Summary

1. The principal factor determining the sharpness of the electrometric end-point with polarized electrodes of pure platinum is the difference in the degree of reversibility of the electrode reaction before and after the end-point. Other factors such as concentration and rate of stirring are of minor importance. The end-point phenomena are more distinct, the more nearly the electrode reactions conform to the requirement of complete reversibility on one side of the end-point and complete irreversibility on the other, but are sharp enough for practical use in analysis in some cases which fall far short of meeting this requirement.

2. Although the polarization sometimes produces a slight displacement of the end-point break of a single electrode, the errors so introduced are generally too small to be of significance in a volumetric analysis.

3. The end-point break in titrations of the ordinary type, based on the single potential of a platinum electrode, may often be improved and the behavior of the electrode made much more dependable and satisfactory by polarizing it with respect to an auxiliary electrode.

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[CONTRIBUTION FROM THE PHYSICAL AND CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

SOLID SOLUTIONS OF THE ALKALI AND AMMONIUM HALIDES

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The purpose of this paper is to establish the limits of miscibility of the alkali and ammonium halides at room temperature and to determine the natures and structures of their solid solutions. The photographic powdered-crystal method of X-ray analysis was employed. The apparatus and method of procedure for precision work have been described.[1] The constitution of metallic alloys has been frequently investigated by the X-ray method, but Vegard[2] seems to have been the only one to have used this procedure in the investigation of solid solutions of salts.

The problem of the miscibility of the alkali halides has often been studied by thermal and optical methods. These methods sometimes lead to ambiguous results, and are not always sufficient to permit definitely deciding whether a pair of salts is miscible at room temperature. X-ray methods, on the other hand, are capable of giving a definite answer to this question, provided only that the system be in equilibrium.

The Nature of Solid Solution.—Solid solution may take place in two different ways. The mechanism of the simpler of these two ways is a more

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[1] Havighurst, Mack and Blake, THIS JOURNAL, **46**, 2368 (1924).

[2] Vegard, *Z. Physik*, **5**, 17 (1921).

or less regular substitution in the space lattice of the solvent by the solute atoms or ions. For this substitution to be possible, at least in the case of salts, the stronger atoms must be chemically similar to the original occupants of the lattice points and they cannot differ greatly in volume from these. The effect upon the space lattice of the crystal is an additive change, depending upon the atomic volumes and the mole fractions of the components. The lattice expands or contracts, causing an *apparent* deformation[2] of both solute and solvent atoms. The deformability of these atoms or ions is limited and the solution will be homogeneous until this limit is reached. Measurements on a 50–50 solution of potassium chloride and potassium bromide enabled Vegard to state this "rule of additivity." It has been confirmed for several series of binary metallic alloys. It seems probable that all completely miscible binary systems follow this rule.

The other type of solid solution is *interstitial*, rather than *substitutional*. The solute atoms do not fit into the space lattice of the solvent, but are crammed in between solvent atoms, causing the enlargement of the unit cell of the solvent, no matter what the size of the solute atoms may be. This type of solution can be possible only in a partially miscible system, and the solute atoms need not be similar, either chemically or in volume, to those of the solvent. Westgren and Phragmen[3] found that the unit cube of γ-iron increases in size with increasing carbon content, although the carbon atoms are smaller than the iron atoms. The type of solution is therefore interstitial. Density measurements upon the iron confirmed this supposition. No case has been recorded of interstitial solution in solid solutions of salts and it may not occur.

Exceptions to the first type of solution might be expected to appear in a system of two salts with a common ion, with such a difference of molar volumes as to make the components only partially miscible. Such a system would be composed of two saturated solutions, each solvent being forced to the limit to hold its solute ions. Under these circumstances, there is a possibility of strains in the lattices which would partially controvert the law of additivity.

In binary systems of the alkali and ammonium halides, therefore, we may look for three types of behavior. First, those systems whose components contain a common ion and are not greatly unequal in molar volume, should be completely miscible, with the dimensions of the unit cube obeying the law of additivity. Second, systems whose components possess a relatively large difference in molar volume should behave anomalously. Third, systems whose components differ greatly in molar volume should not be appreciably miscible and the components should be unaffected by each other's presence.

[3] Westgren and Phragmen, *Nature*, 113, 122 (1924).

The Law of Additivity.—The general expression for the side of the unit cell of a cubic mixed crystal is $a^n = a_1^n + (a_2^n - a_1^n)x$, where a is the length of side of the unit cube of the solid solution, a_1 is the length of side of the unit cube of one pure component, a_2 is the length of side of the unit cube of the other pure component and x is the mole fraction of component a_2.

