[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON]

The Al_2Br_6–HCl–Al_2Cl_6–HBr and Al_2Br_6–Al_2Cl_6 Systems and Mixed Halide Intermediates[1]

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The halogen exchange reactions of HCl with anhydrous $AlBr_3$ and HBr with $AlCl_3$ have been studied at 24, 40 and 70°. At 24°, HCl exchanges readily with two-thirds of the bromine atoms in aluminum bromide, forming a mixed halide phase of composition $AlBrCl_2$. Only a very slow conversion of $AlBrCl_2$ to $AlCl_3$ by HCl is observed. It is suggested that the difficultly replaceable bromine atoms are in the bridges of the dimeric molecules. The mixed halide phase is not formed directly by the reverse reaction of HBr with $AlCl_3$ at 24°; an aluminum bromide phase is produced. At temperatures of the order of 140° a ready redistribution of halogens among aluminum halide molecules occurs. X-Ray powder patterns of annealed mixtures of $AlBr_3$ and $AlCl_3$ show formation of solid solutions with limited solubility at 25° (bromide phase saturated with 15% chloride; chloride with 20% bromide). The $AlBrCl_2$ phase prepared by reaction of HCl and $AlBr_3$ appears to be isomorphous with $AlCl_3$, with unit cell dimensions 2.5 to 3.0% larger. This intermediate phase is not found in the annealed mixtures.

The preparation of $AlBrCl_2$ by reaction of phosgene with aluminum bromide at 100° was reported by von Bartal[4] in 1907. Identification of this substance, described as forming brick-red crystals melting at 142°, was based on analysis. The red color is unexpected as the simple anhydrous halides are white. In recent years patents pertaining to the use of aluminum bromochlorides as isomerization and polymerization catalysts have been issued.[5,6] The patent by Young and Elmore[6] describes enhanced polymerization effects of $AlBrCl_2$, $AlBr_2Cl$ and Al_2Br_5Cl; these substances were said to be prepared by simply fusing aluminum chloride and aluminum bromide in the corresponding stoichiometric proportions.

The mixed halides present interesting questions concerning their stability (tendency to disproportionate) and the structure of the bridge linking the dimeric molecules. Conclusive evidence for the existence of intermediates as well defined chemical substances has not been presented in the references cited; the aluminum chloride–aluminum bromide melting point diagram reported by Isbekow[7] shows only a simple eutectic near 40 mole per cent. chloride (at 73°) and gives no indication of intermediate compound formation. On this diagram the melting point reported by von Bartal corresponds to 70–72 mole per cent. chloride.

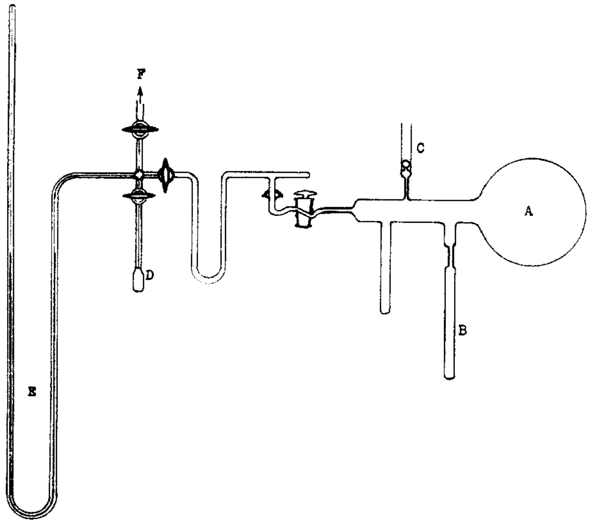

Fig. 1.—Apparatus used for hydrogen halide–aluminum halide equilibrium study.

We have studied the halogen exchange reactions of hydrogen chloride with aluminum bromide and of hydrogen bromide with aluminum chloride, measuring the composition of the gas phase in equilibrium with the solid as the composition of the latter is varied from $AlBr_3$ to $AlCl_3$. Evidence is found in the first reaction indicating formation of a mixed halide phase. X-Ray powder patterns of this phase have been compared with those of annealed mixtures of aluminum chloride and aluminum bromide.

