not involve a mere reversal of the process by which precipitation occurs. Instead the I_2 or HIO formed by solubility in water is converted to NH_2I by the NH_3, the net reaction being

$$N_2H_3I_3 + NH_3 = 3NH_2I$$

(4) In the slow decomposition of $N_2H_3I_3$ a loss in total oxidizing power occurs, corresponding to the conversion of part of the nitrogen to N_2. In the experiment mentioned in (2) the three solutions were permitted to stand overnight and then analyzed. The first (with most precipitate) had lost 39% in total oxidizing power, the second 2%, and the third only 0.5%. From this it would appear that $N_2H_3I_3$ does not exist to more than a minor extent as a molecular compound in solution, but only as a precipitate.

(5) If $N_2H_3I_3$ is precipitated from a solution containing sufficiently low concentration of NH_3 it may undergo spontaneous decomposition into N_2 and I_2 in a series of mild explosions over a period of several minutes. This effect was observed repeatedly when 50 ml. of 0.01 *N* KI_3 (low in KI) solution was added to 200 ml. of 0.01 *N* NH_3. Judging solely from the visible effects one would guess that the reaction is of the Meldrum[6] type with the concentration of NH_3 in the aqueous solution too low to stabilize the $N_2H_3I_3$.

Preparation of NH_4Cl–NH_4OH mixtures: Stock solutions of 4.00 *N* NH_4Cl and NH_4OH were prepared and 100 ml. of the NH_4Cl solution used with 50, 100 or 150 ml. of the NH_4OH solution and diluted to 500 ml. to give mixtures 1, 2 and 3.

Preparation of 0.01 *N* KI_3 solutions: A stock solution was prepared containing 400 g. of KI in 1 liter. Then 25.4 g. of I_2 was dissolved in 200 ml. of this solution and diluted to 2 liters to give a 0.1 *N* KI_3 solution. To 100 ml. portions of this reagent were added 0, 10, 20, 30 and 40 ml. of the stock KI solution and then diluted to 1 liter to give 0.01 *N* KI_3 solutions numbers 1, 2, 3, 4 and 5, with the concentrations of KI accurately adjusted to the ratio 1:2:3:4:5.

Preparation of color standards: Thirteen 500-ml. glass stoppered erlenmeyer flasks were set up with 50 ml. of 0.2 *M* KH_2PO_4, 50 ml. of 0.2 *M* Na_2HPO_4 and 25 ml. of KI solution (2 g. of KI). To these, in order, were added 50, 40, 30, 25, 20, 17, 14, 12, 10, 8, 6, 4, and 2 ml. of 0.01 *N* KI_3 solution and sufficient water to give a total volume of 250 ml. Course of an experiment.

The measured amount of the NH_4Cl–NH_4OH mixture was placed in a 500-ml. glass-stoppered erlenmeyer flask, plus sufficient water to give a volume of 200 ml., then 50.0 ml. of the selected KI_3 solution added. After thorough mixing the color of the solution was checked against the color standards and the per cent. loss of color noted.

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[6] F. R. Meldrum, *Trans. Faraday Soc.*, **34**, 947 (1938); *Proc. Roy. Soc.* (*London*), **A174**, 410 (1940). At low temp and press, dry $N_2H_3I_3$ decomposes as follows

$$N_2H_3I_3 = NH_3 + NI_3$$
$$2NI_3 = N_2 + 3I_2$$

ANN ARBOR, MICHIGAN

RECEIVED APRIL 21, 1951

[FROM THE DEPARTMENT OF CHEMISTRY OF SAINT LOUIS UNIVERSITY]

Reactions between Dry Inorganic Salts. VII. An X-Ray Study of the Reciprocal System $RbCl + KBr \rightleftarrows RbBr + KCl$[1a,b]

BY LYMAN J. WOOD AND L. J. BREITHAUPT, JR.

A detailed X-ray diffraction study of the reciprocal system $RbCl + KBr \rightleftarrows RbBr + KCl$ has been made. This system appears to be unique among reciprocal systems. The unit cell edge of rubidium chloride is very nearly the same as that of potassium bromide and the average unit cell edge of rubidium bromide and potassium chloride is almost the same as that of either rubidium chloride or potassium bromide. The sums of the heats of formation of the two reciprocal salt pairs are very nearly equal. The average melting points are very nearly equal. The molecular weight of rubidium chloride is 120.94 and that of potassium bromide 119.01. The X-ray diffraction results indicate that when any mixture of these salts is melted one solid solution is formed which contains all of the cations and anions in the original mixture.