This formula reduces to Vegard's rule of additivity of the unit cube side when n equals 1. There are other possibilities for n. Grimm and Herzfeld[4] have considered solid solutions in the light of crystal-lattice thermodynamics and have come to the conclusion, on the basis of Born's theory, that n should be 8 for the alkali halides. It seems most natural, however, to believe that the *molar volume* is additive. For such a case, n would equal 3. Grimm and Herzfeld have some evidence in favor of this value, n equals 3, as against the value, n equals 8. We have some further evidence in favor of the values 1 or 3 as against the value 8. The calculated lengths of the unit cube side in the series potassium chloride-potassium bromide, for the three values of n, are shown in Table I. Our X-ray measurements will allow no such departure from additivity of the cube side as that demanded by the value, n equals 8. The difference between the values for n equals 1 and n equals 3 is within experimental error in this system, which is almost at the limit of miscibility for the alkali halides. Since we cannot distinguish between the two cases, we will assume the additivity of the unit cube side for the sake of simplicity.

TABLE I

SIDE OF UNIT CUBE OF KCl-KBr

$a^n = a_1^n + (a_2^n - a_1^n)x$

x is the mole fraction of KBr

x	a ($n = 1$) Å.	a ($n = 3$) Å.	a ($n = 8$) Å.
0.0	6.280	6.280	6.280
.2	6.340	6.342	6.350
.4	6.399	6.403	6.413
.5	6.429	6.433	6.443
.8	6.518	6.521	6.527
1.0	6.578	6.578	6.578

Limits of Miscibility.—In an isomorphous series, the miscibility depends upon the differences in molar volume of the components. As the temperature rises, the degree of miscibility increases. If we have a system which is completely miscible at high temperatures, separation may set in as the temperature is lowered. The curve of unmixing is analogous to the familiar miscibility curve for the system phenol-water. The maximum on the curve is displaced to the side of the component with the smaller space lattice. Table II gives a survey of these volume differences

[4] Grimm and Herzfeld, *Z. Physik*, **16**, 77 (1923).

for systems of the alkali and ammonium halides with a common ion. The quantity δ is a function of the volume difference, or from our present point of view, of the difference in lengths of the cube sides. It is defined as follows: $\delta = 100 \times (a_1 - a_2)/\frac{(a_1 + a_2)}{2}$ where a_1 and a_2 are the cube sides of the pure components. At room temperature the limit of complete miscibility is found to be in the neighborhood of δ equal to 5. The system, sodium chloride-sodium bromide, with δ equal to 5.33, may not be completely miscible, while a 50–50 solution of potassium chloride and potassium bromide, with δ equal to 4.64, showed no sign of unmixing after six months. The miscibility of the system, cesium chloride-ammonium chloride, with δ equal to 6.12, is very limited. Partial miscibility, with anomalous behavior of the unit cube side, exists up to δ equal to 10, when there is an almost complete lack of miscibility. Systems with a value of δ above 15 have not been included in the table. Table III contains a collection of the data for the pure substances, used in the

TABLE II

DIFFERENCES IN UNIT CUBE SIDE OF AMMONIUM AND ALKALI HALIDES

Like lattices stable at room temperature

System	%	System	%	System	%
$RbI-NH_4I$	1.11	$CsCl-NH_4Cl$	6.12	LiBr–LiI	10.27
$KI-NH_4I$	2.69	CsBr–CsI	6.13	CsCl–CsI	10.34
KI–RbI	3.80	RbBr–RbI	6.44	RbCl–RbI	10.85
CsCl–CsBr	4.22	LiCl–LiBr	6.75	NaCl–KCl	10.95
KBr–RbBr	4.31	LiI–NaI	6.93	$NaI-NH_4I$	11.40
RbCl–RbBr	4.42	KBr–KI	6.96	KCl–KI	11.58
KCl–RbCl	4.53	LiBr–NaBr	7.82	NaI–RbI	12.50
NH_4Cl-NH_4Br	4.57	NaBr–NaI	8.50	NaCl–NaI	13.81
KCl–KBr	4.64	NaI–KI	8.72	NaF–KF	14.20
NaCl–NaBr	5.33	LiCl–NaCl	9.22	NaBr–RbBr	14.56
$CsBr-NH_4Br$	5.76	NaBr–KBr	10.26		

Like lattices, with one lattice unstable at room temperature

System	%	System	%
$RbBr-NH_4Br$	0.77	NH_4Br-NH_4I	6.10
$RbCl-NH_4Cl$	0.87	NH_4Cl-NH_4I	10.61
$KBr-NH_4Br$	3.54	$NaBr-NH_4Br$	13.79
$KCl-NH_4Cl$	3.66	$NaCl-NH_4Cl$	14.59

TABLE III

PURE AMMONIUM AND ALKALI HALIDES

	Li	Na	K	Rb	Cs	NH_4 face-centered	NH_4 body-centered
F	4.014	4.621	5.328	...	...	...	...
Cl	5.132	5.628	6.280*	6.571*	4.110*	6.514*	3.866*
Br	5.490	5.936	6.578*	6.868*	4.287	6.810*	4.047*
I	6.03[a]	6.463	7.052*	7.325*	4.558	7.244*	...

