[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ST. LOUIS UNIVERSITY]

Reactions Between Dry Inorganic Salts. VIII. A Refractive Index Study of Solid Solutions Formed by the Reciprocal System RbCl + KBr ⇄ RbBr + KCl[1]

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For some areas of the composition diagrams of the reciprocal system RbCl + KBr ⇄ KbBr + KCl the results of X-ray diffraction analysis expected for a single ternary solid solution and for a co-existing pair of binary solid solutions cannot be distinguished from each other. In these areas the refractive indexes calculated for the two interpretations of the X-ray measurements are very different from each other and a definite choice between the two alternatives becomes possible. All observations are in complete accord with the view that, for each mixture, one solid solution is formed which contains all of the rubidium, potassium, bromide and chloride ions.

Recently an X-ray diffraction study of the reciprocal system

$$RbCl + KBr \rightleftharpoons RbBr + KCl$$

was made and it was then found that, after crystallization of any molten mixture of salts of this system, only one X-ray pattern is observed. The observed unit cell edge is always in good agreement with the cell edge calculated by the use of Vegard's additity law on the assumption that all of the rubidium, potassium, bromide and chloride ions are contained in a single solid solution. Except for the intensities of the odd number index lines, *e.g.*, 111, 311, etc., the single diffraction pattern corresponding to each ternary[3] mixture, can be equally well accounted for on the basis of two co-existing binary solid solutions. The expected intensities for the odd number index lines of each member of a given binary pair are equal to each other but are always greater than the expected intensities for the corresponding ternary solid solution.

A study of this diagram indicates that in the central area the calculated difference in intensities between a pair of binary solid solutions and the corresponding ternary is of such a magnitude as to be readily measurable. For compositions indicated approximately by the shaded areas, this differentiation becomes difficult and after a time impossible as each corner is approached. Furthermore the entire upper right hand side of Fig. 1 is equivalent, point for point, with the lower left hand half and corresponding points in these two halves of the diagram cannot be distinguished from each other by X-ray analysis. (For example compare points D-25 and D-24; D-8 and D-7; D-32 and D-27, and so on.) It has been found possible to use refractive index measurements to supplement the X-ray diffraction analysis in a very satisfactory manner. A study of the refractive indexes of a series of mixtures, whose compositions are shown in Fig. 1, has been made and the results obtained are described in the section on Experimental results.

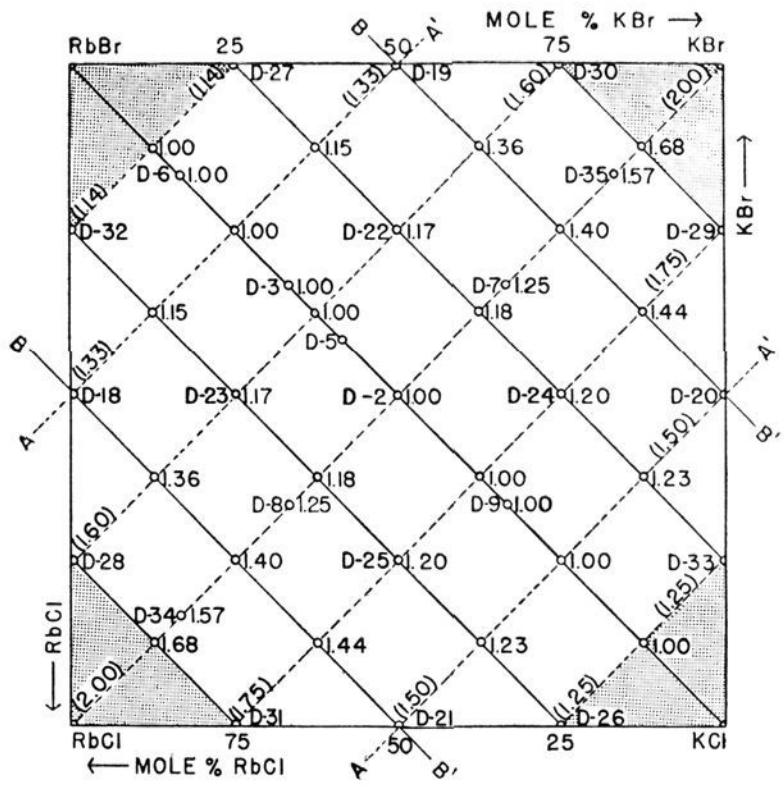

Fig. 1.—Electron ratios in alternate odd number index planes. Experimental mixtures are indicated by D-numbers; electron ratios for the ternary solid solution are indicated by numbers in the direction of BB′; electron ratios for the binary mixtures are indicated by numbers in parentheses in the direction of AA′.