Experimental Part

Aluminum bromide was prepared by reaction of reagent grade bromine and electrolytic, iron-free aluminum sheets in a nitrogen atmosphere, refluxed in the presence of excess aluminum, distilled several times under vacuum, collected in several glass "fingers" and sealed off under vacuum. Aluminum chloride was obtained by resublimation of Baker C.P. analyzed anhydrous $AlCl_3$, and stored in a similar manner. The hydrogen halides (Matheson Co., anhyd.) were dried carefully with P_2O_5 and purified by fractional distillation, using traps cooled with liquid air and Dry Ice. The vapor pressures of the pure gases at $-78.51 \pm 0.01°$ were found to be 1089 mm. (HCl) and 406.5 mm. (HBr).

After thoroughly pumping out the apparatus (Fig. 1) the bottom of tube B was opened and a roughly weighed amount (usually 1 to 5 g.) of aluminum halide introduced in a dry box; the opening was then sealed and the vessel attached to the vacuum line. The halide was sublimed into the one-liter reaction bulb A, dispersed in a thin film, and tube B sealed off. A measured amount of hydrogen halide was then added and the system allowed to equilibrate, either in place on the vacuum line at 24 ± 3° or in an oven at 40 ± 1° or 70 ± 1°. At 70° it was necessary to seal off the reaction vessel near the stopcock (lubricated with fluorocarbon grease) and, after equilibration, reconnect to the vacuum system at C; access was then gained by breaking the fragile glass bulb in this tube with a steel ball (operated with a magnet). For systems equilibrated at 40 and 70° the gas mixture was condensed into the "finger" immediately on removing the reactor from the oven to prevent a significant shift in composition. The gas composition was determined by freezing the mixture into D with liquid air, isolating the sample from the equilibrium vessel, and measuring the

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[4] A. von Bartal, *Z. anorg. u. allgem. Chem.*, **55**, 152 (1907).

[5] E. W. M. Fawcett and E. S Narracott, U. S. Patent 2,393,357 (to Anglo-Iranian Oil Co., Ltd.), January 22, 1946.

[6] D. W. Young and N. M. Elmore, U. S. Patent 2,443,287 (to Standard Oil Development Co.), June 15, 1948.

[7] W. Isbekow, *Z. anorg. u. allgem. Chem.*, **143**, 80 (1925).

vapor pressure of the HCl–HBr mixture at −78.51°.[8] The volume of the manometric system was small: a maximum of 2% of the smallest sample used was in the gas phase during the vapor pressure measurement. The gas mixture was then re-introduced into the equilibrium vessel to check the measurement, or discarded.

The composition of each sample of aluminum halide was followed by means of the gas analyses through a series of equilibration steps and finally checked by direct analysis[9] of the solid for total halide (Mohr), bromide (Kolthoff and Yutzy[10]), and aluminum (8-hydroxyquinoline precipitation in an acetate buffer[11]). The checks were usually good to less than 0.05%; series deviating by more than 1% were discarded.