[a] Wyckoff, *J. Washington Acad. Sci.*, **13**, 393 (1923).

calculation of Table II. The starred values are our own, while the others are due to Davey.[5] It will be noticed that we have omitted rubidium and cesium fluorides. There is some dispute concerning their structures. The structure of ammonium fluoride has never been determined.

Unstable Lattices.—The alkali and ammonium halides, while all cubic, crystallize in one of two different lattices. Most of these salts have face-centered cubic lattices of ions, but ammonium chloride and bromide and cesium chloride, bromide and iodide are composed of simple cubes of ions, interpenetrating to form a body-centered cubic lattice. Miscibility relations between the two types of lattices cannot be simple. Bartlett and Langmuir[6] have shown that ammonium chloride and ammonium bromide change from the body-centered to the face-centered lattice on rise of temperature, Bridgman[7] has observed transition points in all three ammonium salts, accompanied by a volume change of about 15%. The transition temperature for ammonium iodide is —17.6°. Presumably it changes from its normal face-centered lattice to a body-centered lattice. The transition point of ammonium chloride is 184°, the highest of the three. It would seem natural to expect that in a solid solution of ammonium chloride or bromide with an alkali chloride or bromide, the transition point would be lowered; that is, the high temperature lattice would be more nearly stable at room temperature. Furthermore, the ammonium bromide lattice, with a transition point of 138°, would change more easily than the chloride. This effect is illustrated by the systems ammonium chloride-potassium chloride, ammonium chloride-rubidium chloride and ammonium bromide-potassium bromide. By extrapolation, we should get a value for the side of the hypothetical unit face-centered cube of the ammonium salt. It will be observed in Fig. 1 that the extrapolated values for ammonium chloride from the two series, potassium chloride-ammonium chloride and rubidium chloride-ammonium chloride, agree very well.

Cesium chloride has a transition point at 451° and it might be assumed that its lattice becomes face centered at that point and that the other cesium halides also possess an unstable face-centered lattice. The system, cesium chloride-rubidium chloride, should throw some light upon this question. The evidence from this system for a face-centered cesium chloride lattice is not very convincing. Also it might be expected that all the face-centered alkali halides have an unstable body-centered lattice. The results of our work make this possibility seem doubtful.

Structure of Solid Solutions.—The view advocated by Tammann[8]

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[5] Davey, *Phys. Rev.*, **21,** 143 (1923).

[6] Bartlett and Langmuir, THIS JOURNAL, **43,** 84 (1921).

[7] Bridgman, *Proc. Am. Acad. Arts Sci.*, **52,** 89 (1916).

[8] Tammann, *Z. anorg. allgem. Chem.*, **107,** 1 (1919).

and others, that the mechanism of solid solution consists of a regular substitution of solvent groups by solute groups, would require that for certain definite molar ratios of the components, new diffraction lines should appear on the film. These lines would be weak. Vegard could not find them on films from his potassium chloride-potassium bromide solution, and we have observed none of them in our work. Bain[9] has reported these new interference maxima in the case of alloys of copper-gold and molybdenum-tungsten. He took special pains in annealing his alloys. It will be noticed that these alloys have components whose atomic numbers are quite different. The intensity of the new lines is proportional to the difference in atomic number between the solute and solvent atoms or ions. This difference is not great in the case of the miscible alkali and ammonium halides. Also, it is known[10] that diffusion is a much slower process in salts than in metals, with the result that the limit of homogeneity could not be reached so easily in a solid solution of salts.

In the absence of these new diffraction lines, X-rays afford no way of differentiating between a solid solution and a pure compound. That is, *every solid solution of a completely miscible system acts toward X-rays as though it were a pure binary substance, the reflecting power and volume of the compound ion or atom being determined additively by the atomic numbers and volumes of the constituent atoms.* We include in this group of completely miscible systems the ammonium-potassium halide series and the ammonium-rubidium halide series, because if both components had the same stable lattices, they would be completely miscible and they seem to follow the additivity rule up to their limits of miscibility. The above generalization is confirmed by two kinds of evidence. The law of additivity, which is found to hold quite strictly for all the completely miscible systems studied, proves that the volume relations are additive. Certain solutions of rubidium chloride-ammonium chloride and cesium chloride-ammonium chloride confirm the statement that the variation of the reflecting power is additive. A solution of 25 mole per cent. of rubidium chloride in ammonium chloride gave a diffraction pattern which was that of a body-centered cube. Now the heavier chloride ions in the ammonium chloride lattice are at the corners of simple cubes and give a simple cubic pattern, with some of the lines weakened by interference due to the ammonium ions. The addition of rubidium ion to the ammonium ion increases the reflecting power of the latter until, at the limit of miscibility, which is about 20% rubidium chloride, the compounded ion of ammonium-rubidium is practically equal in reflecting power to the chloride ion. The simple cubic lines, which had already been weakened by the ammonium ions, are now completely eliminated, each point of the lattice is equiva-

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[9] Bain, *Trans. Am. Inst. Min. Met. Eng.*, **68**, 625 (1923).