Materials, Apparatus and Methods

The refractive index was determined by the oil immersion method by observing the movement of the Becke line as the focus of the microscope was changed. For this work a set of certified immersion liquids varying in steps of 0.002 unit was used. By comparison an oil was first selected whose refractive index was close to that of the crystal. The temperature of the oil was then carefully raised or lowered by means of water jackets[4] above and below the microscope slide until the crystal disappeared into the oil. The temperature at which the crystal disappeared into the oil was observed and the temperature at which it reappeared was observed and the refractive index of the oil at the middle of this temperature range was taken as the refractive index of the crystal. Under favorable conditions this temperature range was sometimes no greater than 0.5° and since the temperature coefficient of the diffraction liquids was about 0.0004, the refractive indexes could (under favorable conditions) be determined to an accuracy to about ± 0.0001. Illumination was by sodium vapor light.

In order to add to the information gained about the reciprocal system RbCl + KBr ⇄ RbBr + KCl by the X-ray analysis and by the refractive index measurements, the melting point of each mixture was determined. A small amount of each mixture was placed in a small melting tube made of high melting glass (vycor). This melting point tube was placed in a cylindrical melting point block which was then placed in a large vycor test-tube. This test-tube was heated electrically in an insulated tube furnace. The melting of the mixture was observed visually by looking through a small opening passing through the melting point block at 90° to the melting point tube. The temperature

(1) Read before the Ninth Pittsburgh Diffraction Conference.

(2) Lyman J. Wood and L. J. Breithaupt, Jr., THIS JOURNAL, **74**, 727 (1952).

(3) The terms binary and ternary are used in the sense of the phase rule. While all of the evidence indicates that these mixtures are made up of ions it is necessary for purposes of calculation, to assume a "Stoichiometric Molecule" which is invariably taken as an ion pair consisting of one cation and one anion.

(4) Lyman J. Wood and Albert Frank, *Anal. Chem.*, **23**, 695 (1951).

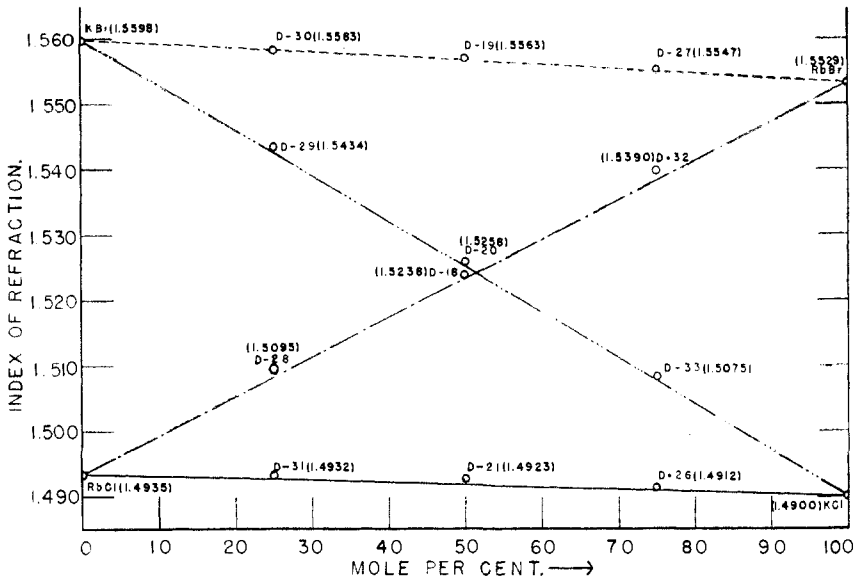

Fig. 2a.—Refractive index *vs.* mole per cent. for the common ion pairs RbBr–RbCl; RbBr–KBr; RbCl–KCl; KBr–KCl. Numbers in parentheses are observed indexes.

was observed by means of a thermocouple and a type K potentiometer. The thermocouple was placed in contact with the melting point tube through an opening along the axis of the melting point block. High precision melting points cannot be expected from this method but the cost of sufficient quantities of high purity rubidium salts for reliable freezing point curves was prohibitive. The most accurate part of the observation appeared to be the end of melting. The observation of the freezing point was completely unreliable.