Some time ago it was reported[2] that the reciprocal system

$$RbCl + KBr \rightleftarrows RbBr + KCl$$

is one of only three of the 60 reciprocal systems of the common alkali halides that do not go to completion in the direction of the pair of balanced mass[3] upon heating. This system is perhaps unique among reciprocal systems. The unit cell edge of rubidium chloride is very nearly the same as that of potassium bromide and the average unit cell edge of rubidium bromide and potassium chloride is almost the same as that of rubidium chloride or potassium bromide. Furthermore the sum of the heats of formation of the rubidium chloride–potassium bromide pair is 199.00 kcal. which is very nearly equal to 200.36 kcal., which is the sum of the heats of formation for the rubidium bromide–potassium chloride pair. The melting point of rubidium chloride is 720° and that of potassium bromide is 731°. The average of the two melting points (725.5°) differs by only a little from the average melting point of rubidium bromide and potassium chloride which is 729.5°. The molecular weight of rubidium chloride is 120.94 and that of potassium bromide is 119.01. In the preliminary investigation two mixtures of this reciprocal system were examined and the tentative conclusion was reached that a single solid solution was formed that contained all of the rubidium, potassium, bromide and chloride in the mixture. An extensive investigation has now been made and the results obtained are described below under experimental results.

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(1) (a) Read at the XIIth International Congress of Pure and Applied Chemistry. (b) For the table of data from which Figures 2, 3 and 4 of this article were drawn order Document 3367 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) E. B. Thomas with Lyman J. Wood, THIS JOURNAL, **57**, 822 (1935).

(3) The salt pair having the heavier cation united with the heavier anion and the lighter cation united with the lighter anion has been designated as the pair of Balanced Mass by Link and Wood [Harold L. Link with Lyman J. Wood, *ibid.*, **62**, 766 (1940)] while the other pair has been called the reactive or reciprocal pair.

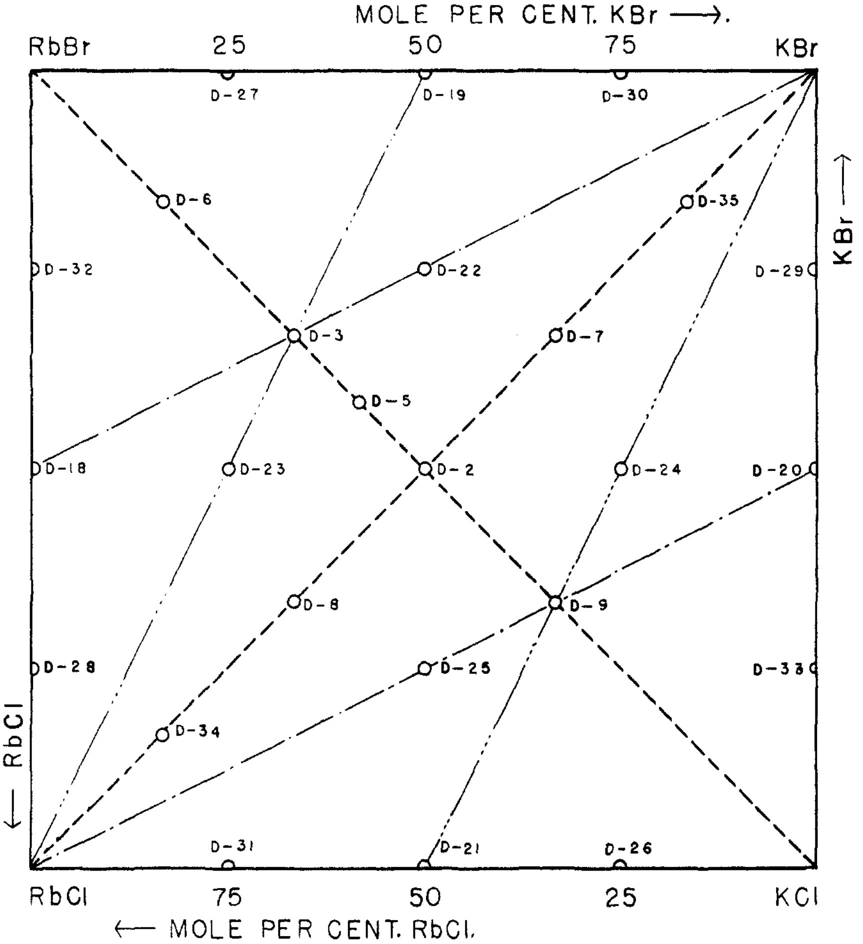

Fig. 1.—Composition diagram of mixtures investigated.