[10] Desch, *Chem. News*, **106**, 191 (1912).

lent in reflecting power, and we get the pattern due to a body-centered cube, just as we do in the case of pure cesium iodide. The same effect is observed in the system cesium chloride-ammonium chloride, where the limit of miscibility of the ammonium chloride side is about 6% of cesium chloride. This much cesium causes the exclusively simple cubic lines of the chloride lattice to become much weaker, all but two or three of these lines disappearing.

Preparation[11] of Solid Solutions.—Some of the alkali iodides and the ammonium salts cannot be melted without decomposition. It is necessary therefore to make their solid solutions by precipitation from aqueous solution. The method used was that described by Fock.[12] A solution of 40–50 g. of the mixture in water at a temperature slightly above that of the room was cooled and vigorously shaken. The crystals that separated were filtered off and quickly dried with filter paper. Since only 2–3% of the substance in solution crystallized, we considered the composition of the solid solution to be constant. For the analyses of solutions made in this way, we drove off the ammonium salts by heating, when possible. Otherwise, we converted a known weight of the sample to the silver salt and calculated the composition indirectly.

Where the pure components melt without decomposing, we weighed out the proper amounts of each, ground them together in a mortar, placed the mixture in a hard glass tube, sealed it and put it in an electric furnace. After the mixture was melted, we cooled the melt gradually by lowering the temperature of the furnace and finally held it at 10° to 25° below the temperature of solidification for various lengths of time. It was thought that during the process of cooling, coring might result, but that a homogeneous solution could be obtained by allowing diffusion to take place at a temperature just below the melting point. A solid solution of rubidium chloride-potassium chloride which was thus annealed for 36 hours gave a diffraction pattern on which the lines were no sharper than those of another pattern due to the same solid solution which had been quenched in mercury from its melting point. These lines, in both cases, were practically as sharp as those due to a pure substance. Consequently, we were led to the belief that annealing is not necessary for the alkali halides. It is possible that the crystallization interval is very short in these systems, and that a high degree of homogeneity is attained, regardless of the method of cooling. After crystallization, the system may be brought to room temperature by very gradually lowering the temperature

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[11] The purity of the salts with which we are working has been established in a previous paper by the present authors (Ref. 1), except for sodium bromide and iodide. These were of the c. p. variety, from a reliable chemical firm, with the analysis given on the purchase bottle.

[12] Fock, *Z. Kryst.*, **28**, 337 (1897).

of the furnace, to give the final equilibrium conditions, or it may be quenched by dipping the glass bulb into mercury. Some work by other investigators indicates that, if the melt be quenched, even though the components are not miscible at room temperature they may be kept in metastable solution for some time.

Tammann and Krings[13] have found some differences in solid solutions made by melting and by crystallization from solution but state that X-ray examination shows no differences. We have observed no difference in a potassium bromide-potassium chloride solution made in each way.

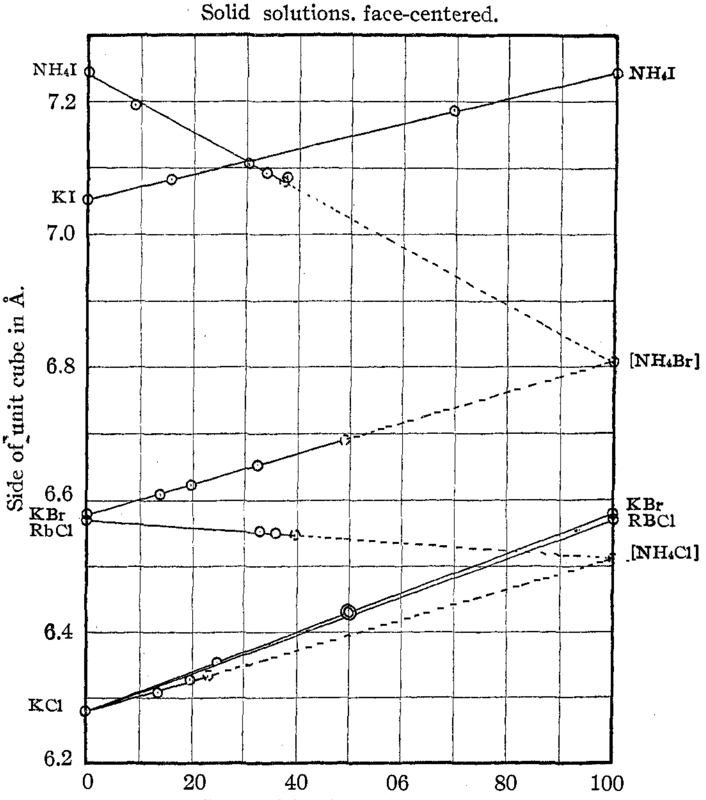

Fig. 1.