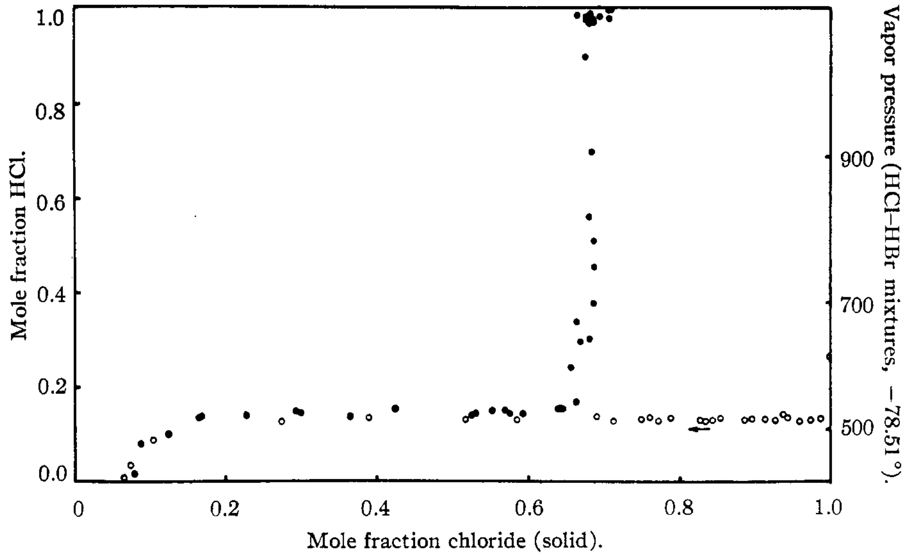

Fig. 2.—Composition of equilibrium HCl–HBr mixtures for the $AlBr_3$–$AlCl_3$ system at 24°.

To prepare annealed samples of the anhydrous aluminum halides for X-ray analysis, mixtures of the desired proportion were sublimed in vacuum ($p < 10^{-4}$ mm.) into Pyrex tubes of about 30-ml. volume, sealed, melted to ensure uniformity, and then quenched in an oil-bath. Each sample was annealed over a period of 3 to 7 days. The temperature was raised to near the melting point and held for one day at each of a series of decreasing values (10 or 15 degree intervals) down to 35°. The sample was then allowed to stand at room temperature for 2 to 6 days and opened in a dry box; portions for powder patterns and analysis were taken from the same small area. The Pyrex powder pattern tubes (0.3 to 0.4 mm., i.d.) were sealed with a flame after filling.

X-Ray exposures of 24 to 30 hours (North American Phillips unit, Cu tube; 30 kv., 20 ma.) were made in a cylindrical camera of 11.49 cm. radius. The ring diameters were measured on a light table calibrated with sodium chloride. A Cu–K wave length value of 1.5418 Å. was used in the calculation of interplanar spacings.

Results and Discussion; Exchange Equilibria

A summary of results for the reaction of HCl with aluminum bromide at 24° (eight series of experiments) is given by the solid circles in Fig. 2. The chlorine atoms exchanged presumably form mixed halide molecules, initially in solid solution with aluminum bromide. At 18 mole per cent. chloride (solid), the equilibrium gas composition reaches 14.5% mole per cent. HCl and does not change on further addition of HCl until the solid phase reaches approximately 65% chloride. This indicates formation of a new solid phase approximating the composition of $AlBrCl_2$.

As the chloride content of the solid is increased beyond 65%, the concentration of HCl rises rapidly, reaching essentially 100% at a solid composition of 68–70%. All of this portion of the curve may be retraced by addition of HBr. Further reaction of the new phase with HCl is inappreciable during the length of time normally required for equilibration (three or four days). However, a very slow reaction does occur. In one experiment the solid changed from 67 to 72% chloride in 40 days while the gas changed from 90 to 83% HCl. This slow reaction causes the composition of the mixed halide phase (at the top of the curve) to vary somewhat, depending on the length of time it is in contact with high concentrations of HCl. A number of experiments were carried out to verify the slow reaction as shown by the many points in the vicinity of 70% in Fig. 2.

The open circles summarize seven independent experiments on the HBr–$AlCl_3$ reaction at 24°. Systems allowed to stand as long as three weeks showed no significant change after four days. The solubility limit of bromide in the chloride lattice is only about 2%; the "equilibrium" gas composition at this point (13.3% HCl) does not change on further addition of HBr as a bromide-rich phase is produced. The latter appears to be the same phase as occurs in the HCl–$AlBr_3$ system; it has about the same composition (at saturation) and addition of HCl results in its conversion to the mixed halide phase (68–70% chloride). Addition of excess HCl before the chloride phase has been completely converted to the bromide phase results in mixtures in the composition range between 70 and 100% chloride (*i.e.*, mixtures of $AlBrCl_2$ and $AlCl_3$).

