

Acknowledgment.—The authors are indebted to Dr. Bernard Lewis for suggestive discussions preceding and during the course of this work.

Summary

A study of the lower explosion limit of the nitrous oxide-hydrogen system reveals the existence of a minimum in the pressure *versus* temperature curve for mixtures of any fixed compositions. The addition of molecular oxygen poisons the explosive reaction, and this suggests that the minimum is due to the poisoning of the reaction by oxygen from the thermal decomposition of nitrous oxide. In view of the results of Melville's study of

the slow reaction, the mechanism of poisoning must be $H + O_2 + M \rightarrow HO_2 + M$.

After passing through the minimum, the explosion limit does not increase indefinitely as the temperature is raised. Above 900° it decreases again in a vycor vessel, but could not be observed to decrease in quartz vessels of the size employed. In vycor above 900°, the explosion is not strongly affected by added oxygen and this insensitivity would be expected from the interpretation of the low temperature results.

ABERDEEN PROVING GROUND, Md.

RECEIVED APRIL 21, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF ETHYL CORPORATION]

Studies in the Lead Chloride-Lead Bromide System¹

BY GEORGE CALINGAERT, FRANCES W. LAMB AND FRED MEYER

The published information on the lead chloride-lead bromide system is incomplete and contradictory, and after a preliminary examination of its X-ray diffraction characteristics it became obvious that previously reported work would have to be repeated in order to arrive at a reliable description of the system. This paper covers an investigation of this system which, in addition to a thorough X-ray diffraction analysis, includes a repetition and an extension of the work of other investigators by thermal analysis, by conductivity and by aqueous preparations.

In a recently published study of the binary and ternary systems of lead halides, Mlle. Delgery,² contrary to the conclusions of previous investigators,³ reported the existence of several compounds and eutectics. Her first two papers gave the results of thermal analyses on the three binary systems of lead chloride, lead bromide and lead iodide,^{2a} and on the ternary system of these lead halides.^{2b} These thermal analyses were supported in a third publication^{2c} on six series of unsaturated aqueous solutions, each containing two of the four halides. In each series, the composition of the solute was varied from that of one halide to that of the other, while the total concentration was kept constant. All the conductivity-composition curves reported showed broad minima and sharp maxima, which latter were interpreted by the author as indicating the existence in solution of compounds of the corresponding solute compositions. Furthermore, Delgery proposed such measurements as a valuable adjunct to thermal

analysis, reporting that peritectic compounds difficult to detect by thermal analysis were readily detected by such conductance measurements.^{2c,2d}

For the lead chloride-lead bromide system Delgery's results indicated the existence of a stable compound, PbClBr, a peritectic compound, PbBr₂·3PbCl₂, a eutectic close to 9PbBr₂·16PbCl₂, and several series of solid solutions, two of which had limited miscibility. These results contradicted the earlier thermal analysis of Mönkemeyer,^{3a} who found that this system was one in which there was a continuous series of solid solutions with the melting (liquidus) points of all intermediate compositions lying on a straight line joining the melting points of the pure components. The work of Mönkemeyer was directly confirmed by Favorskii,^{3b} and indirectly by Matthes^{3c} in a study of the ternary system, lead chloride-lead bromide-lead iodide. A comparison of the results obtained by Delgery, Mönkemeyer and Favorskii is given in Fig. 1.

On the other hand, Thomas,⁴ in 1898, claimed, like Delgery, to have prepared both PbBr₂·3PbCl₂ and PbClBr. His evidence that PbBr₂·3PbCl₂ was a compound rather than a solid solution was based on the constancy of the composition of the material crystallizing out of a hot solution of lead chloride to which potassium bromide had been added. His evidence for the existence of PbClBr was even less satisfactory, since his material was obtained only by heating PbClI in a current of bromine.

Experimental

Materials.—Except for lead bromide, these were of analytical reagent quality; all were used without further purification. Spectrographic analysis of the potassium chloride, lead chloride and lead bromide showed a total metallic impurity of less than 0.007, 0.01 and 0.01%, respectively. Chemical analysis of the lead chloride gave

(4) Thomas, *Bull. soc. chem.*, [3] **19**, 598 (1898); [3] **21**, 532 (1899); *Compt. rend.*, **128**, 1234 (1899).

(1) The X-ray diffraction portion of this study was presented before the Sixth Annual Pittsburgh Conference on X-Ray and Electron Diffraction on November 19, 1948.

(2) (a) Delgery, *Compt. rend.*, **222**, 886 (1946); (b) **223**, 401 (1946); (c) **224**, 274 (1947); (d) **224**, 915 (1947).

(3) (a) Mönkemeyer, *Neues Jahrb. Mineral. Geol. (Beilage Bd.)*, **22**, 1 (1906); (b) Favorskii, *Ann. secteur. anal. phys.-chim., Inst. chim. gén. (U. S. S. R.)*, **13**, 281 (1940); (c) Matthes, *Neues Jahrb. Mineral. Geol. (Beilage Bd.)*, **21**, 342 (1911).

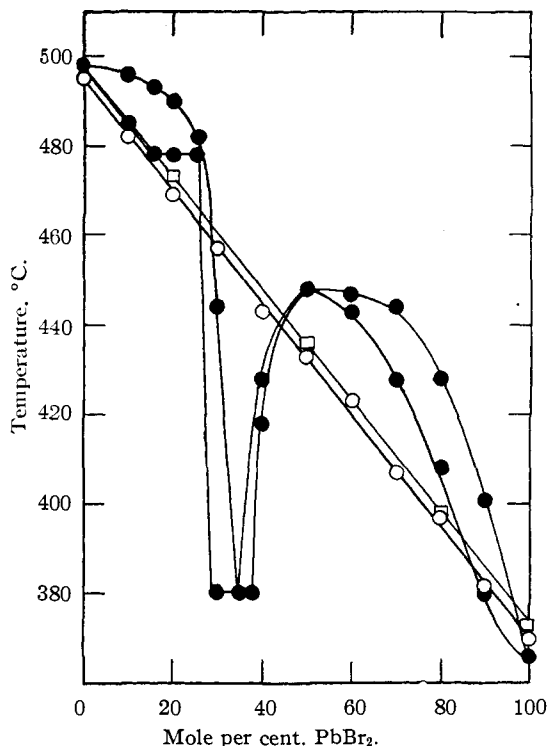


Fig. 1.—Thermal diagram of the lead chloride-lead bromide system as reported in the literature: O, Mönkemeyer; □, Favorskii; ●, Delgery.

the calculated composition; chemical analysis of the lead bromide indicated the presence of less than 0.8% of a basic bromide.

Thermal Analysis.—All cooling and heating curves were run *in vacuo* in a Vycor tube in which was supported a Vitreosil thermal well having a thin-walled capillary end. The runs were made on 40- to 50-g. samples which were vacuum dried for several hours before starting the run. Cooling and heating rates of $1^\circ/\text{minute} \pm 10\%$ were maintained by manual control of the furnace voltage. Temperatures were measured with an L. & N. glass-fiber insulated iron-constantan thermocouple and a K-2 potentiometer. Throughout each run, the Vycor tube was vibrated continuously with a Burgess Vitro-Tool; this gave improved heating and cooling curves and minimized supercooling.

One cooling curve and two heating curves were obtained on each sample. One heating curve was run on an intimate mechanical mixture and the other on the solidified melt, after it had been finely ground. The two heating curves always gave comparable results; that is, in the heating curve run on the mixture, only one thermal arrest, characteristic of the solidus temperature of the corresponding solid solution, was observed. The duration of arrests obtained ordinarily varied from thirty to almost fifty minutes for a 40-g. sample.

Conductivity Measurements. A. Equipment.—Conductance measurements were made at 1000 cycles from a bridge assembled from an L & N precision type slide wire, a shielded 11,111 ohm a. c. decade resistance box, a 1000 mmf. variable air condenser, a Wagner ground and appropriate shielding. The slide wire was used as fixed unit-ratio arms by maintaining the slide wire contact at its effective a. c. center. Two Jones-type conductivity cells were made of 16-mm. Pyrex tubing with platinized electrodes approximately 10 cm. apart. The cells were calibrated at 25° with the 0.01 demal KCl solution of Jones and Bradshaw, and the measurements were made at

$25.00 \pm 0.01^\circ$. The pH was measured with a glass electrode and a Model G Beckman pH meter.