Summary of Solid Solutions.—Figs. 1 and 2 represent those of the systems studied which seem to abide fairly well by the rule of additivity. We have plotted the mole fraction of the component on the right against the side of the unit cube. In case the X-ray analysis showed the presence of two solutions in equilibrium, the circles representing the measurements

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[13] Tammann and Krings, *Z. anorg. allgem. Chem.*, **130,** 229 (1923).

are dotted and placed upon the extrapolated line. All hypothetical lattices are enclosed in brackets; for example, [NH_4Cl].

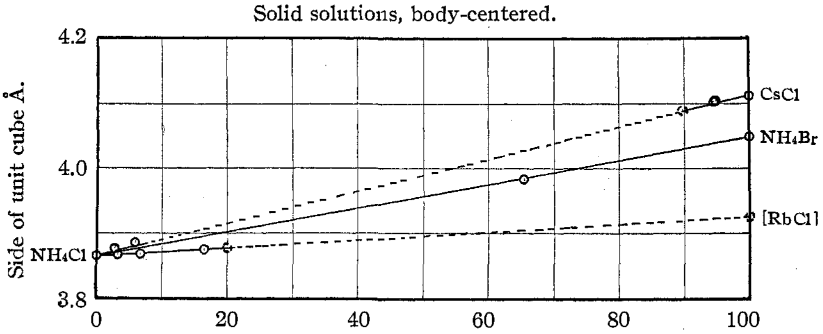

Fig. 2.

System: Potassium Bromide-Potassium Chloride.—This series seems to be completely miscible, the diffraction pattern taken after the melt had stood at room temperature for six months showing no signs of anything but a homogeneous solution.

SYSTEM: POTASSIUM BROMIDE-POTASSIUM CHLORIDE

Composition:	KCl	100.0	75.0	50.0	0.0
	KBr	0.0	25.0	50.0	100.0
Side of Unit Cube, Å.		6.280	6.353	6.431	6.578

System: Rubidium Chloride-Potassium Chloride.—This is also a completely miscible system. The 50–50 solution gave a value for the cube side which was the same as that of the 50–50 potassium chloride-potassium bromide solution. This point lies slightly above the curve, but almost within experimental error of it.

SYSTEM: RUBIDIUM CHLORIDE-POTASSIUM CHLORIDE

Composition:	RbCl	100.0	50.0	0.0
	KCl	0.0	50.0	100.0
Side of Unit Cube, Å.		6.571	6.432	6.280

System: Ammonium Iodide-Potassium Iodide.—The lattices of these two salts are similar and they are completely miscible, following the law of additivity.

SYSTEM: AMMONIUM IODIDE-POTASSIUM IODIDE

Composition:	NH_4I	100.0	98.5	69.4	15.8	0.0
	KI	0.0	1.5	30.6	84.2	100.0
Side of Unit Cube, Å.		7.244	7.242	7.187	7.084	7.052

System: Ammonium Chloride-Ammonium Bromide.—This series is completely miscible, both lattices being body-centered.

System: Ammonium Chloride-Ammonium Bromide

Composition:	NH_4Cl	100.0	34.5	0.0
	NH_4Br	0.0	65.5	100.0
Side of Unit Cube, Å.		3.866	3.982	4.047

System: Sodium Chloride–Sodium Bromide.—This system is at the border line of complete miscibility. A solution of 35% of sodium bromide in sodium chloride gave a diffraction pattern with the sodium chloride lines displaced, but there were faint lines due to sodium bromide or to its hydrate. Atmospheric moisture might affect the stability of this system.

System: Potassium Chloride-Ammonium Chloride.—Fock[12] studied this system without the aid of X-rays and found that the miscibility extended to about 23% ammonium chloride in potassium chloride and 3% potassium chloride in ammonium chloride. We agree with these limits, but observe practically no effect on the ammonium chloride lattice due to the presence of potassium chloride. Vegard[2] made a measurement on a 20% solution of ammonium chloride in potassium chloride and extrapolated to get a value of 6.577 Å. for the side of the hypothetical face-centered cube of ammonium chloride. Our extrapolated value is 6.514 Å. Bartlett and Langmuir[6] obtained a value of 6.532 Å. for face-centered ammonium chloride at 250°.