While it was not felt that high precision melting points were required nevertheless a considerable amount of care was exercised in making these observations. The absolute reading of the thermocouple was checked by making freezing point curves of potassium chloride, aluminum (99.6%) and tin. The melting point of the potassium chloride was taken at 770.3°, the aluminum as 658.9° and the tin as 231.9°. The thermocouple was next calibrated in the melting point block by observing the melting point of potassium chloride as a high point and as a low point the melting point of a eutectic mixture of sodium chloride and sodium sulfate having a composition of $NaCl:Na_2SO_4$ = 30.5:69.5 by weight (51.61 mole per cent. sodium chloride). This mixture of sodium chloride and sodium sulfate was used as a standard in the melting block because molten aluminum is not transparent to light and its melting point could not be observed.

The melting point of this eutectic mixture is listed in the "International Critical Tables" as a secondary standard of fixed temperature. However, the melting point has been erroneously given as 637°. In the original literature[5] the melting point is given as 627 ± 0.5°.[6]

The authors carefully compared a cooling curve of this mixture with the cooling curve of aluminum and obtained a melting point of 626°. The error in the melting points of the pure substances (Fig. 2b) is probably not greater than ±1.0° while the error is probably somewhat greater for the values given for the mixtures.

The salts used in this work were of the same high purity as described in the previous paper and the method of preparation and treatment of the mixtures were also the same.

Experimental Results and Discussion

The observed refractive indexes and melting points for the pure components and mixtures are shown in parentheses in Figs. 2 to 4. In Fig. 2a the refractive indexes of the binary mixtures are plotted against molar composition. The straight lines shown in the figure are drawn on the assumption that the refractive indexes are additive and the points plotted represent experimental observations. It is quite clear that the points are very nearly on the straight lines and that the experimental observations agree remarkably well with the assumption that the refractive indexes are additive.[7]

It is to be seen that the refractive indexes of rubidium chloride and potassium bromide are very different from each other whereas their unit cell edges are very nearly the same. Also the refractive indexes of the common chlorides are very nearly equal to each other and the common bromides are very nearly equal to each other while the respective pairs of unit cell edges are very different from each other. Because of this the X-ray diffraction method and the refractive index method of analysis supplement each other in a very satisfactory manner.

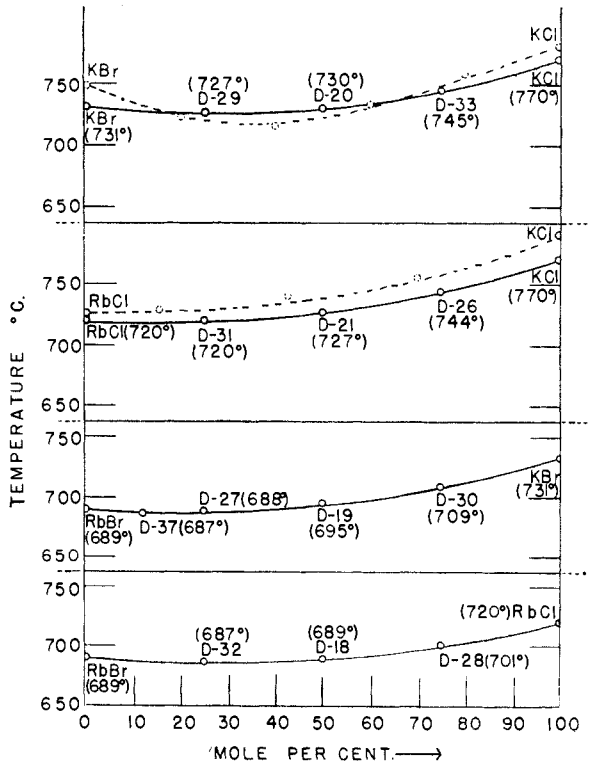

Fig. 2b.—End of melting *vs.* mole per cent. for the common ion pairs RbBr–RbCl, RbBr–KBr, RbCl–KCl, KBr–KCl. Numbers in parentheses are observed melting points.