At 40 and 70°, the behavior is modified by an increase in the solubility limits and a greater ease of conversion of $AlBrCl_2$ to $AlCl_3$. The data at 70° are shown in Fig. 3; the corresponding results at 40° are intermediate between the 24 and 70° curves.[9] The gas phase compositions (mole per cent. HCl) in the invariant regions are: HCl–$AlBr_3$: 40°, 16.5; 70°, 20.1; HBr–$AlCl_3$: 40°, 19.5; 70°, 22.2. It may be noted that the HCl

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(8) This temperature was produced with Dry Ice by a National Bureau of Standards technique; see American Institute of Physics, "Temperature, Its Measurement and Control," Reinhold Publ. Corp., New York, N. Y., 1941, p. 242. The properties of the HCl–HBr system at −78.51° will be reported later.

(9) For details, see the Ph.D. Dissertation of J. D. Corbett, University of Washington, 1952. Methods for the analyses were investigated extensively.

(10) I. M. Kolthoff and H. Yutzy, *Anal. Chem.*, **9**, 75 (1937). This method was found satisfactory for determination of bromide (or iodide) in the presence of chloride (probable error, 0.3% in mole fraction bromide).

(11) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 327.

concentration in the invariant region for the reaction between HBr and $AlCl_3$ at 40 and 70° is sufficiently high to make the mixed halide phase more stable than the bromide phase, contrary to the behavior at 24°. True equilibrium between the solid phases (Fig. 3) is still not attained in the region between 65 and 100% chloride in as long as fourteen days; the equilibration time allowed for the points shown was usually three or four days.

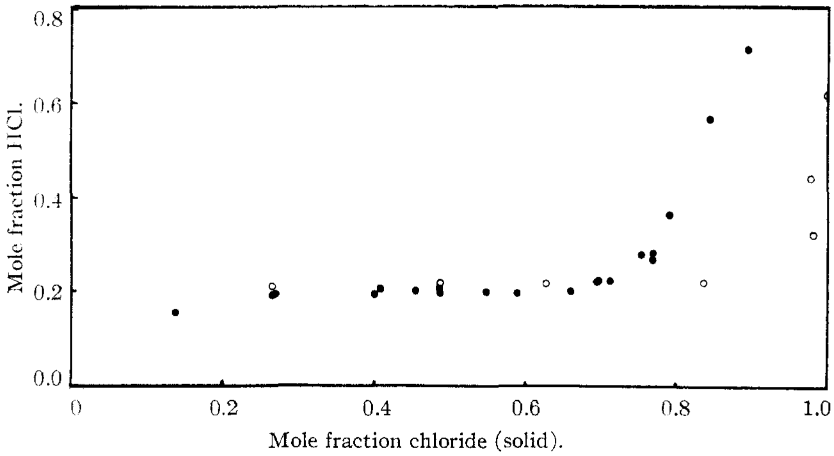

Fig. 3.—Composition of equilibrium HCl–HBr mixtures for the $AlBr_3$–$AlCl_3$ system at 70°.

It is not yet possible to give mechanisms for these reactions, but it is interesting to speculate that the reaction between $AlBrCl_2$ and HCl to produce $AlCl_3$ is slow because it involves the more tightly held bridge atoms in the original Al_2Br_6 molecule.[12] Such non-reactivity of bridge halogens has been observed before. In Mo_6Cl_{12} and similar tantalum and tungsten compounds, eight chlorine atoms, presumably located in bridges, are found to be unreactive in solution.[13] On the other hand, a similar effect is not observed in the reaction of HBr with aluminum chloride, at least a special phase corresponding to $AlBr_2Cl$ is not observed. The identity of the bridge halogens and the structural characteristics of the solid phases seem clearly important in determining the stability of the intermediates.