Materials, Apparatus and Methods

The potassium and rubidium salts used in this work were of the highest quality obtainable and were carefully tested for impurities. The rubidium salts contained less than 0.1% potassium and only traces of other elements such as cesium, barium, calcium and strontium. These salts were fused, ground and passed through a 250 mesh screen after which they were used to make up the mixtures whose compositions are represented in Fig. 1 in mole per cent. The points on the composition diagram are arranged in straight lines so that the unit cell edge (or sin θ) can be plotted against composition in a systematic manner. The compositions of the common ion salt pairs are arranged around the perimeter of the diagram, the two common cation pairs along the sides and the two common anion pairs along the top and bottom.

The composition of any point inside the perimeter may be expressed in either one of two ways. For example the starting composition of a point on one of the diagonals such as D-3 may be a $33^1/_3$% molar mixture of each of the components rubidium bromide, rubidium chloride and potassium bromide as indicated by the numbers above the equation, or the starting composition may be 66 $^2/_3$ mole per cent.

$$\overset{100}{\mathrm{RbCl}} + \overset{100}{\mathrm{KBr}} \rightleftarrows \underset{200}{\overset{100}{\mathrm{RbBr}}} + \underset{100}{\mathrm{KCl}}$$

rubidium bromide and $33^1/_3$% potassium chloride as indicated by the numbers under the equation. It does not matter which starting composition is used, the final state of the system is always the same. The purpose of this investigation was to determine the final state of the system at each point after the mixture had been melted and allowed to crystallize.

Each crystalline mixture was annealed at 400° for several hours and analyzed by the method of X-ray diffraction. An XRD-3D direct recording General Electric X-ray diffraction apparatus with a copper target tube was used for the X-ray analysis. This apparatus makes use of a Geiger-Mueller tube for the detection of the diffracted beam. For qualitative and semi-quantitative work the intensity of the diffracted beam is automatically recorded on a moving chart. For quantitative work the intensity of the diffracted beam is determined by counting the amplified signals from the Geiger-Mueller tube by means of a scalar circuit and a stop watch with an automatic switch. In this apparatus all voltages are stabilized by means of electron circuits and the high voltage applied to the X-ray tube is rectified by means of two kenetron tubes so that quantitative intensity measurements can be made quite satisfactorily.

The samples were annealed in a well insulated electric oven whose temperature was carefully controlled by means of a photoelectric circuit. A thyratron tube with a 1.5 amperes rating was placed in series with the oven in such a way that the phase of the current through the tube was controlled by a phototube. The phototube was activated by light from a mirror galvanometer in the thermocouple circuit. The response of the mirror galvanometer was made very sensitive to changes in temperature by making use of a balanced circuit consisting of a high grade storage cell and a voltage divider. The operation of this shift-phase circuit was found to be more reliable than relay containing circuits and also more responsive to temperature changes since an increase or decrease in current through the oven began to be realized as soon as needed. The temperature was read by means of a thermocouple and a type K potentiometer and remained constant within ± 0.25°.

Experimental Results and Discussion

The results of the X-ray analysis of the pure components and the binary mixtures are shown in Table I. Each of the four pure substances crystallizes in a face-centered cubic lattice and each mixture produced one X-ray pattern which was that of a face-centered cubic lattice whose dimensions were intermediate between those of the pure salts contained in the binary mixture. The 2θ values for the face planes shown in Table I were obtained by observing the second order diffraction peaks directly on the goniometer of the diffraction apparatus. These observations were carefully rechecked by measurement of the recorder chart. At the comparatively high value of 2θ for the second order the α_1 and α_2 lines of the K_α doublet of the copper anode could be resolved satisfactorily in nearly all cases. The α_1 peaks were used to obtain the 2θ values recorded in the table and the variation is not much more than ±0.01°.

TABLE I

PROPERTIES OF BINARY MIXTURES OF THE RECIPROCAL SYSTEM $RbCl + KBr \rightleftarrows RbBr + KCl$

	Molar composition, %				2θ 200	
	RbCl	KBr	RbBr	KCl	Calcd.[a]	Obsd.
D-16	100					27.03
D-1		100				27.04
D-10			100			25.81
D-17				100		28.35
D-32	25		75		26.11	26.11
D-18	50		50		26.41	26.41
D-28	75		25		26.72	26.71
D-26	25			75	28.00	27.99
D-21	50			50	27.67	27.64
D-31	75			25	27.35	27.32
D-27		25	75		26.11	26.10
D-19		50	50		26.41	26.40
D-30		75	25		26.72	26.70
D-29		75		25	27.35	27.32
D-20		50		50	27.68	27.64
D-33		25		75	28.01	28.04

[a] Calculated on the assumption that unit cell edges are additive.