(5) H. S. Roberts, *Phys. Rev.*, **23**, 386 (1924).

(6) The erroneous listing of this melting point has also been confirmed in a private communication from the Temperature Measurements Section of the National Bureau of Standards.

(7) If molar refractivities are calculated they are found to be additive also.

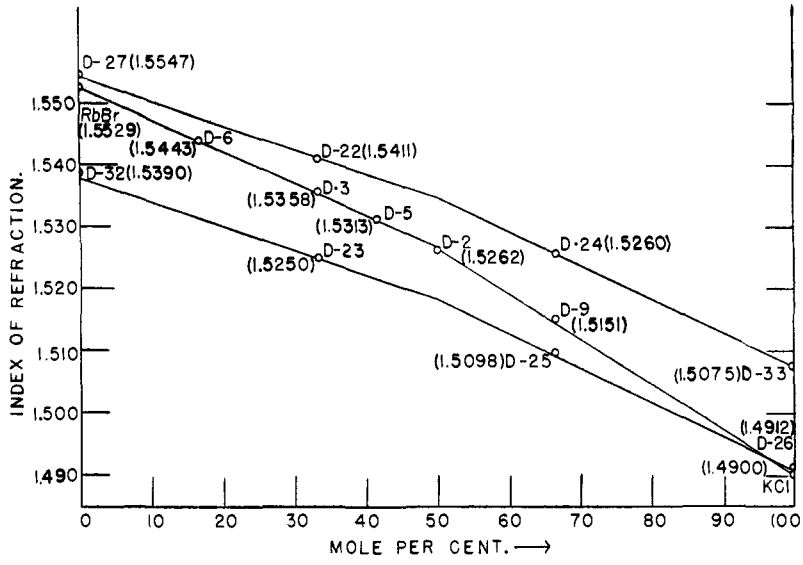

Fig. 3a.—Refractive index *vs.* composition in the direction of the RbBr–KCl diagonal.

In Fig. 2b the melting points of the binary mixtures are plotted against molar composition. The curves here are, of course, not straight lines. They are, however, smooth curves and the melting points vary gradually from one pure substance to the other. Melting points have been reported for the potassium bromide–potassium chloride system[8,9] which are not in good agreement with our melting points (Fig. 2b). The beginning of freezing as reported by Vrzhesneskii is shown by the dotted curve and while the curve is typical of a system forming only solid solutions, the melting points of both potassium chloride and potassium bromide are unexplainably high. The melting point of potassium chloride is listed in the table of primary standards of fixed temperatures as 770.3°. Several of the most recently determined melting points of potassium bromide as listed in Gmelin's Handbook of Inorganic Chemistry range from 728 to 733°, which are to be compared with our melting point of 731°. The melting point of potassium bromide reported by Vrzhesneskii is undoubtedly much too high.

Melting points have been reported for the rubidium chloride–potassium chloride system[10] and these results are also not in good agreement with our melting points (Fig. 2b). Again the dotted curve represents the beginning of freezing as reported by Zemczuzny and Rambach. The melting point of rubidium chloride taken from the dotted curve is 726°, the most recently determined value reported in Gmelin's Handbook is 722° while our value is 720°. Our melting point value for rubidium bromide is 689° while the most recently determined value listed in Gmelin's Handbook is 681°. In view of the difficulty encountered in removing potassium from rubidium salts it is quite possible that our rubidium salts containing less than 0.1% of potassium were of much higher purity than most rubidium salts used in the past.

(8) Amadori and Pampanini, *Atti accad. Lincei*, **20II**, 572 (1911).
(9) Vrzhesneskii, *Z. anorg. allgem. chem.*, **74**, 98 (1912).
(10) Zemczuzny and Rambach, *ibid.*, **65**, 403 (1910).