System: Potassium Chloride-Ammonium Chloride

Composition:	KCl:	100.0	86.7	80.4	76.7	30.1	2.2	1.0	0.0
	NH_4Cl	0.0	13.3	19.6	23.3	69.9	97.8	99.0	100.0
Side of Unit Cube, Å.:									
face-centered		6.280	6.308	6.328	6.336	6.333			
body-centered						3.863	3.863	3.867	3.866

System: Potassium Bromide-Ammonium Bromide.—As would be expected, ammonium bromide has a greater solubility in potassium bromide than that of ammonium chloride in potassium chloride. Fock's curve for this system shows the limit of miscibility to be about 42% ammonium bromide. The limit on our curve comes at 48%. The extrapolated value of the face-centered cube side for ammonium bromide is 6.810 Å. Bartlett and Langmuir give the value 6.900 Å. Our value is much more nearly what would be expected from a consideration of other bromides and ammonium salts. The differences between the cube sides of ammonium bromide and potassium bromide and ammonium chloride and potassium chloride, are practically the same. The same holds true

System: Potassium Bromide-Ammonium Bromide

Composition:	KBr	100.0	86.1	80.5	67.5	38.7	1.5	0.0
	NH_4Br	0.0	13.9	19.5	32.5	61.3	98.5	100.0
Side of Unit Cube Å.:		6.578	6.609	6.624	6.655	6.690		
face-centered								
body-centered						4.042	4.048	4.047

for the relations between the rubidium and ammonium bromides and chlorides. Potassium bromide does not seem to be soluble to the extent of more than 1% or 2% in ammonium bromide.

System: Rubidium Chloride-Ammonium Chloride.—This is a very interesting system, as the two components are almost equal in molar volume, but possess different normal lattices. Ammonium chloride is soluble in rubidium chloride up to 40% and the extrapolated value for its face-centered cube side is 6.514 Å., agreeing with that from the potassium chloride-ammonium chloride series. On the other hand, as seen in Fig. 2, rubidium chloride is soluble in ammonium chloride to the extent of 20% and the points lie upon a straight line. This would seem to indicate an unstable body-centered lattice for rubidium chloride, with cube side 3.924 Å. This value is somewhat larger than would be expected from a consideration of ionic radii and we are inclined to doubt the reality of such a hypothetical lattice.

SYSTEM: RUBIDIUM CHLORIDE-AMMONIUM CHLORIDE

Composition: RbCl	100.0	67.1	64.0	59.8	44.5	30.3	25.1	16.4	6.8	3.3	0.0
NH_4Cl	0.0	32.9	36.0	40.2	55.5	69.7	74.9	83.6	93.2	96.7	100.0
Side of Unit Cube, Å.:											
face-centered	6.571	6.554	6.551	6.550	6.549	6.546	faint				
body-centered				faint	3.879	3.877	3.878	3.875	3.868	3.867	3.866

System: Ammonium Iodide-Ammonium Bromide.—If ammonium iodide changes to the body-centered form at —17.6°, we should expect this lattice to be formed in solution in ammonium bromide. There is no evidence for such a lattice. Now δ for this system is 6.10 and even if both components had the same lattice normally, they would be far from completely miscible. This may explain the rather peculiar behavior of this system. Ammonium bromide is soluble to the extent of 37% in ammonium iodide, with the face-centered lattice. The points fall fairly well upon a straight line, and the extrapolated value for the face-centered cube of ammonium bromide is in good agreement with that obtained from the system ammonium bromide-potassium bromide. This agreement is not necessarily to be expected, for in the system, cesium chloride-ammonium chloride, with almost the same value for δ, the law of additivity is not well followed. The rather large degree of miscibility of ammonium bromide and ammonium iodide is surprising, in view of their large difference in molar volumes and suggests that there may be other factors in addition to volume relationships which help to determine the limits of miscibility. There is a definite decrease in size of the body-centered ammonium bromide cube when it takes up some ammonium iodide. This is contrary to expectation and we have no explanation to offer. The same effect seems to be existent in the system, potassium bromide-potassium iodide. Ammonium iodide is soluble in ammonium bromide somewhat in excess of 5%.

System: Ammonium Iodide-Ammonium Bromide

Composition: NH_4I	100.0	91.3	69.9	66.5	62.4	30.1	5.2	4.4	2.5	0.0
NH_4Br	0.0	8.7	30.1	33.5	37.6	69.9	94.8	95.6	97.5	100.0
Side of Unit Cube, Å.:										
face-centered	7.244	7.194	7.105	7.092	7.089	7.077				
body-centered						4.039	4.040	4.048	4.050	4.047

System: Ammonium Chloride–Cesium Chloride.—Here the bounds of complete miscibility have been exceeded and the law of additivity is not well followed. The normal lattices of both components are body-centered. Cesium chloride is soluble to the extent of 6% in ammonium chloride and ammonium chloride dissolves to about 10% in cesium chloride. This latter limit is only approximate, as a solution containing 14.6% of ammonium chloride gave no lines due to the solution rich in ammonium chloride. We believe that some of this other solution was present, but on account of its relative lightness and poor reflecting power it did not show on the diffraction pattern.