B. Preparation of Solutions.—Two sets of stock solutions of lead chloride and lead bromide were prepared, corresponding to the two series of solutions whose conductivities were to be measured.

In the first set, sufficient lead halides were dissolved in carbon dioxide-free, hot conductivity water, in calibrated Pyrex volumetric flasks, so that after hydrolysis products were removed, the solutions would be exactly 0.02 molar in lead ion. After solution of the halides was complete, the solutions were allowed to reach hydrolytic equilibrium at 25° , adjusted to final volume and filtered through a Jena sintered-glass filter. The final concentration of the lead bromide solution was calculated from the weight of Pb(OH)Br recovered, and the final concentration of the lead chloride solution was computed on the basis of pH. The second set of stock solutions was prepared by dissolving the desired amount of each lead halide in a hot dilute solution of its hydrohalic acid. The pH's of both hydrobromic and hydrochloric acid solutions, prepared by dilution of concentrated acids with conductivity water, were close to 3.30, this being nearly the maximum pH at which the more easily hydrolyzed lead bromide would dissolve completely. The compositions of both sets of stock solutions were finally confirmed by analysis.

Solutions for conductivity measurements were prepared by mixing at room temperature appropriate volumes of each stock solution from calibrated Pyrex burets into Pyrex volumetric flasks. No appreciable change in volume occurred on mixing. This method of preparation insured that both the relative composition (Cl/Br) and the actual total concentration (0.0200 molar lead halides at 25°) were accurately controlled.

C. Conductance measurements on each solution were made in both cells, and were considered satisfactory when consecutive measurements of the cell resistance were constant to 3 parts in 10,000 and the resistance ratio of the cells was within 5 parts in 10,000 of the value found in calibration.

Aqueous Preparations. A. The Preparation of PbBr₂·3PbCl₂ was attempted according to the method of Thomas,⁴ using four times his scale, and by collecting the entire crystalline product for three temperature intervals. A Glas-Col electrical beaker jacket was used to maintain close temperature control. Forty ml. of a 10% potassium bromide solution was added slowly with stirring at 95° to one liter of carbon dioxide-free water containing 20 g. lead chloride. The resulting clear solution was slowly cooled with constant stirring, and crystallization began at 90° . The solution was further cooled to 70° , where it was maintained for two hours before removing the first crop of crystals. A second crop of crystals was similarly obtained from the supernatant solution for the interval from 70° to 50° . The resulting supernatant solution was then allowed to cool overnight to room temperature (approx. 23°) for the last crop. Each crop of crystals was separated from adhering mother liquor by washing with 95% ethyl alcohol, transferring to a Buchner funnel and draining as completely as possible. The crystal meals were then ground, and dried overnight at 75° *in vacuo* with constant pumping.

B. Other solid solutions of lead chloride and bromide of predetermined composition were attempted. The appropriate volumes of standardized hydrochloric and hydrobromic acids (approx. 1.1 N) required to prepare 1.021 equivalents of mixed acid (equivalent to 900 ml. of the hydrobromic acid solution) of the desired chlorine-bromine ratio were placed in "Low-Actinic" flasks and 66.7 ml. of a 1.5 M lead acetate solution was added dropwise with stirring. The flasks were stoppered and kept for three weeks at room temperature (approx. 23°), with occasional shaking. The products recovered were found to be well-formed tiny crystals which were drained as completely as possible on a filter, and then vacuum-dried at 110° to remove the final traces of acids.

X-Ray Diffraction.—The following is a description of the samples used and the technique of specimen preparation:

A. **Fused preparations** were obtained by heating under nitrogen an intimate mixture of the appropriate weights of lead chloride and lead bromide at about 525° in fused alumina crucibles. After melting, they were stirred for ten or fifteen minutes and allowed to cool.

B. **Heat-treated Preparations:** H 1.—One of the 50 mole % compositions used for thermal analysis, and having a forty-minute crystallization period, was kept at 420 ± 3° for sixty hours, and then allowed to cool in air.

H 2.—This is a 50 mole % lead bromide melt which had a three-hour crystallization period and was cooled to room temperature in the furnace.

H 3.—The same as H 2 except that, following the three-hour crystallization period, the sample was annealed at 416 ± 3° for forty-six hours, after which it was cooled to 100° over a period of ten hours.

H 4.—The same as H 2 except that the crystallization and annealing times were fifteen hours each, and the cooling time three hours.

C. **The preparation of specimens** which would show a minimum of preferred orientation and give patterns of reproducible relative intensities was a problem of major importance, which is inherently more difficult with the Geiger-Counter Spectrometer than with camera units. Lead chloride and lead bromide crystallize in long needles along their *a* axes, and there is a tendency for these axes to line up parallel to the surface on which they are mounted. A method was developed for making reproducible collodion films of 30-mg. samples on microscope slides, as follows:

(1) The 200-mesh material was ground an additional ten minutes. Grinding is important not only for particle size reduction but also to obtain particles of equal dimensions in all three directions in order to avoid possible orientation during the drying of the collodion film.

(2) Two drops of dilute collodion (1 part collodion in 2 parts of a 3:1 absolute alcohol-ether solution) was added to 30 mg. of the fine powder placed in a small glass cone. The mixture was worked with a stirring rod (the end of which was shaped to fit the bottom of the cone) until the solvent evaporated, leaving a fine powder coated with collodion. About 0.5 ml. of dilute collodion was added, and the dried powder was suspended by stirring, forming a fine, stable suspension.

(3) This suspension was poured on a microscope slide to cover the full width of the slide for one inch of its length, and was stirred rapidly until it became tacky and formed a thick gel. After drying, the preparation was ready for use.

The reproducibility of this method of specimen preparation was checked on nine lead chloride and ten lead bromide preparations. The average deviation from the mean relative intensity of 31 of the lead chloride reflections and 29 of the lead bromide reflections was found to be approximately 10% for each of the reflections.

Collodion films are also well suited for use with the back-reflection camera, since they can be readily removed from the glass slide, are smooth, flexible and may be accurately held to the curvature of the focusing circle of the camera. For this purpose a denser film was prepared by using 100 mg. of sample and 1 ml. of dilute collodion.

D. A calibration of the goniometer was made before and after each series of 2θ measurements, using alpha-quartz. The lattice constants, $a = 4.91310$ Å. and $c = 5.40461$ Å., given by Wilson and Lipson,⁵ were used to calculate the 2θ values of suitable lines occurring in the forward-reflection region. These are listed in Table I. The calibration of the goniometer readings showed very little variation throughout the series of measurements made in this study.

^a Calculations were made using 1.5418 Å. as the wave length of the weighted mean of the $\text{CuK}\alpha$ radiation, except for the indicated reflections where 1.54050 and 1.54435 Å. were used as the wave lengths of α_1 and α_2 , respectively.

E. **Lattice constants** were computed for each fused composition from measured angles of reflection (2θ)

(5) Wilson and Lipson, *Proc. Phys. Soc., (London)*, **53**, 245 (1941).

TABLE I
ALPHA-QUARTZ CALIBRATION DATA^a

<i>hkl</i>	2θ calcd.	<i>hkl</i>	2θ calcd.
100	20.877 ^{oa}	103	55.381°
101	26.663°	121	60.017°
110	36.578°	121 α_1	59.961°
102	39.504°	121 α_2	60.126°
200	42.490°	302	75.738°
112	50.187°	302 α_1	75.662°
202	54.927°	302 α_2	75.886°

found for five planes in the forward-reflection region by manual scanning measurements after correcting for systematic errors (based on the previous calibration), using a weighted least squares solution of the equation

$$d^{-2} = (2/n\lambda)^2 \sin^2 \theta = h^2 a^{-2} + k^2 b^{-2} + l^2 c^{-2} \quad (1)$$

The weighting factor, determined by least squares theory, is proportional to $\csc^2 2\theta$. Since the numerical solution of simultaneous equations obtained from Eq. (1) by least squares is not sensitive to small variations in weights, it was possible to assign an average relative weight for each plane satisfactory for all compositions (Table II) and, consequently, to obtain by matrix algebra a general solution of the least squares equations for the lattice constants for all compositions.

