

solution, and chloride ion determined volumetrically. It was definitely shown that the presence of ethyl chloride did not affect this determination. Carbon dioxide and hydrogen chloride were then determined together by absorption on ascarite, and carbon dioxide found by difference. The residual gas was analyzed for ethylene by the micro-method of Blacet, MacDonald and Leighton.⁵ Ethyl chloride was determined on samples from which carbon dioxide and hydrogen chloride had been removed by exploding the sample with three times its volume of oxygen at reduced pressure, absorbing the liberated chloride ion in sodium hydroxide solution, and titrating. The accuracy of this method was tested on synthetic gas mixtures of composition approximating that of the mixtures resulting from the pyrolyses. The results of a series of representative analyses are shown in Table I. Compositions were found to vary somewhat, as shown, and the variation showed no regular trend with temperature. It may be attributed to the complexity of the reaction, obscure surface effects, and difficulties of analysis.

TABLE I

COMPOSITION OF GAS MIXTURES OBTAINED FROM THE THERMAL DECOMPOSITION OF ETHYL CHLOROCARBONATE

t, °C.	HCl, %	C ₂ H ₄ , %	CO ₂ , %	C ₂ H ₅ Cl, %	P ₁ /P ₂
300	16.1	15.0	42.9	27.1	2.31
310	16.1	16.3	41.9	26.0	2.33
320	15.6	17.8	42.0	24.4	2.38
325	16.0	16.4	42.4	24.1	2.31
325	19.9	20.1	41.6	21.5	2.42
330	17.1	18.7	40.8	21.8	2.37
330	20.4	20.9	39.2	18.5	2.46

(5) F. E. Blacet, Geo. D. MacDonald and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).

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Interpretation of the Refractive Index Measurements on the Ternary System RbCl-RbBr-KBr-KCl

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The X-ray diffraction study by Wood and Breithaupt¹ of the ternary crystalline solids obtained from mixtures of the salts RbCl, RbBr, KBr and KCl indicated that the salts formed a continuous ternary solid solution as sole solid phase, as was to be expected from the fact that each of the four common-ion binary combinations forms a continuous

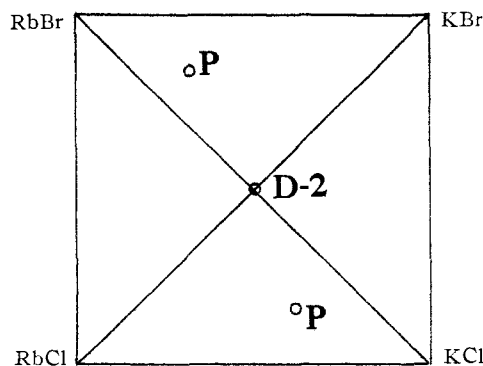


Fig. 1.—Composition diagram of the system RbCl-RbBr-KBr-KCl.

(1) L. J. Wood and L. J. Breithaupt, *This Journal*, **74**, 727 (1952).

solid solution with a very shallow minimum in its melting point curve. In consideration of the subtle uncertainty that the X-ray data might not unequivocally distinguish between a single ternary solid solution and a heterogeneous mixture of two common-ion binary solid solutions, the same investigators, in a subsequent study,² sought to decide the question by means of refractive index measurements; their article also reports melting point observations on the ternary system further corroborating the conclusion of continuous ternary solid solution. It is claimed that the refractive index data, unlike the X-ray diffraction data, are unequivocal in establishing the nature of the solid as a single homogeneous ternary solid solution. Although the conclusion regarding a continuous ternary solid solution seems to be correct, the argument used is inconsistent and faulty and other accompanying conclusions are incorrect.