It has been determined that rearrangement of halogens among the aluminum halide molecules occurs quite readily at temperatures well above 24°. Three separate mixtures of $AlBr_3$ and $AlCl_3$ (with initial mole fractions chloride at 0.74, 0.53, 0.66) were heated at 40, 70 and 140° for 28, 19 and 5 days, respectively, quenched to room temperature and then allowed to react with excess HCl. If one assumes that all dimers (after quenching) with bromine atoms in the bridge will react with HCl to form the mixed halide phase $AlBrCl_2$, and all dimers with chlorine atoms in the bridge react to form aluminum chloride, an estimate of the redistribution can be made from the amount of HCl reacting. The composition of the mixtures after this treatment changed to 0.84, 0.72 and 0.76 mole fraction chloride, respectively. Although the information gained from this method of analysis is limited, evidence for redistribution is apparent in each case.

Partial sublimation of samples of $AlBrCl_2$ (prepared by the HCl–$AlBr_3$ reaction at 24°) in vacuum (25°) gives evidence that some rearrangement occurs at room temperature. The sublimate was found to contain more bromide than $AlBrCl_2$ (*e.g.*, $^2/_3$ of a sample (7 g.) sublimed in 8 days; the chloride analysis changed from 68% (original) to 65% (sublimate)). The mixed halide seems somewhat more volatile than aluminum bromide at 25°; the latter is much more volatile than aluminum chloride at this temperature.[14] Redistribution of halogens obviously affords a possible mechanism for the slow reaction of HCl with the mixed halide.

The solid solutions formed complicate attempts to calculate thermodynamic properties of the mixed halide ($AlBrCl_2$). An estimate may be made by assuming that the ratio of activities of the solids in the equilibrium constant expression for the reaction

$$Al_2Br_6(s) + 4HCl(g) = Al_2Br_2Cl_4(s) + 4HBr(g)$$

is unity when the two saturated phases are in equilibrium.[15] On this basis, ΔF^0 is -4.18 kcal. at 24°. With free energy values for the hydrogen halides and aluminum bromide[16] this gives a standard free energy of formation for $Al_2Br_2Cl_4$ of -286.4 kcal./mole. Utilizing the data at 40 and 70° also, we estimate values of ΔS^0 and ΔH^0 of 9.0 e.u. and -1.5 kcal. for the reaction, and of 68.5 e.u. and -312.5 kcal. for the standard entropy and heat of formation of $Al_2Br_2Cl_4(s)$.

These values indicate a thermodynamic stability for the mixed halide quite apart from its kinetic inertness toward HCl. The free energy of formation estimated leads to a value of ΔF^0 of 3.0 kcal. for the disproportionation reaction

$$Al_2Br_2Cl_4(s) = 1/3Al_2Br_6(s) + 2/3Al_2Cl_6(s)$$

Hence one would estimate that 1.5% of the mixed halide would disproportionate at equilibrium at 24° if ideal solid solutions were formed. While these values are obviously very rough, they are generally consistent with the properties discussed above.

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(12) Aluminum bromide exists as a molecular dimer in the solid, liquid and gas phases: see P. A. Renes and C. M. MacGillavry, *Rec. trav. chim.*, **64**, 275 (1945); H. Gerding and E. Smit, *Z. physik. Chem.*, **B50**, 171 (1942); K. J. Palmer and N. Elliott, *ibid.*, **60**, 1852 (1938). A pair of bromine atoms forms a bridge between the two aluminum atoms.

(13) H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1952, p. 156.

(14) W. Fischer and O. Ralphs, *Z. anorg. u. allgem. Chem.*, **205**, 1 (1932).

(15) The actual activity ratio is probably somewhat larger than unity (*i.e.*, the $AlBr_3$ phase is more dilute) which would give a more negative value of ΔF^0, indicating a greater stability of the mixed halide. It is interesting to note that the activity of the chloride species in the bromide phase falls to very low values at mole fractions chloride <0.05. The partial pressure of HCl in the gas phase is very small between 0 and 0.05 N_{Cl}.

(16) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circ. 500, Series I, U. S. Govt. Printing Office, Washington, D. C., 1950.