TABLE II
RELATIVE WEIGHTS USED IN CALCULATION OF LATTICE CONSTANTS

Plane	$\csc^2 2\theta / \csc^2 2\theta_{200}$			<i>w</i>
	PbCl ₂	50% PbBr ₂	PbBr ₂	
002	7.51	7.58	7.77	7.6
020	5.40	5.51	5.61	5.5
103	2.47	2.50	2.53	2.5
123	1.81	1.82	1.85	1.8
026	1.00	1.00	1.00	1.0

Results

Thermal Analysis.—Liquidus and solidus temperatures were determined from cooling and heating curves, respectively, on nine compositions ranging from pure lead chloride to pure lead bromide in steps of one-eighth mole fraction except that the 37.5 mole % lead bromide was replaced by 35 mole % lead bromide which is the eutectic composition of Delgery's thermal diagram.

A summary of the data obtained is given in Table III and Fig. 2. Where more than one run

TABLE III
THERMAL ANALYSIS OF PbCl₂-PbBr₂ SYSTEM

Composition in mole % PbBr ₂ ^a	Liquidus, T, °C.	Solidus, T, °C.
0	496.3 ^b	496.0 ^b
12.5	478.9	474.6
25	464.0	457.5
35	452.3	443.3
50	435.9	425.0
62.5	420.7	410.2
75	403.4	394.2
87.5	386.5	381.5
100	370.1 ^c	369.8 ^c

^a The compositions are based on the weights of reagents used. ^b Mönkemeyer, Favorskii and Delgery give 495, 498 and 498°, respectively. ^c Mönkemeyer, Favorskii and Delgery give 370, 373 and 366, respectively.

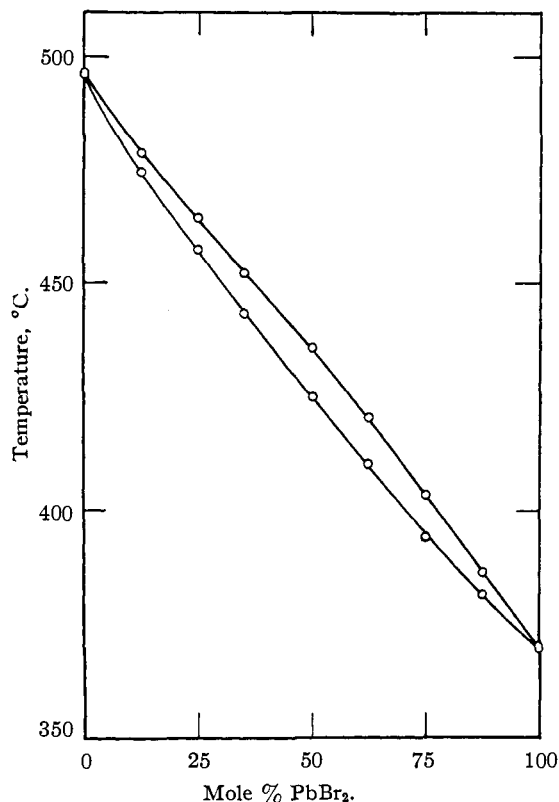


Fig. 2.—Thermal diagram of lead chloride-lead bromide system obtained in the present work.

was made, the values shown represent an average of those values for which the extrapolation of the thermal breaks was the least arbitrary. For this reason, solidus values from cooling curves and liquidus values from heating curves were ignored. The points given in this Table are believed to be precise to one degree; but judging from a calibration with zinc, they may be from zero to 2.5° low.

The thermal diagram obtained for this system is an ideal example of the diagram obtained for a binary system in which the two components form a continuous series of solid solutions, where all the melting points are intermediate between those of the pure components. As a consequence, no compounds exist in the lead chloride-lead bromide system; at least, not in the temperature-composition region above and possibly somewhat below the solidus curve of the system. This is in complete agreement with Mönkemeyer^{3a} and Favoriskii,^{3b} and in complete disagreement with Delgery.^{2a,2b}

Conductivity Measurements.—The variations in conductivity with varying anion composition which Delgery observed^{2c,2d} are considerably different in character from those observed by Sandonnini⁶ for similar systems in which complex compounds are known to exist, and are in such complete contradiction with accepted theories of

conductivity that we decided to subject them to extremely careful experimental verification.

Because no experimental details, other than the concentrations used, were given in Delgery's brief communication,^{2c} it was not possible to carry out these measurements under conditions identical with those which she employed; nor, did it seem desirable to do so on the basis of the following considerations. First, it was estimated from a study of the system $\text{PbCl}_2\text{-PbBr}_2\text{-H}_2\text{O}$,⁷ that the minimum solubility of this system at 20° is 0.020 mole of lead halides per liter.⁸ Therefore, nearly saturated solutions were avoided by using a total halide concentration of 0.020 molar at 25° rather than 0.0245 molar as used by Delgery. Second, because of the appreciable hydrolysis of both lead chloride and lead bromide, some free acid is always present in their solutions, and the solution of either halide in water is always accompanied by the separation of some insoluble hydrolysis products. Variations in the composition of the solutions and, consequently, in their conductivities would depend, therefore, on the method used to prepare the solutions.

Two methods were used; each involved mixing appropriate volumes of stock solutions of lead chloride and lead bromide. In the first, the stock solutions were prepared with the minimum amount of free acid by dissolving the proper excess of lead halide in conductivity water so that after the products of hydrolysis were removed the solutions were of the desired concentration. This method has the principal disadvantage that a solution of lead bromide is more acidic than a solution of lead chloride of the same concentration (about 1 pH unit for 0.020 molar solutions at 25°), so that the pH of a series of solutions prepared from them varies continuously. Also some investigation of the nature and degree of the hydrolysis of these lead halides was required.⁹ This method was used only because it seems similar to Delgery's. Since she does not mention hydrolysis, it was assumed that her stock solutions were prepared by dilution from saturated solutions. In the second method, the lead bromide stock solution was prepared by using as the solvent the most dilute hydrobromic acid solution which would prevent the precipitation of hydrolysis products. The lead chloride stock solution was prepared by using a hydrochloric acid solution of the same pH as the hydrobromic acid. These lead halide solutions form a series of isohydric solutions and so do the hydrohalic acid solutions used to prepare them.

The results of the conductivity measurements

(7) Meyer, *Rec. trav. chim.*, **42**, 301 (1923).

(8) The temperature of this study was not stated, but assuming that the work was done at constant temperature, it was estimated from the ratio of solubilities reported by G. Meyer for the lead halides and from the solubility-temperature data of these compounds reported in the "International Critical Tables."

(9) The products of hydrolysis were identified as the basic salts $\text{Pb}(\text{OH})\text{X}$, and 0.020 molar lead bromide and lead chloride solutions were found to be 2.1 and 0.2% hydrolyzed at 25°, respectively.

(6) Sandonnini, *Gass. chim. Ital.*, **46**, II, 205-219 (1916).

are given in Table IV and are plotted against composition in Fig. 3. Series A, varying pH , is the series of solutions for which the lead halide stock

TABLE IV

CONDUCTIVITY MEASUREMENTS FOR THE LEAD CHLORIDE-LEAD BROMIDE AND HYDROCHLORIC-HYDROBROMIC ACID SERIES

Series A, 25.00 \pm 0.01°C. 0.02003 M PbBr₂, 0.02000 M PbCl₂

Solu- tion	Vol. % PbBr ₂ soln.	Spec. cond. ^a ohm ⁻¹ cm. ⁻¹ $\times 10^3$	pH	Solu- tion	Vol. % PbBr ₂ soln.	Spec. cond. ^a ohm ⁻¹ cm. ⁻¹ $\times 10^3$	pH
1	0	3.761	4.41	6	50.03	3.721	3.63
2	20.00	3.746	3.97	7	59.99	3.712	3.56
3	25.01	3.742	3.90	8	79.98	3.695	3.43
4	30.03	3.737	3.83	9	100.00	3.676	3.36
5	40.04	3.729	3.71				

Series C, 25.00 \pm 0.01°C. 0.02000 M PbCl₂ in HCl, 0.02000 M PbBr₂ in HBr

Solu- tion	Vol. % PbBr ₂ soln.	Spec. cond. ^a ohm ⁻¹ cm. ⁻¹ $\times 10^3$	pH	Solu- tion	Vol. % PbBr ₂ soln.	Spec. cond. ^a ohm ⁻¹ cm. ⁻¹ $\times 10^3$	pH
1	0	3.942	3.27	6	50.03	3.828	3.27
2	20.00	3.897	3.28	7	59.99	3.804	3.27
3	25.01	3.886	3.27	8	79.98	3.756	3.27
4	30.03	3.874	3.27	9	100.00	3.707	3.28
5	40.04	3.851	3.27				