In Fig. 3a refractive indexes are plotted against molar composition along the rubidium bromide–potassium chloride diagonal and along lines parallel to the diagonal. The points represent observed refractive indexes. Because the sums of the refractive indexes of the two reciprocal pairs are not quite equal to each other (this is true also if molar refractions are used) two sets of calculated refractive indexes for the ternary solid solution can be obtained. If it be assumed that the reaction goes as far as possible in the direction of the rubidium chloride–potassium bromide pair (the R pair) before the solid solution forms, the refractive indexes are additive and the solid lines of Fig. 3a result. If the reaction is assumed to go in the other direction, corresponding calculations for the ternary solid solutions are 0.002 to 0.004 lower and differ from the observed refractive indexes by as much as five to ten times the experimental error.

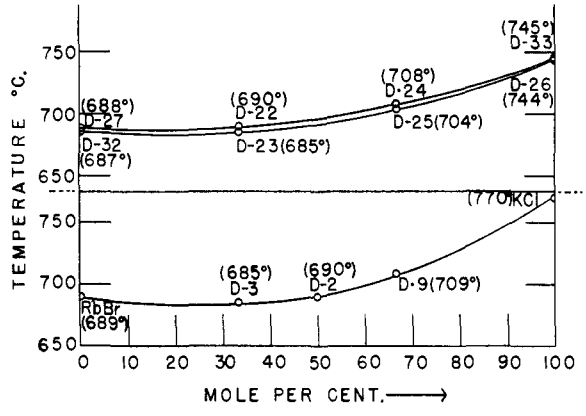

Fig. 3b.—End of melting *vs.* composition in the direction of the RbBr–KCl diagonal.

The observed refractive index measurements can tentatively be explained as follows: Let it be assumed that when a given mixture is heated (a) the reaction goes as far as possible in the direction of the rubidium chloride–potassium bromide pair; (b) the rubidium chloride and potassium bromide, together with the residual rubidium bromide or potassium chloride, form the two binary solid solutions described in Fig. 1; (c) the two binary solutions form the ternary solid solution consisting of all of the rubidium, potassium, bromide and chloride ions distributed in a random fashion throughout the crystal. It is hoped that studies of ion migration under the fusion point now in progress in our laboratory will make some contribution to the solution of this problem.

The refractive index calculated for the pair of binary solid solutions (Fig. 1) corresponding to each point in Fig. 3a are listed in column 10 of Table I. The calculated indexes for each member of the binary pair are very different from each other and from

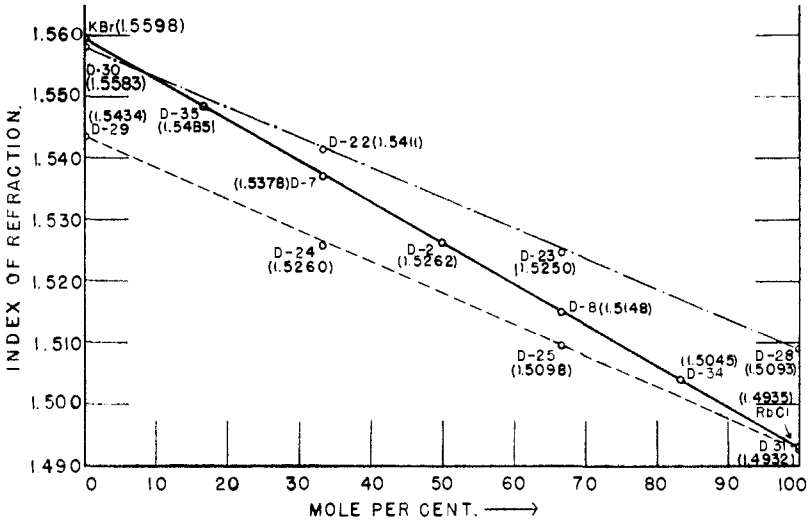

Fig. 4a.—Refractive index *vs.* composition in the direction of the RbCl-KBr diagonal.

the calculated value for the ternary solid solution. A study of Table I will make it clear that refractive indexes can be used for distinguishing between the ternary and binary solid solutions far into the shaded regions of Fig. 1 where the X-ray diffraction cannot be used. The refractive indexes for these mixtures give positive evidence for the absence of binary solid solutions and the existence of one ternary solid solution in each case. This is in complete agreement with the results of the X-ray results.