The argument begins with assuming, from a plot of the binary data, that the refractive index of each of the four binary solid solutions, RbCl-RbBr, RbBr-KBr, KBr-KCl and KCl-RbCl (the edges of the composition diagram shown here in Fig. 1), is strictly additive with respect to the refractive indexes of the component salts, and that the resulting ternary solid solution should likewise be additive with respect to two adjacent binary solid solutions. It is expected, in other words, that the refractive index of the ternary solid solution with composition P (Fig. 1) should be additive with respect to either the pair of binary solid solutions RbCl-RbBr and RbBr-KBr (possibility A) or the pair RbBr-KBr and KBr-KCl (possibility B). It is furthermore expected that if possibility A holds for point P, then point P', for example, will be additive with respect to the pair RbCl-KCl and KCl-KBr and not with respect to the pair RbCl-RbBr and RbCl-KCl. On examining their data on the basis of this expected additivity, the authors conclude that the system is divided according to possibility A, or that all original mixtures in the square of Fig. 1 react to form RbCl and KBr as a "stable salt pair," plus excess of either RbBr or KCl, and that the agreement with the additivity expected on this basis is indeed "striking." Such strict additivity is of course at least as consistent with a heterogeneous mechanical mixture of two binary solid solutions as with any sort of single solid phase formed from them, but heterogeneity is ruled out on the basis of detailed observations reported on "every particle" of the sample D-2 (Fig. 1). Hence the following two conclusions are drawn: (1) that the system forms a single continuous ternary solid solution, and (2) that the refractive index of this continuous solid phase is additive with respect to the salts RbCl-RbBr-KBr on the RbBr side of the diagonal RbCl-KBr and additive with respect to the salts RbCl-KCl-KBr on the KCl side.

These two conclusions, however, are self-contradictory, and the second one is in itself impossible. If the refractive index is represented as a vertical axis upon the composition square of Fig. 1, with a, b, c and d as the values of the refractive indexes for the salts RbCl, RbBr, KBr and KCl, respectively.

(2) L. J. Wood and L. J. Breithaupt, *ibid.*, **74**, 2355 (1952).

the refractive index of the ternary solid solution falls on a surface joining the points **a**, **b**, **c**, **d** (Fig. 2). If each binary system is strictly additive the four edges **ab**, **bc**, **cd** and **da** are straight lines. If the ternary solid solution on the RbBr side of the diagonal RbCl-KBr is additive with respect to **ab** and **bc**, or, that is, with respect to the points **a**, **b** and **c**, its refractive index falls on the plane **abc**; and if the ternary solid solution on the KCl side is additive with respect to **ad** and **cd** its refractive index lies on the plane **acd**. The gradual introduction of KCl into crystalline RbBr, forming, at equilibrium, always a continuous, homogeneous solid solution with composition lying on the diagonal RbBr-KCl of Fig. 1, would then cause a linear change in the value of the refractive index up to the 1:1 proportion. At this point the rate of change would change abruptly, to follow a second linear rate up to pure KCl. This is, in fact, exactly the way in which the refractive index for the diagonal RbBr-KCl is plotted in Fig. 3a of ref. 2, with "very good agreement" with the data; and the present Fig. 2 summarizes what the authors present as the argument for continuous ternary solid solution.

But such a relation, involving two such intersecting planes (or even two such intersecting curved surfaces) for a property surface, is of course impossible if the solid phase is homogeneous and continuous for the whole system, requiring a similarly smooth and continuous property surface throughout. The relation is also in itself an impossibility in an equilibrium phase diagram, for if there were actually a discontinuity in the solid solution, with a miscibility gap, then the property surface would have to be divided differently, into regions pertaining to homogeneous phases and regions pertaining to heterogeneous mixtures, not into the two intersecting planes of Fig. 2. One-phase, homogeneous areas cannot be adjacent to each other in a composition diagram.

That these inconsistencies could be overlooked is probably the result of the undue concern with the notion of a "stable pair" of salts in a system with complete, continuous solid solution. Given continuous solid solution the real significance of reciprocity of composition and of the stability relation of pairs vanishes from the point of view of the phase rule, even though energy relations may allow us to calculate which pair is theoretically "stable." Neither the pair RbBr + KCl nor the pair RbCl + KBr is stable as a pair of salts, or as a pair of phases, that is. The two salts of either pair, taken as an original mixture, must interact or undergo a phase reaction, since the only stable phase is a common, identical solid solution; the two interactions can differ only in respect to the energy change and in respect to velocity. In fact, the authors' explanation (p. 2357 of ref. 2) suggests no way in which, starting with the "stable pair" RbCl + KBr, the final ternary solid solution should even begin to form, if this ternary solid solution consists either of the two binaries RbCl-RbBr and RbBr-KBr or of the two binaries RbCl-KCl and KCl-KBr. If RbCl + KBr is the stable pair, in other words, these two salts must dissolve directly in each other without first forming binary solid solutions.