Series B, 25.00 \pm 0.01°C. HBr, HCl approx. 5.4×10^{-4} N

Solu- tion	Vol. % HBr soln.	Spec. cond. ^a $\times 10^3$	pH	Solu- tion	Vol. % HBr soln.	Spec. cond. ^a $\times 10^3$	pH
1	0	2.194	3.29	6	50.03	2.209	3.30
2	20.00	2.204	3.30	7	59.99	2.209	3.30
4	29.98	2.204	3.31	8	79.97	2.217	3.34
5	39.98	2.207	3.31	9	100.00	2.217	3.30

* Measurements were made in each case on two cells and their average and maximum deviation from the average value shown above was 0.015 and 0.025%, respectively.

solutions were prepared with water, and where the acidity, due to hydrolysis, is the minimum possible for each solution of the series. Series C, constant pH , is the series of solutions for which the lead halide stock solutions were prepared with their respective dilute acids, each of the same pH . Series B, constant pH , is a series of solutions made by mixing the hydrochloric and hydrobromic acid solutions used for preparing the stock solutions of Series C. The conductivities of all three series show very slight positive deviations from a simple additive relation with composition, and no evidence whatever of the sharp maxima reported by Delgery. The results for the two halide series can be shown to be consistent by evaluating the contribution of the acids present in each solution of each series, assuming as a first approximation that the conductivities of these solutions are an additive function of all the ions present, and that the ionization equilibria of the lead halides are independent of the acid concentration.

Corrections for solutions of Series C were obtained directly from the smooth curve drawn through the conductivity values obtained for Se-

ries B as in Fig. 3. The curve of these corrected values for Series C (C minus B), shown in Fig. 3 as C - B, is almost exactly parallel to the original curve C.

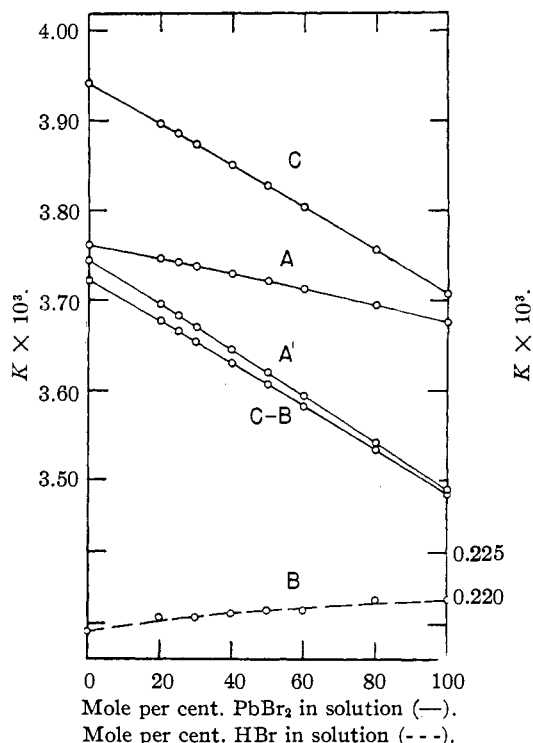


Fig. 3.—Conductivity of aqueous solutions of PbCl₂-PbBr₂ system, and of HCl-HBr system (pH 3.30).

The corresponding corrections for solutions of Series A were made from an estimate of the total acid present, using the value of 425 as a composite equivalent conductance for both acids. That no appreciable change in the amount of each acid occurred on mixing the stock solutions is shown in Table V by the agreement between the values of the pH calculated and observed for each Series A solution. The corrected conductivities for Series A are shown in Table V and in Fig. 3, as A'.

TABLE V

CORRECTED CONDUCTIVITIES OF SERIES A SOLUTIONS

Solution	Estimated acidity $\frac{N}{V} \times 10^4$		pH		Specific conductivity $\times 10^3$	
	HCl	HBr	Calcd.	Found	Mixed acid	Corrected
A1	0.39	..	(4.41)	4.41	0.017	3.744
A2	.31	0.87	3.93	3.97	.050	3.696
A3	.29	1.09	3.86	3.90	.059	3.683
A4	.27	1.31	3.80	3.83	.067	3.670
A5	.23	1.74	3.70	3.71	.084	3.645
A6	.20	2.18	3.62	3.63	.101	3.620
A7	.16	2.62	3.56	3.56	.118	3.594
A8	.08	3.49	3.45	3.43	.152	3.543
A9	..	4.36	(3.36)	3.36	.185	3.480

The failure of the two corrected curves, A' and C - B, to superimpose exactly must be attributed

to the fact that the ionic equilibria involved in each series, particularly with regard to intermediate ions formed from the lead halides, are influenced by the amount of halogen acids present. The closer agreement obtained for the lead bromide end is, of course, due to the similarity of the compositions of the two lead bromide solutions, so that there is really no assurance that these corrected conductivities are a measure of the "conductivity of lead bromide" independent of the pH of the solutions used.

Another interesting point is that, for both series, the conductivity of the lead bromide solution was lower than that of the lead chloride solution. This was unexpected, inasmuch as the Br^- ion has a higher limiting ionic conductivity than the Cl^- ion. It is also contrary to the report of Delgery,^{2c} who, strangely enough, shows the bromide to be more conducting than the chloride in the two more concentrated solutions, and less conducting in the most dilute solution she measured.

For comparison, the conductivity results reported by Delgery^{2c} for the lead chloride-lead bromide system are shown in Fig. 4 for 0.0245 molar Pb, together with the present results. These results, as well as those for the other binary halide solution systems, which seemed improbable, must now be considered erroneous and should be disregarded.

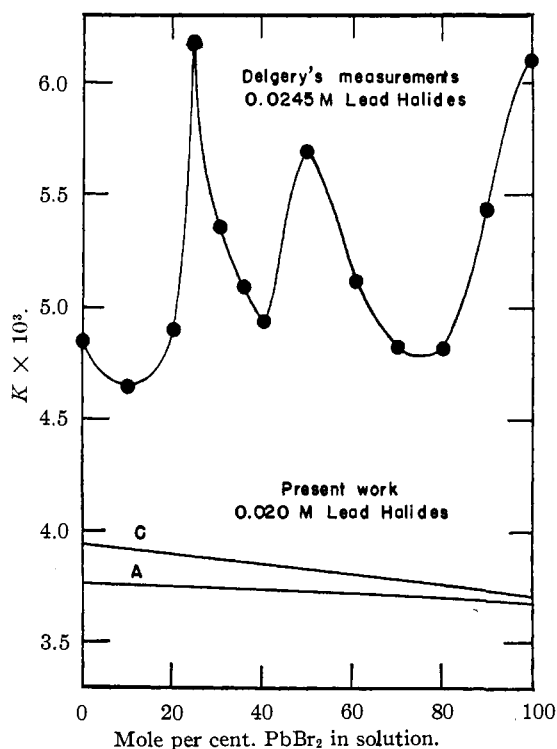


Fig. 4.—Comparison of conductivity of aqueous solutions of the lead chloride-lead bromide system.

Aqueous Preparations.—These were undertaken to check the claim by Thomas⁴ that a com-

pound $PbBr_2 \cdot 3PbCl_2$ could be prepared from an aqueous solution; to determine whether it was possible to prepare from aqueous solutions any given solid solution of this system; and to determine whether the X-ray diffraction characteristics of solid solutions of this system prepared from aqueous solution were different from those of solid solutions prepared by fusion.

A. The preparation of $PbBr_2 \cdot 3PbCl_2$ was attempted using the method of Thomas⁴ but on a larger scale and by collecting the entire crystalline product for three temperature intervals (see Experimental Part). The results are given in Table VI. The estimated ranges of composition of the solid solutions are given in the last column, where the smallest figure is based on the assumption that the contaminant is entirely potassium bromide and the largest on the more plausible assumption that it is entirely potassium chloride. These results show that the composition of the solid solution crystallizing out is not constant as Thomas claimed.