In Fig. 4a refractive indexes are plotted against composition along the rubidium chloride–potassium bromide diagonal and along directions parallel to this diagonal. As in Fig. 3a the positions of the lines represent calculated refractive indexes for the ternary solid solutions while the points represent observed indexes and the agreement is excellent. Along this diagonal the two binary solid solutions are replaced by the two pure substances rubidium chloride and potassium bromide and the unit cell edge calculated for the ternary solid solution at any point is equal (very nearly) to the unit cell edge of rubidium chloride or potassium bromide. The electron ratio for the alternate odd number index planes of rubidium chloride and potassium bromide is two and for the ternary solid solutions along this diagonal this electron ratio decreases from two at either end to zero at the middle. In the previous paper it was shown that observed intensities for the odd number index X-ray diffraction lines decrease from high values for rubidium chloride or potassium bromide to zero for mixture D-2 as would be expected if a single ternary solid solution is formed. Toward the ends of the diagonal these intensities for the ternary solid solution approach those of the pure components and the X-ray method will not distinguish between the ternary solution and the pure substances (shaded areas of Fig. 1).

A study of Fig. 4a makes it clear that refractive indexes could be used for making this distinction far into these shaded areas. For example a mixture of 99 mole per cent. of rubidium chloride and one mole per cent. potassium bromide would have a calculated refractive index of 99% of 1.4935 + 1% of 1.5598 = 1.4942 (Fig. 2a). The difference between this calculated value and the observed index of rubidium bromide is 0.0007 while the average difference between the observed and calculated indexes in Table I is 0.0003.

Toward the middle of the rubidium chloride–potassium bromide diagonal the expected intensities of the odd number index X-ray diffraction lines for the ternary solid solutions decrease to small values as they approach zero at the middle. Over most of the distance between D-7 and D-8 these intensities are so low that it is difficult or impossible to detect them and since the unit cell edge does not vary along this diagonal, the X-ray results for mixtures in this region cannot be distinguished from each other. However, the calculated refractive indexes for points between D-7 and D-8 are very different from each other and from the pure components. Amounts of rubidium chloride or potassium bromide too small to produce detectable odd number index lines or to affect unit cell edge results measurably could still be detected by the refractive index method. Heterogeneity due to a series of solid solutions of slightly varying composition that might go undetected by the X-ray analysis could also be detected within narrow limits by refractive index observations.[11] For mixture D-2 the unit cell edge was very near the calculated value for the ternary solid solution and no odd number index lines were observed. Each particle of this mixture examined had an index very close to 1.5262 which is in good agreement with the calculated value of 1.5267. These results indicate that this mixture is quite homogeneous, and that it is made up of one solid solution with no left over rubidium chloride or potassium bromide.

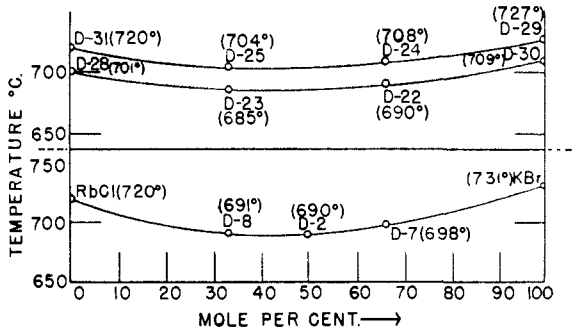

Fig. 4b.—End of melting *vs.* composition in the direction of the RbCl-KBr diagonal.

Additivity of refractive indexes can be demonstrated in a very striking manner by considering constant ratio lines extending from each corner of the composition diagram (Fig. 1). Take for example the line running from rubidium chloride

(11) L. J. Wood and A. J. Frank, *Anal. Chem.*, **23**, 695 (1951).