If sin θ_{200} values for any of the common ion mixtures are plotted against molar composition the points are found very nearly at positions expected from Vegard's additivity law.[4] The calculated values for sin 2θ fall on slightly concave curves that deviate only a little from straight lines. Because the unit cell edge of potassium bromide is almost exactly equal to that of rubidium chloride, the potassium bromide–potassium chloride curve coincides with the rubidium chloride–potassium chloride curve and the potassium bromide–rubidium bromide curve coincides with the rubidium chloride–rubidium bromide curve. In no case does an experimental point deviate from the calculated curve by more than the experimental error.

The mixtures corresponding to the mid-points of each of the binary curves have previously been investigated by the author and his co-workers[5,6] and the potassium bromide–potassium chloride pair has also been investigated by Vegard[7] and by Havighurst,[8] who made use of the X-ray diffraction method of analysis. All of these results are in essential agreement. These measurements have been repeated here because these points represent the beginnings of the ternary curves (see below) and it was desired to make all observations in such a way that they would be readily comparable.

The data recorded in Table I leave no doubt that the four common ion pairs of the reciprocal system

$$RbCl + KBr \rightleftarrows RbBr + KCl$$

all form a continuous series of solid solutions that remain stable at room temperature. This is most unusual. The senior author has made an extensive study of solid solution formation among the common ion pairs of the 60 reciprocal systems of the alkali halides and has represented the results graphically.[9] The study included 30 common cation pairs and 40 common anion pairs. In none of the other 59 reciprocal systems did all four of the common ion pairs belonging to a given system form continuous stable series of solid solutions.

The compositions for the ternary mixtures examined are represented by points inside the perimeter of Fig. 1. In no case was more than one X-ray pattern found and in each case the positions of the diffraction peaks and their intensities were in quantitative agreement with values that would be expected for one solid solution containing all of the cations and all of the anions in the mixture. In Fig. 2 sin θ values for the 200 peaks are plotted against composition along the rubidium bromide–potassium chloride diagonal. The line positions are calculated from the additivity law and the experimental points are plotted so that laboratory observations are readily compared with theoretical calculations. In each case, without exception, the observed points are in slightly better agreement with calculations based on the rubidium bromide–potassium chloride pair. This is not in agreement with work previously reported by the senior author, but this lack of agreement is believed to be without significance because the difference between the average unit cell edge of the balanced pair and that of the reciprocal pair does not exceed the experimental error.

The unit cell edges for mixtures along the rubidium bromide–potassium chloride diagonal could be accounted for on the basis of a mixture of two binary solid solutions instead of one ternary solution. Take mixture D-3 as an example. Let it be assumed that after melting and cooling the mixture is $^1/_3$ rubidium chloride, $^1/_3$ potassium bromide and $^1/_3$ rubidium bromide. A binary solid solution containing $^1/_3$ of a mole of rubidium chloride and $^1/_6$ of a mole of rubidium bromide would have the same calculated unit cell edge as a binary solid solution containing $^1/_3$ of a mole of potassium bromide and $^1/_6$ of a mole of rubidium bromide. Furthermore, the calculated unit cell edge for the binary solid solutions would be equal to that calculated for the ternary. This is so because the unit cell edge of rubidium chloride is very nearly equal to that of potassium bromide.

While the X-ray diffraction patterns for these binary and ternary solid solutions would be similar they would not be identical. The binary solutions

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(4) Vegard, *Z. physik.*, **5**, 16 (1921).

(5) E. B. Thomas with Lyman J. Wood, THIS JOURNAL, **57**, 822 (1935).

(6) Harold L. Link and Lyman J. Wood, *ibid.*, **62**, 766 (1940).

(7) Vegard, *Z. Physik*, **5**, 16 (1921).

(8) Havighurst, Mack and Blake, THIS JOURNAL, **47**, 29 (1925).

(9) Lyman J. Wood, *J. Sch. Sc. and Math.*, **45**, 623 (1945).