TABLE VI
ATTEMPTED PREPARATION OF $PbBr_2 \cdot 3PbCl_2$ USING
THOMAS' METHOD

Frac- tion	Temp. range, °C.	Yield, g.	Analyses, %				Composi- tion, mole % $PbBr_2$
			Pb	Br	Cl	K	
1	90-70	7.3	68.21	14.96	16.55	0.10	28.3-28.7
2	70-50	5.4	68.56	14.34	17.01	.08	27.0-27.3
3	50-23	4.0	69.22	12.33	18.23	.09	22.8-23.2

X-Ray diffraction patterns in the back-reflection region of these samples were among the sharpest obtained for solid solutions of this system, and a comparison of these patterns clearly showed a progressive shift in lines, again demonstrating the difference in composition of these samples. The non-existence of this "compound" is further supported by the fact that except for very slight line shifts, forward-reflection patterns of the first and third samples were identical with those of the fused 25 mole % preparation.

B. The Preparation of Solid Solutions of Predetermined Composition.—It has been shown in a study of the effect of alkali and alkaline earth chlorides and bromides on the solubility of lead chloride and lead bromide,¹⁰ that all the solubility curves obtained possess a common minimum for a range of concentration of soluble halides from about 0.3 to about 0.7 *N*. It was therefore expected that if no compounds or favored composition existed, the addition of lead ion to a solution containing both bromide and chloride ions in this concentration range would result in the precipitation of a solid solution containing the same chlorine-bromine ratio as the solution. To simplify the problem of purification of the product, hydrobromic and hydrochloric acids were selected as the soluble halides and lead acetate as the soluble lead salt. (Even if salts were used for the

(10) Herz and Hellbrant, *Z. anorg. allgem. Chem.*, **130**, 188 (1923).

halides, some acid would have been necessary to avoid hydrolysis.) The effect of hydrochloric acid on the solubility of lead chloride^{10,11} fits into the same general picture. As far as the authors are aware, no comparable data exist for the effect of hydrobromic acid on the solubility of lead bromides.

The actual preparations are described in the Experimental Part. The preparations were analyzed chemically and studied by X-ray diffraction. The results of analysis showed the products to vary in composition from 48.3 to 57.5 instead of from 35 to 65 mole % lead bromide, as expected. The data for these experiments are summarized in Table VII. The last column of Table VII gives the estimated composition of the mixed acid remaining after the addition of lead acetate and is based on the estimate made from Herz and Hellabrant's data¹⁰ that 0.004 mole of lead ion remains in solution. That aging was not an important factor in determining composition was shown in an experiment in which the initial precipitate from a solution of the same composition as that used for Aq 1 was immediately recovered and was found, by X-ray diffraction, to be close to 50 mole % lead bromide.

TABLE VII

COMPOSITION OF SOLID SOLUTIONS OF LEAD CHLORIDE AND LEAD BROMIDE OBTAINED BY PRECIPITATION FROM MIXED HCl-HBr SOLUTIONS

Solid solution	Initial mole % HBr of mixed acid	Analysis of precipitates		Mole % PbBr ₂ in precipitates	Calcd. mole % HBr in soln. in equil. with precipitate
		% Br	% Cl		
Aq 1	35	23.96	11.39	48.3	32.0
Aq 2	45	25.60	10.40	52.2	43.3
Aq 3	50	25.73	10.39	52.4	49.5
Aq 4	50	25.64	10.40	52.2	49.5
Aq 5	55	26.29	10.09	53.6	55.3
Aq 6	65	27.88	9.14	57.5	66.7

The last two columns of Table VII correspond to the equilibrium compositions obtained by G. Meyer⁷ for the solid solution and the solute in the system PbCl₂-PbBr₂-H₂O. For comparison, the two sets of data are shown in Fig. 5. The similarity between the two systems is striking. In fact, the only effect of the presence of 0.85 N mixed acids (considering the 0.21 N acetic acid present to be without influence) is to shift the equilibrium compositions of the solid solutions about 2% toward the lead bromide axis. This effect may in part be ascribed to the greater acid strength of hydrobromic acid, and is apparently superimposed on the tendency to form the 50 mole % lead bromide solid solution.

While G. Meyer pointed out that this relationship between the equilibrium compositions of solute and solid solution of the PbCl₂-PbBr₂-H₂O system is exactly similar to that found for the

(11) Kendall and Sloan, *THIS JOURNAL*, **47**, 2306 (1925).

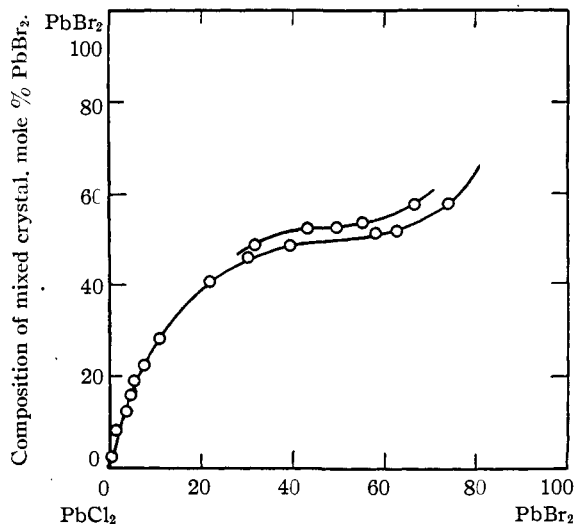


Fig. 5.—Lead chloride-lead bromide mixed crystals in equilibrium with their aqueous solution: lower curve, PbCl₂-PbBr₂-H₂O system from G. Meyer; estimated temperature, 20°; upper curve, present data for 0.85 N mixed acid; approximate temperature, 23°.

permutites by Hisschemöller¹² and was therefore explainable on the basis that a compound, PbCl₂-PbBr₂, existed, he felt that it could also be due to physical forces alone. The present results, however, clearly demonstrate that not all compositions of solid solutions of lead chloride and lead bromide are equally likely to form; in other words, chloride and bromide ions do not enter the crystal lattice on the basis of statistical probability alone.

The results obtained in repeating Thomas' preparation of the 25 mole % lead bromide solid solution can now be qualitatively explained on the basis of the tendency to form the 50 mole % composition, if the same relationship between the composition of the solid solution and the solute in aqueous solution is assumed to hold for the system PbCl₂-KBr-H₂O at the various temperatures used as for the PbCl₂-PbBr₂-H₂O system at 20°.

On this basis, the composition of the solid solutions for the various fractions would have been 34.5, 28 and 19 mole %, respectively, instead of the 28.5, 27, and 23 mole % lead bromide actually obtained.

X-Ray Diffraction.—Lead chloride and lead bromide¹³ are orthorhombic, with four molecules per unit cell, and belong to space group V_h¹⁶, with all atoms occurring in special positions (c). Their lattice constants (Table IX) differ from their mean value by less than 3%, and they would be expected to form a continuous series of solid solutions and to obey Vegard's law for solid solutions.

An X-ray diffraction study was made of nine

(12) Hisschemöller, *Rec. trav. chim.*, **40**, 394 (1921).

(13) (a) Bräkken, *Z. Krist.*, **83**, 222 (1932); (b) Bräkken and Harang, *ibid.*, **68**, 123 (1928); (c) Döll and Klemm, *Z. anorg. Chem.*, **241**, 247 (1939); (d) Nieuwenkamp and Bijvoet, *Z. Krist.*, **84**, 49 (1933); (e) Wyckoff, "The Structure of Crystals," 2nd ed., suppl., Chemical Catalog Co., New York, N. Y., 1935, p. 27.

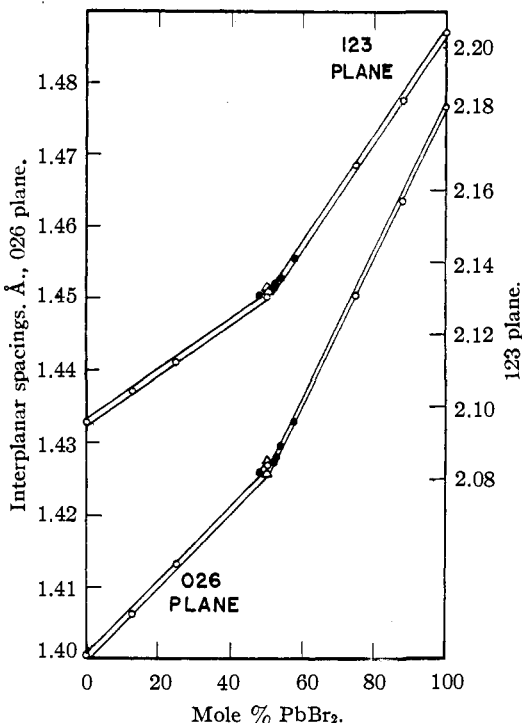


Fig. 6.—Relationship between interplanar spacings and compositions for the 123 and 026 planes in the $\text{PbCl}_2\text{-PbBr}_2$ system. The lines show the effect of an error of $\pm 0.02^\circ$ in 2θ . Legend: \circ , fused; \bullet , aqueous; Δ , heat-treated preparations.