System: Ammonium Chloride-Cesium Chloride

Composition: NH_4Cl	100.0	97.2	93.2	14.6	5.4	5.1	0.0
$CsCl$	0.0	2.8	6.8	85.4	94.6	94.9	100.0
Side of Unit Cube, Å.:							
NH_4Cl-rich	3.866	3.877	3.887				
$CsCl$-rich			4.091	4.094	4.102	4.106	4.110

System: Potassium Chloride–Cesium Chloride.—Cesium chloride is apparently not at all soluble in potassium chloride, while potassium chloride can dissolve to the extent of a few per cent. in cesium chloride. Five per cent. of potassium chloride hardly changed the size of the cesium chloride lattice, but there was no trace of potassium chloride lines. The saturated solution of potassium chloride in cesium chloride seems to raise the value for the cube side of cesium chloride. This may be an example of interstitial solution. We can hardly believe that this measurement of 4.115 Å. represents experimental error, although the value is quite close to that for the pure salt.

System: Potassium Chloride-Cesium Chloride

Composition: KCl		100.0	85.0	5.0	0.0
$CsCl$		0.0	15.0	95.0	100.0
Side of Unit Cube, Å.:	face-centered	6.280	6.279		
	body-centered		4.115	4.111	4.111

System: Sodium Chloride–Potassium Chloride.—Eitel[14] studied this system, noting the beginning of unmixing by an ultramicroscopic method. He observed that melts which were rich in potassium chloride, after being quenched, showed no signs of unmixing for a long time. Our solutions were allowed to cool gradually. Potassium chloride with 5% of sodium

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[14] Eitel, *Centr. Min. Geol.*, **1919**, p. 173.

chloride gave a faint sodium chloride pattern, only three or four lines being visible. The potassium chloride pattern was strong. Sodium chloride as a standard was mixed with this sample,[15] the original sodium chloride lines being too faint to cause an error in the measurement of the lines of the standard. The potassium chloride had a cube side of 6.267 Å., showing the probability of the solution containing about 2% sodium chloride. Sodium chloride with 35% potassium chloride, when arbitrarily used as a standard and assigned the value 5.628 Å., gave for the potassium chloride pattern a cube side of 6.279 Å. Presumably, then, since the potassium chloride actually measured 6.267, the sodium chloride lattice must have expanded to bring this value up to 6.279. The sodium chloride, which was assumed to have a cube side of 5.628 Å., must have actually measured about 5.640 Å., indicating the solution of a few per cent. of potassium chloride in sodium chloride.

SYSTEM: SODIUM CHLORIDE-POTASSIUM CHLORIDE

Composition: NaCl		100.0	65.0	5.0	0.0
KCl		0.0	35.0	95.0	100.0
Side of Unit Cube, Å.:	NaCl-rich	5.628	5.628[a]	faint	
	KCl-rich		6.279	6.267	6.280

[a] Assumed.

System: Sodium Chloride-Potassium Iodide.—This system, without a common ion and with components far different in molar volume, should not be appreciably miscible. A 50–50 melt, when the sodium chloride pattern was assigned the value 5.628 Å., gave for potassium iodide, 7.041 Å. Pure potassium iodide has a cube side of 7.052 Å. The potassium iodide may have decreased in size slightly, the sodium chloride may have increased slightly, or both effects may have occurred.

SYSTEM: SODIUM CHLORIDE-POTASSIUM IODIDE

Composition: NaCl		100.0	50.0	0.0
KI		0.0	50.0	100.0
Side of Unit Cube, Å.:	NaCl-rich	5.628	5.628[a]	
	KI-rich		7.041	7.052

[a] Assumed.

System: Rubidium Chloride-Cesium Chloride.—If cesium chloride has an unstable face-centered lattice, it might be expected to be somewhat soluble in rubidium chloride and to follow the rule of additivity. The solutions exhibit a peculiar behavior. The addition of cesium chloride seems at first to increase the size of the rubidium chloride lattice, then to decrease it again. Rubidium chloride accommodates over 15% of cesium chloride, and cesium chloride, in turn, holds in solution over 11.5%

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[15] Our method of calibration of films requires that sodium chloride be mixed with the sample.

of rubidium chloride. The change of size of the cesium chloride lattice is not regular. This system requires more detailed work.