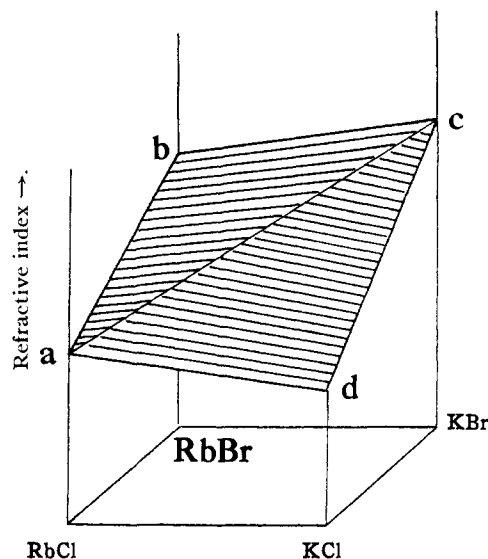


Fig. 2.—Schematic representation of the conclusions in ref. 2.

Whether or not the "unstable pair," RbBr + KCl, first forms the "stable pair" (plus excess of one salt), then two binary solid solutions and finally a single ternary solid solution (this being the scheme proposed by the authors as "explaining" their equilibrium measurements as represented in Fig. 2), is a question of the mechanism (the *process*, involving rates) of arriving at final equilibrium; but the final equilibrium must be independent of the path, and the properties of a single homogeneous phase must vary continuously and smoothly with its composition.

A solution for the difficulty in interpreting the observed refractive indexes of the ternary solid solution may be offered on the basis of a reconsideration of the authors' data on the four binary systems, or the edges **ab**, **bc**, **cd** and **da** of Fig. 2. The question involved is that of the shape of the single smooth and continuous surface which must join these edges if these edges are straight lines, as they were assumed to be by Wood and Breithaupt. These edges are straight lines if the refractive indexes of the binary solid solutions are strictly additive in respect to composition, and in such a case there would seem to be no reason for expecting that their common ternary solid solution should not similarly be strictly additive, whereupon the ternary refractive index surface should be a single plane with the points **a**, **b**, **c** and **d** as its corners. But the ternary surface cannot be a plane unless $a + c = b + d$, which is not the case for the present system, in which $a + c > b + d$ and $c > b \gg a > d$. The numerical values² are: $a = 1.4935$, $b = 1.5529$, $c = 1.5598$ and $d = 1.4900$.

It is to be expected, therefore, and it seems indeed to be an experimental fact on the basis of the authors' own measurements, that the binary systems are not additive, despite the impression given by Fig. 2a of ref. 2. Strict additivity in all four binary pairs would imply constant and independent atomic or ionic contributions, and then the sum of **a** and **c** would equal the sum of **b** and **d**, which is not the case.

Actually, the refractive index of each of the four

binary solid solutions is (irregularly) greater than that of a mechanical mixture of the two salts involved; each of the experimental curves lies above the straight lines of Fig. 2a of ref. 2. For the twelve binary points plotted the average algebraic deviation from the straight lines is +5.2 units (in the fourth decimal) while the experimental accuracy is claimed to be "about ± 0.0001 ." The only negative deviation (0.5 unit) occurs on the curve **bc** (RbBr-KBr), which is itself the nearest to a straight line, with deviations +2, -0.5 and +1. For curve **ad** the deviations are +6, +5.5, +3; for **cd**, +10.5, +9, +0.5; and for **ab**, +9.5, +6, +9.5. The last two binary systems, each with a common cation, seem to differ most from strict additivity.

It is possible, of course, that the experimental uncertainty is much greater than 0.0001, and that the binary systems may still be taken as (practically) additive. However, even if the four edges of the surface are practically straight lines, the surface connecting them, which must be smooth and continuous if the solid phase is a single continuous solid solution, must nevertheless be a curved surface, since the four points **a**, **b**, **c** and **d** are not on the same plane, which would require $a + c = b + d$. Moreover, since at least the two sides **ab** and **cd** appear to be curved above their straight lines, the surface may be expected to be concave downward; this is apparent from the schematic diagram of Fig. 3. Finally, the curvature of the two diagonals of