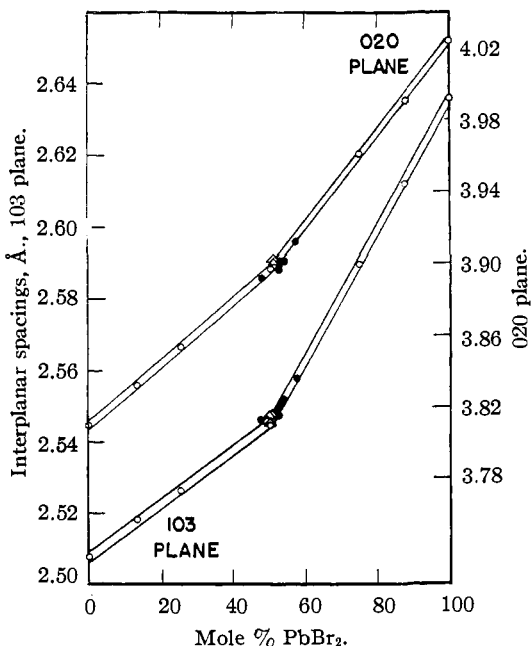


Fig. 7.—Relationship between interplanar spacings and compositions for the 020 and 103 planes in the $\text{PbCl}_2\text{-PbBr}_2$ system. The lines show the effect of an error of $\pm 0.02^\circ$ in 2θ . Legend: \circ , fused; \bullet , aqueous; Δ , heat-treated preparations.

fused preparations of the lead chloride-lead bromide system. In a preliminary examination of 2 r. p. m. automatic recordings in the forward-reflection region obtained with a Norelco Geiger-counter X-ray spectrometer using $\text{Cu K}\alpha$ radiation, line-shift measurements showed a discontinuity at the 50 mole % composition indicative of a compound, PbClBr , isomorphous with lead chloride and lead bromide and forming a complete series of solid solutions with each of these compounds. The preliminary investigation also reveals discontinuities in the progressive changes in relative intensities of a number of lines at the 50 mole % composition, which gave further support to the above hypothesis.

In view of these unexpected results more accurate determinations of the Bragg angles were made by manual scanning measurements, which gave 2θ values reproducible to $\pm 0.01^\circ$. Making allowance for error in applying the calibration data, the total experimental error in 2θ measurement should not be over $\pm 0.02^\circ$.

Manual scanning data were obtained for the 002, 020, 026, 103, 123 and the unresolved 212, 114 planes of most of the fused preparations. The average d values in Ångström units for the first five planes are given in Table VIII. The interplanar spacings-composition data are shown in Figs. 6 and 7 for the 123, 026, 020 and 103 planes. From

TABLE VIII
INTERPLANAR SPACING VALUES FOR LEAD CHLORIDE-LEAD BROMIDE SYSTEM

Sample	Mole % PbBr_2	Interplanar spacing values in Å.				
		Plane 026	Plane 123	Plane 103	Plane 020	Plane 002
F 0	0.00	1.4008	2.0958	2.5079	3.8101	4.5193
F 1	12.8	1.4071	2.1044	2.5182	3.8324	4.5393
F 2	25.2	1.4133	2.1128	2.5262	3.8536	4.5564
F 4	50.0	1.4268	2.1307	2.5448	3.8971	4.5944
F 6	74.9	1.4503	2.1672	2.5897	3.9611	4.6796
F 7	88.1	1.4635	2.1850	2.6122	3.9902	4.7164
F 8	100.0	1.4768	2.2040	2.6360	4.0238	4.7612
Av. dev. ^a		± 0.0001	0.0004	0.0005	0.0006	0.0028
H 1	49.9			2.5451		
H 2	50.2	1.4264	2.1322	2.5473	3.8992	
H 3	50.3	1.4273	2.1321	2.5483	3.8995	
H 4	50.0			2.5463		
Aq 1	48.3	1.4260	2.1310	2.5458	3.8921	
Aq 2	52.2	1.4277	2.1337	2.5483	3.8989	
Aq 3	52.4	1.4280	2.1342	2.5504	3.9001	
Aq 4	52.2	1.4284	2.1341	2.5496	3.8973	
Aq 5	53.6	1.4295	2.1360	2.5525	3.9008	
Aq 6	57.5	1.4329	2.1413	2.5581	3.9123	
Av. dev. ^a		± 0.0002	0.0003	0.0004	0.0006	
Calcd. = ex- ptl. error ^b		0.0004	0.0010	0.0013	0.0031	0.0046

^a Each of the individual interplanar spacing values represents the average of 2 or 3 determinations. The average deviation for each plane is based on 18 to 20 individual determinations for the fused preparations and 24 to 29 for the heat-treated and aqueous preparations.

^b The calculated experimental error is based on a $\Delta 2\theta$ of $\pm 0.02^\circ$.

these figures, discontinuities in interplanar spacings can be seen at the 50 mole % composition, which is in agreement with the preliminary observations made from the automatic scanning records.

In order to determine whether the results of X-ray diffraction were in any way due to a distortion of the crystal lattice in the fused preparations, an investigation was made of heat-treated and aqueous preparations. The compositions of the heat-treated preparations were held close to the 50 mole % composition, since the effect of line-shift measurements should be most pronounced at this composition. Heat treatment included slow crystallization, prolonged annealing and slow cooling. Manual scanning data were obtained for the heat-treated and aqueous preparations. The average interplanar spacing values are given in Table VIII, and Figs. 6 and 7. It is evident that any changes produced in interplanar spacing values for the 026, 123 and 020 planes by heat treatment are within the experimental error. The increases in d values noted for the 103 plane are only slightly greater than the experimental error and may or may not be real. If real, a possible explanation might be that the adjustment of the crystal lattice took place primarily along the a -axis. Preparations from aqueous solution likewise show no significant differences.

A least squares treatment was used to calculate the lattice constants for each composition from the manual scanning data obtained on the 002, 020, 026, 103 and 123 planes. The lattice constants, axial ratios and unit cell volumes are given in Table IX. The lattice constants for lead chloride and lead bromide show good agreement with the literature values.

TABLE IX

LATTICE CONSTANTS, AXIAL RATIOS AND UNIT CELL VOLUMES FOR LEAD CHLORIDE-LEAD BROMIDE SYSTEM

Mole % PbBr ₂	Lattice constants in Å.			Axial ratios			Unit cell vol., Å. ³
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	
0.0	4.5301	7.6220	9.0375	0.594	1	1.186	312.1
12.8	4.5424	7.6644	9.0767	.593	1	1.184	316.0
25.2	4.5477	7.7074	9.1147	.590	1	1.183	319.5
50.0	4.5616	7.7949	9.1985	.585	1	1.180	327.1
74.9	4.6511	7.9209	9.3520	.587	1	1.181	344.5
88.1	4.6850	7.9798	9.4384	.587	1	1.183	352.9
100.0	4.7249	8.0461	9.5255	.587	1	1.184	362.1

VALUES CALCULATED FROM THE LITERATURE^a

PbCl ₂	4.534	7.623	9.048	0.595	1	1.187	(B. ^{13a} 1932)
PbCl ₂	4.529	7.620	9.045	.594	1	1.187	(D. & K. ^{13b} 1939)
PbBr ₂	4.725	8.036	9.504	.588	1	1.183	(N. & B. ^{13d} 1933)
PbBr ₂	4.727	8.054	9.537	.587	1	1.184	(D. & K. ^{13b} 1939)

^a Lattice constants converted from kX. units to Ångström units.

The relationships of lattice constants and unit cell volume with composition are shown in Fig. 8.