TABLE I

A COMPARISON OF BINARY SOLID SOLUTION MIXTURES WITH THE TERNARY SOLID SOLUTION THAT HAS THE SAME UNIT CELL EDGE

		Molar composition, %				Odd no. index X-ray lines			Refractive index	
						Rel. no. of electrons				
		RbCl	KBr	RbBr	KCl	Cation plane	Anion plane	Nature of line expected	Calcd.	Obsd.
D-6	R[a]	1/6	1/6	2/3	..	33.0	33.0	None	1.5442	1.5443
	1[a]	1/6	..	1/3	..	36.0	30.0	Very low	1.5380	
	2[a]	..	1/6	1/3	..	30.0	36.0	Very low	1.5546	
D-3	R	1/3	1/3	1/3	..	30.0	30.0	None	1.5354	1.5358
	1	1/3	..	1/6	..	36.0	24.0	Mod. strong	1.5133	
	2	..	1/3	1/6	..	24.0	36.0	Mod. strong	1.5575	
D-5	R	5/12	5/12	1/6	..	18.5	18.5	None	1.5310	1.5313
	1	5/12	..	1/12	..	36.0	21.0	Strong	1.5034	
	2	..	5/12	1/12	..	21.0	36.0	Strong	1.5587	
D-9	R	1/3	1/3	..	1/3	24.0	24.0	None	1.5144	1.5151
	1	1/3	..	..	1/6	30.0	18.0	Strong	1.4923	
	2	..	1/3	..	1/6	18.0	30.0	Strong	1.5365	
D-22	R	1/4	1/2	1/4	..	27.0	31.5	Very weak	1.5415	1.5411
	1	1/4	..	1/12	..	36.0	22.5	Mod. strong	1.5084	
	2	..	1/2	1/6	..	22.5	36.0	Mod. strong	1.5581	
D-23	R	1/2	1/4	1/4	..	31.5	27.0	Very weak	1.5249	1.5250
	1	1/2	..	1/6	..	36.0	22.5	Mod. strong	1.5084	
	2	..	1/4	1/12	..	22.5	36.0	Mod. strong	1.5581	
D-24	R	1/4	1/2	..	1/4	22.5	27.0	Very weak	1.5258	1.5260
	1	1/4	..	..	1/12	31.5	18.0	Strong	1.4926	
	2	..	1/2	..	1/6	18.0	31.5	Strong	1.5424	
D-25	R	1/2	1/4	..	1/4	27.0	22.5	Very weak	1.5092	1.5098
	1	1/2	..	..	1/6	31.5	18.0	Strong	1.4926	
	2	..	1/4	..	1/12	18.0	31.5	Strong	1.5424	

[a] In the lines marked R the refractive indexes are calculated on the assumption that the reaction has gone as far as possible in the direction of the reactive or reciprocal pair. In lines 1 and 2 are shown the compositions of binary solid solutions having the same calculated unit cell edge as that shown in line R.

to D-19. The calculated index for D-23, half-way between rubidium chloride and D-19, is 1.5249 (obsd. 1.5250) and for D-3 at two thirds of the way between these points, it is 1.5345 (obsd. 1.5358). Similar calculations can be made for other constant ratio lines leading from the other corners.

In Figs. 3b and 4b the melting points of mixtures represented in Figs. 3a and 4b, respectively, are plotted against composition. As for the common ion pairs (Fig. 2b) these curves are not straight lines but the melting point changes gradually with composition, in any direction, along smooth curves as would be expected for a continuous series of solid solutions. All of the diffraction patterns, refractive index measurements and melting points are in complete accord with the view that, for each mixture, one solid solution is formed which contains all of the rubidium, potassium, bromide and chloride ions.

Acknowledgments.—The authors wish to thank Dr. Edward Marshall of the Aluminum Company of America for assistance in making the melting point curve of aluminum. They wish also to thank Dr. John S. Burlew of the Carnegie Institution of Washington and Dr. H. F. Stimson and Mr. E. F. Meuller (retired) of the National Bureau of Standards for assistance in confirming the erroneous listing of the melting point of the eutectic mixture of sodium chloride and sodium sulfate in the "International Critical Tables."

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