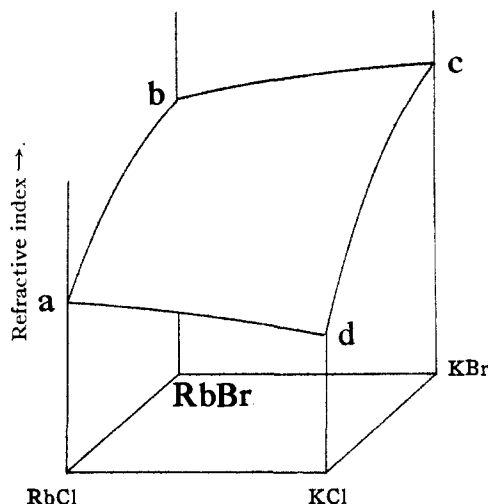


Fig. 3.—Schematic representation of the ternary refractive index surface.

the surface, **ac**, and **bd**, will not be the same, and since $a + c > b + d$, the diagonal **ac** will be flatter, or more nearly a straight line, than the diagonal **bd**. This expected difference is apparent in the experimental data plotted in Figs. 3a and 4a of ref. 2. The refractive indexes parallel to the diagonal **ac** (Fig. 4a) fall, within what must be considered an uncertain experimental error, upon practically straight lines. Those parallel to the **bd** diagonal (Fig. 3a) are actually plotted on straight lines intersecting above the single straight line demanded by continuous additivity (the impossible conception pictured here as Fig. 2), but they may equally well be fitted by continuous curves concave downward.

In conclusion, it appears that all that can be done experimentally is to investigate the shape of the surface, which must be continuous if the ternary solid is continuous, and which may be expected beforehand, on the basis of the bounding binary curves, to be generally concave downward. On the question whether the solid is homogeneous or not, however, any observation of strict additivity with respect to adjacent pairs of binary solid solutions should be taken as indicating heterogeneity, or the presence of a mechanical mixture of such pairs of binary solids, and it would be the very opposite, or evidence of non-additivity, that would suggest a homogeneous ternary solid solution. Practically, the data are useful only in the usual sense that if the property measured varies smoothly over the entire surface the solid is a single phase, while if it varies with abrupt changes, as might be suggested by the unjustified intersecting straight lines of Fig. 3a of ref. 2, then it is heterogeneous. Within a somewhat uncertain experimental error all the data may apparently be fitted by smooth curves across the surface. On this basis, therefore, the data corroborate the thermal study and the X-ray analysis of the system indicating that the only solid formed is a continuous ternary solid solution of all four salts.

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The Reactivity of the Halogen in Some Halogenated Anilines

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In a previous report¹ it was shown that ortho halogen atoms increase the susceptibility of *p*-nitrosubstituted aryl halides toward substitution by nucleophilic reagents. This is no doubt due, mainly, to the unique behavior of halogens when attached to the benzene ring. Halogens have a large induction moment directed away from the ring and at the same time, owing to resonance, the electron density is the lowest at the meta carbon atoms. The over-all effect is to bring about activation for nucleophilic substitution, the order of which is $m > o > p$.

Conversely one would expect deactivation, of the order $m > o > p$ for electrophilic substitution.²

The authors of the present paper have examined in a qualitative way, the behavior of *p*-iodoaniline, 3,4-diiodoaniline, 3,4,5-triiodoaniline and 2,6-dibromo-4-iodoaniline toward acid stannous chloride. The reaction is probably an electrophilic attack by hydrogen ion on nuclear carbon, the *p*-iodine being displaced as positive ion.³ The presence of the

(1) R. B. Sandin and M. Liskear, *THIS JOURNAL*, **57**, 1304 (1935).

(2) For some recent interesting work and reviews on aromatic nucleophilic and electrophilic substitution reactions, see W. M. Schubert, *THIS JOURNAL*, **71**, 2639 (1949); E. Berliner, M. J. Quinn and P. J. Edgerton, *ibid.*, **72**, 5305 (1950); E. Berliner and L. C. Monack, *ibid.*, **74**, 1574 (1952); J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951); L. N. Ferguson, *ibid.*, **50**, 47 (1952).

(3) (a) B. H. Nicolet, *et al.*, *THIS JOURNAL*, **43**, 2081 (1921); **49**, 1796 (1927); **49**, 1801 (1927); **49**, 1805 (1927); **49**, 1810 (1927). (b) A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 408.