The mixed halide phase is similar in appearance to the simple aluminum halides. On repeating the reaction of phosgene with aluminum bromide at 100°, a red product as reported by von Bartal[4] was observed; however, the coloration disappeared readily on evacuation, and was presumably due to adsorbed bromine. The product otherwise resembled annealed mixtures of $AlCl_3$ and $AlBr_3$ rather than our mixed halide phase. Other bromochlorides reported by Young and Elmore such as Al_2Br_5Cl, etc., did not occur as separate phases in the exchange reactions. The observed rearrangement of halogens on heating mixtures of aluminum chloride and aluminum bromide suggests that fusion of these components results in a mixture of simple and mixed halide molecules rather than a single component.

Structural Properties of Annealed Aluminum Bromide-Aluminum Chloride Mixtures and of Aluminum Bromodichloride

The crystal structure of aluminum chloride[17] (monoclinic, C2/m) is similar to the hexagonal structure of $CrCl_3$ and $FeCl_3$ (ionic double layer lattice in which the halide ions are in cubic close-packed arrangement). The halogens in $AlCl_3$ are not all in equivalent positions, however. Aluminum bromide[18] forms a monoclinic lattice with close packed molecular dimers. In Fig. 4 the interplanar spacings, as determined from powder patterns for the simple trihalides and sixteen annealed mixtures, are plotted (open circles) against the (bulk) mole fraction chloride. Two strong reflections corresponding to *d*'s of 5.8 and 6.2 Å. have been omitted because of the high experimental error in this region. Other observed spacings greater than 3.8 Å. were faint and uncertain.

It is apparent that solid solution occurs with solubility limits at *ca.* 15 and 80 mole per cent. chloride.[19] The intermediate mixtures give no evidence of a mixed halide phase as observed in the reaction of HCl with $AlBr_3$. The chloride phase contains considerably more bromide than can be introduced by reaction of HBr with $AlCl_3$ at 24°.

Three independent samples of the $AlBrCl_2$ phase (66-70% Cl) all gave substantially the aluminum chloride pattern except for a slight increase in the unit cell parameters (solid circles, Fig. 4).[20] Table I presents the average interplanar and approximate relative intensities along with the indices of the corresponding lines of the aluminum chloride pattern. (Indices in parentheses are those that intensity calculations show do not contribute appreciably to the diffractions in $AlCl_3$, while a plus mark indicates that the list for that spacing is incomplete). These indices lead to calculated interplanar spacings in excellent agreement with observed values if one uses the unit cell parameters $a = 6.06$ ($AlCl_3$[17]; 5.92%; % expansion, 2.5), $b = 10.50$ (10.22; 2.7%), $c = 6.34_5$ (6.16; 3.0%) and $\beta = 108.5°$ (108°).