SYSTEM: RUBIDIUM CHLORIDE-CESIUM CHLORIDE

Composition: RbCl	100.0	92.0	85.0	50.0	11.5	5.0	0.0
CsCl	0.0	8.0	15.0	50.0	88.5	95.0	100.0
Side of Unit Cube, Å.:							
face-centered	6.571	6.602	6.600	6.586			
body-centered				4.099	4.104	4.105	4.110

System: Potassium Bromide-Potassium Iodide.—Here the lattices are the same, but the molar volumes are too far separated for complete miscibility. Potassium bromide is soluble in potassium iodide to between 15% and 20%. The side of the unit cube does not follow the law of additivity. Solutions rich in potassium bromide show marked peculiarities. Five per cent. of potassium iodide brings the unit cube side down below that of pure potassium bromide. More potassium iodide causes the lattice to expand. A source of difficulty with this series was the fact that the solutions were very hygroscopic, thus permitting the possibility of some changes after the samples were prepared. The effect of moisture upon a solid solution, with one component much more soluble than the other, can hardly be predicted.

SYSTEM: POTASSIUM BROMIDE-POTASSIUM IODIDE

Composition: KBr		100.0	95.0	65.0	15.0	10.0	0.0
KI		0.0	5.0	35.0	85.0	90.0	100.0
Side of Unit Cube, Å.:	KBr-rich	6.578	6.561	6.597			
	KI-rich			6.978	6.988	7.019	7.052

System: Sodium Iodide-Potassium Iodide.—The lattices are similar, but the molar volumes are rather far apart and the miscibility is very limited. Measurements on potassium iodide containing small amounts of sodium iodide showed hardly any change of the potassium iodide lattice. With more sodium iodide, a large number of lines appeared which were probably due to the hydrate of sodium iodide. This system cannot be satisfactorily worked out unless special precautions are taken to keep the samples dry.

Summary

The nature of solid solution and the rule of additivity of unit cube side are discussed. Binary systems of the alkali and ammonium halides are shown to be completely miscible at room temperature and to obey the rule of additivity to a point where the difference in cube sides of the pure components exceeds 5% of the mean of the two. The law of additivity does not hold strictly beyond this point.

Extrapolated values are obtained for the sides of the unit face-centered cubes of ammonium chloride and ammonium bromide.

X-ray measurements are given for solid solutions of a number of binary systems of the alkali and ammonium halides.

It is concluded that for completely miscible systems, each solid solution behaves toward X-rays *as though it were a pure substance*, the reflecting power and volume of the new compound ion or atom being determined additively by the atomic numbers and volumes of the constituent atoms.

COLUMBUS, OHIO

THE REDUCTION OF METALS FROM THEIR SALTS BY MEANS OF OTHER METALS IN LIQUID AMMONIA SOLUTION

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Mechanism of the Reduction Process

It is known that the alkali metals and the metals of the alkaline earths are soluble in liquid ammonia and ionize in solution with the formation of positive ions which are identical with the ions of the salts of the same metals in solution in the same solvent, and negative ions which consist of the negative electrons. If we reduce the salt MX_m of a metallic element M whose positive valence is m, by means of another metal N of positive valence n, then the problem presented is similar to that of a solution of two salts without a common ion, the ionic constituents being M^{m+}, N^{n+}, X^- and e^-.[1] We have, then the reaction equations,

$$\begin{array}{llll} MX_m = M^{m+} + mX^- & (a) & \qquad Me_m = M^{m+} + me^- & (c) \\ NX_n = N^{n+} + nX^- & (b) & \qquad Ne_n = N^{n+} + ne^- & (d) \end{array}$$

Corresponding to these reaction equations we have the equilibrium equations,

$$\begin{array}{llll} (M^{m+})\,(X^-)^m = (K_1)\,(MX_m) & (1) & \qquad (M^{m+})\,(e^-)^m = (K_3)\,(Me_m) & (3) \\ (N^{n+})\,(X^-)^n = (K_2)\,(NX_n) & (2) & \qquad (N^{n+})\,(e^-)^n = (K_4)\,(Ne_n) & (4) \end{array}$$

Here K_1, K_2, K_3, K_4 represent the mass-action functions of the reactions in question. They will have definite values for definite conditions of the system, but will vary as a function of the concentration of the various constituents present, approaching definite limiting values at low concentrations. The reaction taking place in the solution will depend upon the values of the mass-action functions and the solubilities of the constituents MX_m, NX_n, Me_m and Ne_n. We may distinguish a number of different cases, depending upon the relative values of the mass-action functions and the solubilities of the various constituents.

(1) The mass-action functions have approximately the same value for all constituents and the solubility of these constituents is high and of the same order of magnitude. In this case interaction will take place between the salt MX_m and the reducing metal Ne_n but, because of the high value

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[1] For the sake of simplicity we may assume that the negative ions are univalent.