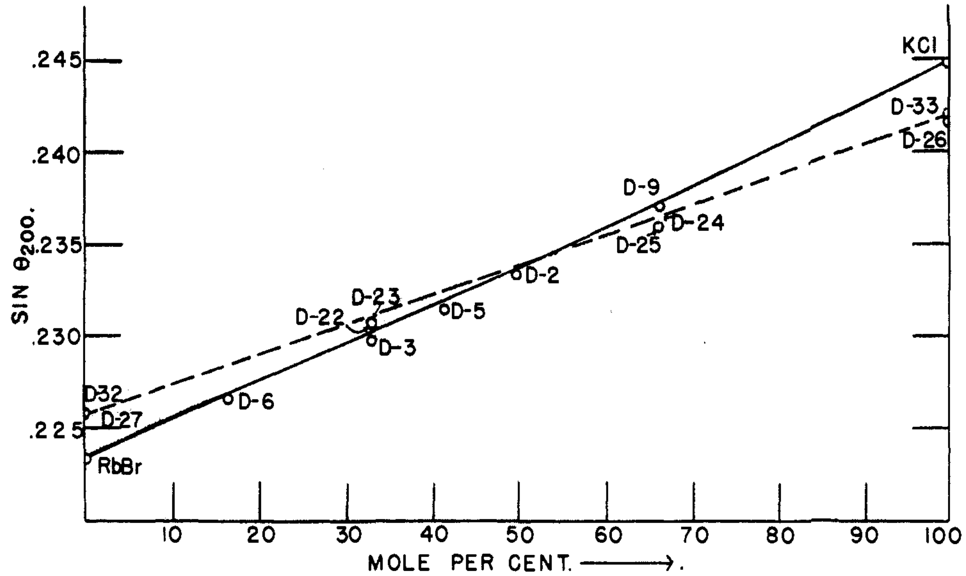

Fig. 2.—Sin θ *vs.* composition in the direction of the RbBr–KCl diagonal.

would produce odd number index lines, *e.g.*, 111, 311, etc., while the ternary would not. This follows from a consideration of the arrangement of the ions in these crystals. The odd number index planes consist alternately of all cations and all anions. If the cation planes contain only rubidium ions (36 electrons) and the anion planes contain only bromide ions (36 electrons) no odd number index lines would be obtained. From similar considerations rubidium chloride or potassium bromide would give relatively strong odd number index lines while potassium chloride would give none. The alternate odd number index planes for the D-3 ternary would contain $^2/_3$ of a mole of rubidium ion plus $^1/_3$ of a mole of potassium ion in the cation planes and $^2/_3$ of a mole of bromide plus $^1/_3$ of a mole of chloride ion in the anion planes. The electron balance would be one to one and no odd number index lines would be expected. In either of the binary solid solutions the electron balance would not be one to one and these planes would be expected. This would be true for the pair of binary solid solutions for any point along the rubidium bromide–potassium chloride diagonal. The intensities for these odd number index lines should increase from zero at either end of the diagonal to a maximum at D-2. For corresponding ternary solid solutions none of these lines would be expected. A very careful examination of mixtures along this diagonal was made with the intensity counting scalar circuit and no evidence for any odd number index peak was found. It seems necessary to conclude that the final mixture is one solid solution which contains all four kinds of ions rather than two different common ion binary solid solutions.

This conclusion is supported entirely by an investigation of points along the rubidium chloride–potassium bromide diagonal. If only one solid solution is formed the unit cell edge along this diagonal would be expected to remain essentially constant (Fig. 3) while the intensities of the odd number index lines would be expected to decrease from rubidium bromide to zero at D-2 and then to increase to potassium bromide (Table II).

TABLE II

RELATIVE INTENSITIES IN COUNTS PER SECOND FOR THE 311 INTERFERENCE LINE ALONG THE RbCl-KBr DIAGONAL

Sample no.	Composition RbCl	KBr	Rel. no. of electrons In cation plane	In anion plane	Rel. intensity in C.P.S.
D-16	100		36	18	103
D-34	5/6	1/6	33	21	70
D-8	2/3	1/3	30	24	Very low
D-2	1/2	1/2	27	27	0
D-7	1/3	2/3	24	30	Very low
D-35	1/6	5/6	21	33	23
D-1		100	18	36	65
D-2	1/2	1/2	36	18	105
(not fused)			18	36	
D-36[a]	1/3	2/3	22.5	32.5	19

[a] The average composition of this mixture is the same as D-7. Equal amounts of potassium bromide and fused D-2 were mixed but the final mixture was not melted.

