of interest since it has been found to be the chief component on the tips of spark plug insulators under certain conditions of engine operation. The interplanar spacing values for the silicate are given in Table V.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE SIGNAL CORPS ENGINEERING LABORATORIES]

Solid Phases in the System Ag_2HgI_4–Cu_2HgI_4

BY LAWRENCE SUCHOW AND PAUL H. KECK

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Solid solutions of Ag_2HgI_4 and Cu_2HgI_4 have been prepared by simultaneous precipitation from aqueous solution. X-Ray diffraction studies and measurement of color transition temperatures have led to the construction of a phase diagram with a miscibility gap from 39 to 54 mole % Cu_2HgI_4 at room temperature, and a eutectoid point at 34° and 43 mole % Cu_2HgI_4. All low temperature or β-phases are pseudocubic tetragonal with the c/a ratio equal to unity below 68 mole % Cu_2HgI_4. Outside the heterogeneous range, the β-phases exhibit steady changes in lattice parameters with composition. The high temperature or α_1-phase of a preparation at the eutectoid composition has been found to consist of a single cubic phase with lattice constant intermediate between those previously reported in the literature for the parent compounds. A considerable transition temperature hysteresis has been observed in all materials. Munsell color specifications and spectral reflectance measurements have been made for both high and low temperature phases. The β-phases exhibit colors from yellow to red, and the α_1-phase from red to dark red-purple, as the copper content increases. The energy difference corresponding to the shift of the reflectance edge occurring with the color transition in each case is very nearly constant.

Introduction

The compounds silver(I) iodomercurate(II), Ag_2HgI_4, and copper(I) iodomercurate(II), Cu_2HgI_4, are thermochromic, each having low and high temperature phases (called β and α, respectively). Ketelaar[1,2] in reporting the crystal structures of the two phases of both compounds, states that they are isomorphous with each other in both phases. The low temperature forms are both of pseudocubic tetragonal symmetry, although in the case of Ag_2HgI_4 the unit cell is actually isometric. The high temperature forms of both compounds are cubic. Ketelaar has also given an explanation of the mechanism of the phase transition based on ionic mobility and an order–disorder rearrangement and has confirmed it by specific heat and conductivity measurements.[3,4]

Because of the close proximity of the lattice constants of the two compounds, and the apparently similar transition mechanism in each case, it seemed quite likely that solid solutions of Ag_2HgI_4 and Cu_2HgI_4 could be formed which would show similar transitions. The objectives of the work to be reported below were, therefore, to study the possibility of preparation of solid solutions in this system and to determine the relations of structure, transition point, and color with composition.

Preparation and Chemical Analysis.—The preparations were made by simultaneous precipitation from solutions

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(1) J. A. A. Ketelaar, *Z. Krist.*, **80**, 190 (1931).

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