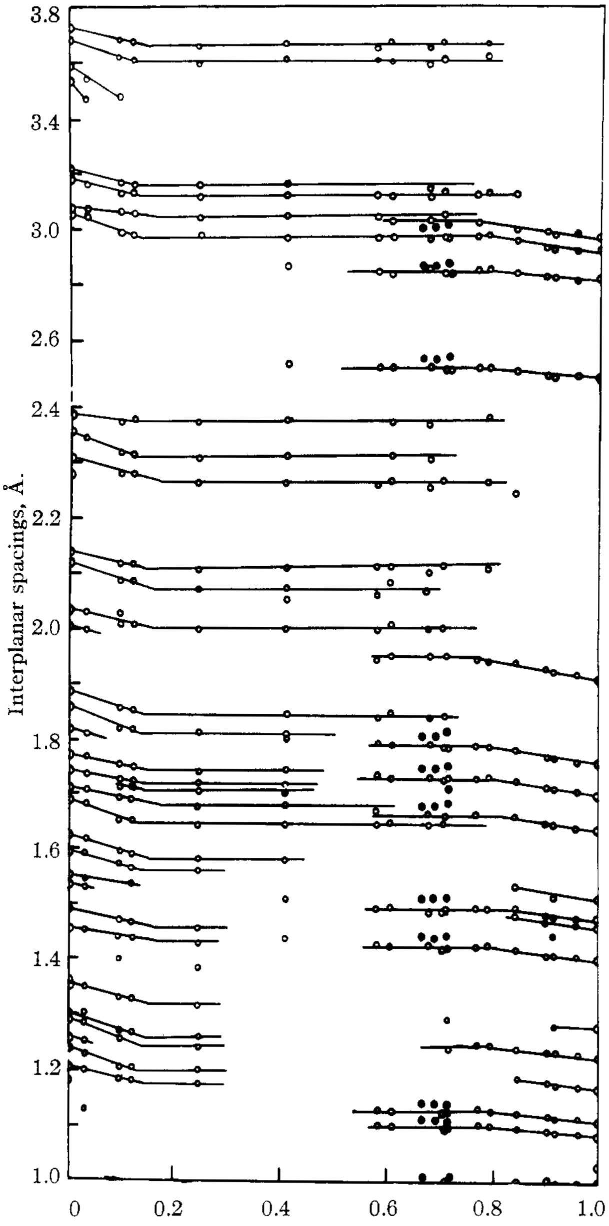

Fig. 4.—Powder pattern spacings for annealed $AlBr_3$-$AlCl_3$ mixtures.

Intensity calculations were carried out for those lines indexed in Table I (the contribution of all planes included where superposition occurs) in an effort to support the proposal that the bromine atoms are in the bridge of the mixed halide molecule. The trichloride atomic positions were assumed. However, a significant conclusion could not be reached because of the superposition of lines. For example a plane such as 220, for which the intensity should be markedly increased by replacement of the bridge chlorine atoms by bromine, has any such increase masked by the strong contribution of 131 and $20\bar{2}$ at the same spacing. Single

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(17) J. A. A. Ketelaar, C. H. MacGillavry and P. A. Renes, *Rec. trav. chim.*, **66**, 501 (1947).

(18) P. A. Renes and C. H. MacGillavry, *ibid.*, **64**, 275 (1945).

(19) A solubility of 33% chloride (bromide phase) at a eutectic temperature of 75° has been reported by N. Pusin and J. Makuc, *Z. anorg. u. allgem. Chem.*, **237**, 177 (1938). The limit for the chloride phase was not well defined.

(20) The slight variation in composition is attributed to the presence of varying amounts of $AlCl_3$ as discussed in the previous section. The small amount of chloride does not appear to change the spacings significantly.

crystal studies are planned in an attempt to determine the positions of the halogens in $AlBrCl_2$.

TABLE I

POWDER PATTERN DATA AND INDICES FOR $AlBrCl_2$

d., Å. Experimental	Intensity	Indices
6.00	s	001
5.24	vf	020
3.05	vf	?
3.01	s	$002, (130)(20\bar{1})$
2.86_8	vs	$13\bar{1}, 200$
2.53_3	vs	$131, 20\bar{2}, (220)$
1.813	f	$202, 13\bar{3}(22\bar{3})(24\bar{2})$
1.752	s	$33\bar{1}, 060(241)$
1.714	f	222, 113
1.682	f	$061, 33\bar{2}, 330$
1.514	m	331, 062 +
1.443	f	$400, 13\bar{4}, 203, (42\bar{2})(024)$
1.142	f	$064, 333, 46\bar{2}, +$
1.113	f	$460, 40\bar{5}, 53\bar{3} +$
1.010	vf	$60\bar{2} +$
0.998_6	vf	0102 +
0.995_4	vf	+

The difference in the solubility limit of the chloride phase in the annealed mixtures and the exchange studies is of interest. We believe this to be associated with different solute species present in the two experiments. The reaction of HBr with aluminum chloride does not appear to form $AlBrCl_2$ directly at 24°; an aluminum bromide phase separates at 13.3% HCl concentration. The 2% solubility limit in the chloride phase shows that $AlBr_3$ (and closely similar species, *e.g.*, Al_2Br_5Cl) will not dissolve appreciably in $AlCl_3$. On the other hand, rearrangement of halogen atoms occurs readily at the temperatures used in forming and annealing the mixtures of $AlBr_3$ and $AlCl_3$; thus appreciable amounts of $AlBrCl_2$ can be produced which, on cooling, would be expected to form solid solution with $AlCl_3$. Hence, it is suggested that the bromide content of the saturated chloride phase of the annealed mixtures is largely present in the form of $AlBrCl_2$.