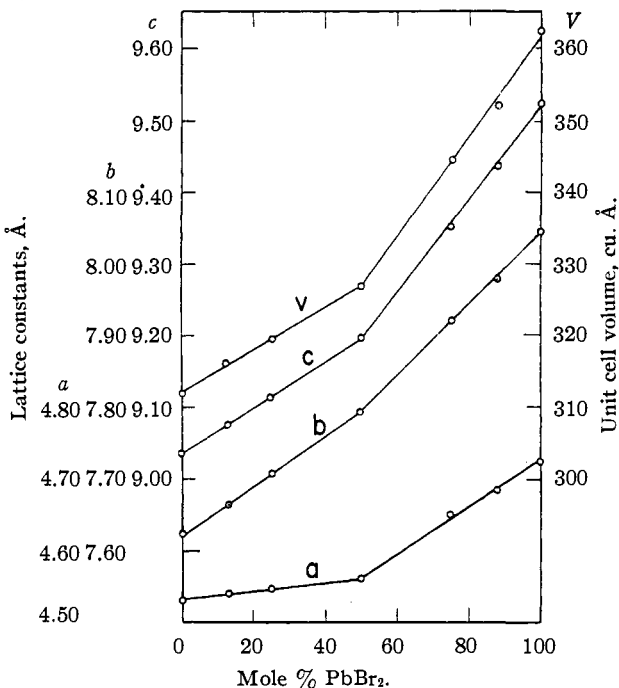


Fig. 8.—Relationship of lattice constants and unit cell volume with composition for the PbCl₂-PbBr₂ system.

As would be expected from the interplanar spacings-composition relationships, these data are best represented by two straight lines intersecting at the 50 mole % composition. From this it may be concluded: (1) that the replacement of chloride ions by bromide ions expands the crystal lattice at a slower rate from 0 to 50 than from 50 to 100 mole % lead bromide. This difference in rate of expansion is most pronounced for the a -axis and least for the b -axis (Fig. 8; also the 020 plane, Fig. 7); (2) that the compound or ordered structure at the 50 mole % composition has definite axial ratios independent of the method of preparation. These axial ratios are unique, being minimum values for the system.

According to Nieuwenkamp and Bijvoet,^{13d} the halide ions of the isomorphous compounds lead chloride and lead bromide occupy two inequivalent positions in the crystal lattice, designated as X' and X''. Also, the Cl'' and Br'' ions have a slightly larger space volume around them in their respective lattices than the Cl' and Br' ions. From this it was theorized that a preferential replacement of the Cl'' ions is taking place from the 0 to 50 mole % lead bromide compositions, leaving only the Cl' ions for replacement from the 50 to 100 mole % compositions. This would explain the lower rate of expansion of the unit cell from 0 to 50, since there is more space for the larger bromide ion at the Cl'' ion positions than at the Cl' ion positions in the crystal lattice. On the basis of this theory, the 50 mole % composition might then be considered to be a preferential-replace-

TABLE X
 RELATIVE INTENSITIES FOR LEAD CHLORIDE-LEAD BROMIDE SYSTEM

Mole % PbBr ₂	Miller indices										
	002	101	012	020	111	121	103	113	032	123	212, 114
0.0	0.30	0.42	1.00	0.42	0.94	0.56	0.65	0.09	0.27	0.45	0.31
12.8	.21	.34	0.91	.47	1.00	.72	.62	.09	.35	.43	.32
25.2	.18	.29	.99	.46	0.98	.86	.63	.12	.37	.43	.33
36.0	.15	.28	.92	.39	.98	.96	.58	.14	.39	.42	.36
50.0	.07	.22	.93	.35	.90	1.00	.57	.18	.42	.38	.34
62.5	.11	.21	.75	.35	.80	1.00	.58	.15	.41	.38	.32
74.9	.20	.24	.74	.40	.84	1.00	.66	.13	.39	.42	.28
88.1	.28	.26	.68	.35	.78	1.00	.82	.13	.43	.48	.26
100.0	.64	.37	.74	.45	.70	0.94	1.00	.17	.41	.55	.22

 TABLE XI
 COMPARISON OF CALCULATED AND EXPERIMENTAL INTENSITIES FOR LEAD CHLORIDE-LEAD BROMIDE SYSTEM

Plane	Observed relative intensities ^a I/I_1 50 mole %			Calculated intensities ^a $I \times 10^{-5}$				
	PbCl ₂	PbBr ₂	PbBr ₂	PbCl ₂	PbCl'Br''	PbCl''Br'	Random	PbBr ₂
002	0.30	0.07	0.64	0.20	0.12	0.33	0.21	0.21
101	0.43	.22	.37	.17	.05	.25	.13	.10
012	1.00	.93	.74	.47	.44	.32	.38	.29
020	0.42	.35	.45	.80	.71	.87	.79	.78
111	.94	.90	.70	.63	.64	.43	.53	.44
121	.56	1.00	.95	.34	.55	.36	.45	.57
103	.65	0.57	1.00	.95	.98	1.34	1.15	1.37
113	.09	.18	0.17	.008	.012	0.011	0.012	0.016
032	.27	.42	.41	.60	.70	.72	.71	.82
212, 114	.31	.34	.22					
212				.33	.31	.21	.26	.19
114				.009	.068	.0003	.015	.022
212 + 114				.329	.378	.210	.275	.212
123	.45	.38	.55	.61	.59	.66	.63	.65

^a The experimentally determined relative intensities have not been corrected, and the calculated intensities have not been converted to relative intensities, so that while comparisons of intensities may be made for any one plane for various structures, they cannot be made from plane to plane for any one structure.

ment structure, PbCl'Br'', and would explain the discontinuity observed in the lattice constant-composition relationships.

As a further check on the existence of the preferential-replacement form PbCl'Br'', a comparison was made of calculated and experimental relative intensities of a number of the reflections. This was of particular interest since discontinuities were noted in the progressive changes in relative intensities of several lines at the 50 mole % composition. The relative intensities (I/I_1) of 11 lines were evaluated for the fused compositions from 1 r. p. m. automatic recordings taken on quadruplicate specimen preparations. A rotating sample mount was used to decrease preferred orientation effects. A summary of the average observed relative intensities for each composition is given in Table X, from which it is noted that at the 50 mole % composition there is either an actual reversal in the progressive changes of relative intensities, as for the 002 plane, or there is an abrupt change in their rate, as for the 121 plane.

Using the structure factor formula¹⁴ for lead chloride and lead bromide, the intensities for the

above 11 reflections were calculated for lead chloride, lead bromide and the three possible forms at the 50 mole % composition: namely, the form in which there is random replacement of Cl' and Cl'' by Br' and Br'' and the two forms in which there is preferential replacement, PbCl'Br'' and PbBr'Cl''. The calculated intensities and the experimental relative intensities are given in Table XI. The calculated intensity values for the "ordered" form, PbCl'Br'', fit the trend of the experimental relative intensities at the 50 mole % composition better than either the "ordered" form PbBr'Cl'', or the random form. This is true for each of the planes calculated except the 113 and 032 planes where the calculated intensities for the three forms are nearly the same. It is interesting to note that the sum of the calculated intensities for the 212 and 114 planes of the "ordered" form, PbCl'Br'', is in good agreement with the trend of the observed relative intensity for the 212, 114 plane (not resolved) at the 50 mole % composition. The results of the intensity study thus support the theory that a preferential-replacement structure occurs at the 50 mole % composition and indicate that it is PbCl'Br''. Thus, the line-shift and intensity data both indicate that the "ordered" form is a "compound"

(14) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. I, rev. ed., The Chemical Catalog Co., New York, N. Y., 1944, p. 138.

stable at room temperature, isomorphic with lead chloride and lead bromide and forming a complete series of solid solutions with both pure components.

Discussion

The present thorough study of the lead chloride-lead bromide system shows it to be a somewhat unique salt system, containing an "ordered" structure at the 50 mole % composition, stable at room temperature. Since the lattices of the two isomorphous components possess two sets of halogen positions with different space volumes, the opportunity arises for the formation of a unique type of ordering as one halogen is replaced by the other in such a way as to cause the least dimensional change in the lattice. Consequently, as bromine is substituted for chlorine in the lead chloride lattice, it preferentially replaces the chlorine from the more spacious Cl^{II} positions until these are completely replaced, forming a continuous series of solid solutions culminating in the formation of the "ordered" structure, PbCl^IBr. Upon further substitution of bromine for chlorine, the less spacious Cl^I positions are occupied, and this forms another continuous series of solid solutions ending with lead bromide. In this second series, the rate of expansion of the unit cell with change in composition is necessarily greater than in the first series of solid solutions. This interpretation not only accounts for the discontinuities observed in the lattice constants-composition relationships for the system, but it has also been shown to account for the discontinuities observed in the relative intensities-composition data.