To test further the conclusion that one and only one solid solution is formed by the reciprocal system

$$RbCl + KBr \rightleftarrows RbBr + KCl$$

several mixtures were made up having compositions off either diagonal of Fig. 1, *viz.*, D-22, D-23, D-24 and D-25. These points in the open field fall on lines parallel to the diagonals and on constant ratio lines. Along a line from D-32 to D-26 (Fig. 1) parallel to the rubidium bromide–potassium chloride diagonal, the calculated values of sin θ will be very nearly the same as along the parallel line from D-27 to D-33. The dashed line of Fig. 2 has been drawn to represent the sin θ values for these two parallels. The dotted circles represent points along the line connecting D-27 and D-33 while the solid circles represent points along the parallel connecting D-32 and D-26.

The three lines of Fig. 3 represent the variation of sin θ values with composition along the direction of the rubidium chloride–potassium bromide di-

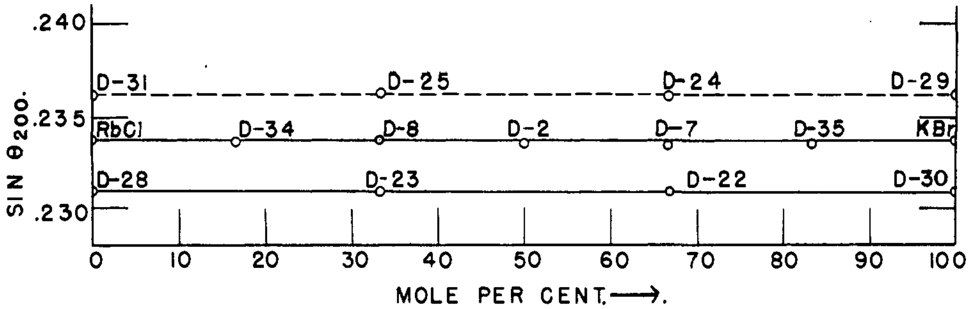

Fig. 3.—Variation of sin θ_{200} with composition along the RbCl-KBr diagonal and along lines parallel to this diagonal.

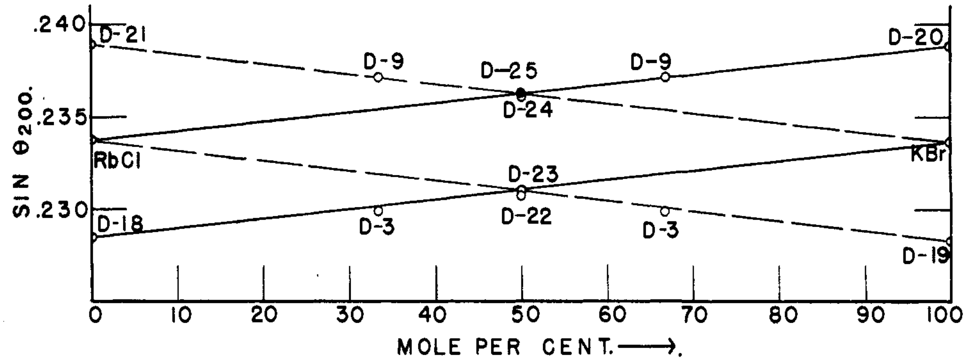

Fig. 4.—Variation of sin θ with the mole per cent. of one ternary component as the other two are kept in a constant ratio to each other.

agonal. The mixtures along the line from rubidium chloride to D-20 in Fig. 4 all have a potassium chloride to potassium bromide ratio of 1:1. In a similar manner mixtures along the line from rubidium chloride to D-19 have potassium bromide to rubidium bromide in a 1:1 ratio and the two lines from potassium bromide have the base components in similar ratios. These two pairs of lines make up two sets of parallel lines across the composition diagram (Fig. 1). Other similar pairs of lines could be drawn from the potassium chloride and rubidium bromide corners. When Figs. 2, 3 and 4 are considered it is found that sin θ changes gradually and continuously with composition in any direction across the composition diagram. This is precisely what would be expected if any mixture of the RbCl + KBr ⇄ RbBr + KCl reciprocal system of whatever composition, always forms one and only one solid solution when melted. Due to the use of rubidium salts in the early part of the work that were later found to contain considerable amounts of potassium salts,[10] several other points in the field of the composition diagram were examined. These points are not shown on the diagram but in no case was more than one X-ray diffraction pattern found.

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St. Louis, Mo. Received July 16, 1951

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(10) Rubidium salts can now be purchased that contain less than 0.1% potassium. Some rubidium salts obtained from a well known supply house contained rather large quantities of potassium.