It is not believed that the equilibria obtained in and between the phases in the annealed samples are effectively frozen above room temperature. No significant variation in spacings could be observed in patterns taken from the same sample after several months. The small variations in distances observed for the saturated phases also indicate no appreciable difference in the equilibrium temperature for the various samples. The aluminum halides have vapor pressures between 10^{-2} and 10^{-4} mm. at room temperature which makes it unlikely that any phase could remain appreciably supersaturated over a long period of time.

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SEATTLE, WASH.

[CONTRIBUTION FROM THE SIGNAL CORPS ENGINEERING LABORATORIES]

Electrical Conductivity of Ag_2HgI_4, Cu_2HgI_4 and their Eutectoid

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The specific electrical conductivities of Ag_2HgI_4, Cu_2HgI_4 and their eutectoid (containing 43 mole % Cu_2HgI_4) have been determined as a function of temperature, and activation energies have been calculated. All the preparations exhibit sharp rises in conductivity at characteristic phase transition temperatures. The activation energies for the two phases of the eutectoid have been found not to be averages of the values for the parent compounds. Combined plots of specific conductivity *vs.* temperature upon heating and cooling appear in the form of hysteresis loops. In the case of the eutectoid, the loop indicates a lag of about 8° on returning to the low temperature phase.

Introduction.—The compound Ag_2HgI_4 has been shown by Ketelaar[1,2] to possess ionic conductivity of considerable magnitude, especially above a transition point at 50.7°, at which a sharp rise is observed. He also reported that Cu_2HgI_4 exhibited ionic conductivity, but with electronic conductivity superimposed upon it. However, he did not give data on the actual measurement of specific conductivity of Cu_2HgI_4. The purpose of the present work was to reinvestigate the specific conductivity of these two compounds as a function of temperature, and more especially, to make a similar investigation on the eutectoid of the two compounds containing 43 mole % Cu_2HgI_4, which was recently reported by this Laboratory.[3]

Experimental Procedure.—The materials to be tested were prepared as by Suchow and Keck.[3] In order to measure specific conductivity as a function of temperature, the powders were pressed into pellets of 0.75 inch diameter and 0.05 to 0.1 inch thickness at a pressure of about 5 tons/in.^{2}. Such pellets were found to be of the same colors as the original powders. However, higher pressures (such as 12–20 tons/in.^{2}) were found to cause uneven darkening in the pellets and to lead to higher transition temperatures and higher conductivity values. The pellet's dimensions were determined accurately with a micrometer and its two flat surfaces were coated with graphite from an IBM Electrographic Pencil. It was then placed between two discs of platinum foil to which leads were attached. Adequate electrical contact between the platinum and the pellet was ensured by placing the pellet and the platinum foil discs between two Bakelite plates held tightly together by bolts insulated from the electrical system. This assembly was then placed inside a metal cylinder surrounded by an asbestos-wrapped metal jacket through which thermostated water could be passed in order to maintain the temperature at desired levels. The temperature in the vicinity of the pellet was controlled within ±0.2° and determined by means of an iron–constantan thermocouple connected to a Leeds and Northrup Potentiometer. The temperature was brought to each desired level and kept there for about ten minutes to ensure that equilibrium had been reached. Measure-

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(1) J. A. A. Ketelaar, *Z. physik. Chem.*, **B26**, 327 (1934).

(2) J. A. A. Ketelaar, *Trans. Faraday Soc.*, **34**, 874 (1938).

(3) L. Suchow and P. H. Keck, THIS JOURNAL, **75**, 518 (1953).