If the structure PbCl^IBr were a compound which was at all stable in the range of temperatures defined by the thermal diagram of the system, one would expect the liquidus and solidus curves to approach or meet at the 50 mole % composition, as in the bromine-iodine system.¹⁵ Since this is not the case (Fig. 2), it is clear that PbCl^IBr does not exist as a compound in this temperature range. For this reason, the preferential-replacement structure may be considered a borderline compound which is stable only at lower temperatures.

The fact that no transition temperature was observed, even in the annealing and slow-cooling of the 50 mole % composition may be due either to the fact that the heat of transition is too small for detection with the present method, or to the fact that the transition occurs over a range of temperatures.¹⁶ Furthermore, two samples of 50 mole % composition which were quenched from the solidus temperature, where they had been held for an hour, to that of a Dry-Ice-chloroform bath, showed no measurable degree of randomness at room temperature. If the transition to the preferential-replacement structure does not occur in the

(15) Terwogt, *Z. anorg. Chem.*, **47**, 203 (1905).

(16) See, for example, the discussion of ordered and disordered phases for Seitz, "Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 35-36 and 502-511.

temperature-composition region immediately below the solidus curve for the system, it occurs rapidly and completely at lower temperatures, since the X-ray diffraction characteristics of any solid solution of this system appear to be independent of sample history.

The results obtained in the attempted preparation of solid solutions of lead chloride and lead bromide of predetermined composition by precipitation from solutions containing excess hydrochloric and hydrobromic acid, and those of G. Meyer on the lead chloride-lead bromide-water system, demonstrated the definite tendency of the 50 mole % composition to crystallize out, which appears to further support the existence of the "ordered" structure PbCl^IBr as a borderline compound.

The results and conclusions of the present study are completely at variance with those reported by Delgery for this system.² Furthermore, we are unable to account for the striking differences which exist between her thermal analysis and those of other investigators⁸ (Fig. 1), including the present one (Fig. 2). Based on her thermal analysis, Delgery claimed the existence of a high-temperature stable compound, PbClBr, and a peritectic compound, PbBr₂·3PbCl₂, both of which Thomas⁴ had previously claimed to prepare. Thomas' preparation of the first composition by heating PbClI in a current of bromine is obviously no evidence for a compound, and we were unable to confirm his preparation of the second. Likewise, we are unable to account for the striking differences which exist between Delgery's conductivities for this system and our own (Fig. 4). We have shown that hydrolysis does not account for the unexpected variations in conductivity which she reported; neither would the possible presence of excess solid phase in her lead chloride-lead bromide solutions, since the system possesses only one minimum in solubility. All her conductivity-composition curves for solutions of binary lead halide systems show sharp conductivity maxima, of a type never observed before, and not readily interpretable on the basis of accepted theories. It is also noteworthy that these maxima are reported at compositions which were precisely the same as those of compounds which she had initially observed or was able to confirm afterward by thermal analysis.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Loren M. Knowles in making the thermal runs and completing several aqueous preparations, and of Gordon E. Noakes and Berol L. Robinson in securing X-ray diffraction data. We are also indebted to Profs. Lewis S. Ramsdel and A. L. Ferguson, University of Michigan, respectively for valuable suggestions in the interpretation of the X-ray diffraction data and for making electrochemical equipment available for the conductometric studies.

Summary

The lead chloride-lead bromide system has been studied by means of thermal analysis, conductivity, aqueous preparations and X-ray diffraction. No binary compounds exist in this system other than the preferential-replacement structure, $\text{PbCl}'\text{Br}''$, whose existence was

demonstrated by the X-ray diffraction data. This "ordered" structure is stable at room temperature but not at the melting point, is isomorphous with lead chloride and lead bromide, and forms a complete series of solid solutions with both.

DETROIT, MICHIGAN

RECEIVED APRIL 25, 1949

[CONTRIBUTION FROM THE LABORATORIES OF DISTILLATION PRODUCTS, INC.]

Vapor Pressures of Phlegmatic Liquids. I. Simple and Mixed Triglycerides¹

BY E. S. PERRY, W. H. WEBER AND B. F. DAUBERT²

The vapor pressure measurements of phlegmatic³ liquids, such as the triglycerides, require a method which imposes a minimum of thermal hazard to the substance under examination. Of the available methods capable of accommodating materials of this kind, the static method of Hickman, Hecker and Embree⁴ employing the pendulum tensimeter appeared to be more promising than the dynamic methods proposed by Verhoek and Marshall⁵ and Kapff and Jacobs.⁶ In application, the dynamic methods have been limited to the vapor pressure measurements of plasticizer-type esters in the range of 10^{-2} to 10^{-4} mm. at 40 to 160°. The pendulum-tensimeter method, however, has been used with substances of lower volatilities which have perhaps even less thermal stability than the ester materials, such as, for example, 1,4-dipropyldiaminoanthraquinone. In addition, the method gives absolute pressure measurements in that the pressure of the vapor is measured directly as a force per unit area. In contrast to the dynamic methods, therefore, the results are independent of the theoretical equations of the kinetic theory and errors introduced by inaccuracies in accommodation coefficients are obviated. For these reasons the pendulum-tensimeter method seemed most generally applicable for the measurements reported below. In the present paper are presented the vapor pressures for a large number of triglycerides, including all of those having an even number of carbon atoms in the acid radical from tributyrin to tristearin; for mixed triglycerides, both saturated and unsaturated; and for several fractionated natural fats. In a subsequent paper⁷ there will be presented the vapor pressures of a number of high molecular weight esters of the plasticizer and diffusion pump fluid types.

The theory for the pendulum-tensimeter method

(1) Communication No. 151 from Laboratories of Distillation Products, Inc.

(2) Department of Chemistry, The University of Pittsburgh.

(3) Hickman and Weyerts, *THIS JOURNAL*, **52**, 4714 (1930).

(4) Hickman, Hecker and Embree, *Ind. Eng. Chem.*, **9**, 264 (1937).

(5) Verhoek and Marshall, *THIS JOURNAL*, **61**, 2737 (1939).

(6) Kapff and Jacobs, *Rev. Sci. Instruments*, **18**, 581 (1947).

(7) Perry and Weber, *THIS JOURNAL*, **71**, 3726 (1949).

has been reported by the original authors,⁴ therefore only the final equations will be reproduced here for convenience. The vapor pressure P is calculated from the effective weight of the pendulum M , the area of the orifice A , and the angular displacement θ , according to the relationship: $P = M/A \times \sin \theta$. For our specific apparatus the vapor pressure in mm. mercury is: $P = 1.075/8.96 \times 13.6 \times 10 \times \sin \theta = 0.0882 \times \sin \theta$.

Experimental

Apparatus.—A pendulum-tensimeter similar to that of Hickman, Hecker and Embree,⁴ but incorporating the orifice heater recommended by Verhoek and Marshall,⁵ was used. A small liquid trap was added to the reflux line to prevent loss of vapor from the boiler. The usual oil-bath was replaced by an air-bath so that the temperature range could be extended. This consisted of an aluminum box approximately $9'' \times 9'' \times 5''$, lagged with asbestos paper. The first air-bath contained a single heater element wound in a flat coil and mounted just off the floor of the box. The heater was shielded and baffled to prevent irregular heating by radiation. Heat distribution in the box was examined by placing 8 thermometers at various points and recording the temperatures of each as the heat was progressively increased to 300°. A satisfactory heat distribution was not obtained by this method regardless of the baffle used and it was finally discarded in favor of one which responded better to the test. The new heater element consisted of a glass rod frame on which was wound asbestos-covered resistance wire equivalent to 1000 watts. The glass frame was cubical in shape and dimensioned so as to leave a half-inch space between it and the walls of the box on all sides. Resistance wire was wound evenly on all 12 rods of the frame. Power was controlled by a variable transformer. Air temperatures measured at various points in the box by means of thermometers as discussed above showed that the total disparity in temperatures was not over 2°. The bath was therefore used as such without any further attempts to better distribute the heat.

The aluminum box with heating element hung from a yoke which straddled the tensimeter and was supported so that it could rotate with the tensimeter. Two Pyrex windows were provided for better illumination and direct observation of the pendulum at the orifice. One window was located on the front wall of the box and the other on the rear wall. The use of the air-bath greatly facilitated the observation of the equilibrium point of the pendulum and thereby increased the reproducibility of the readings. It also extended the effective temperature range to well over 300°.

While collecting data, temperature measurements were made with a well-thermometer which protruded into the