

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

IONIC SIZES AND THEIR RELATIONSHIP TO CRYSTAL STRUCTURE TYPE, SOLID SOLUTION AND DOUBLE SALT FORMATION AND THE STABILITIES OF HYDRATES AND AMMONIATES

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Introduction

The crystal structures of a large number of salts have been determined by means of x-rays, but no one has yet presented a satisfactory explanation for the preference of some substances for one type of structure and of others for other types. In this paper a partial solution of this problem will be proposed, after which a number of related problems will be considered.

If ions all behaved as point charges or as uniformly charged spheres of equal size, we should expect them to crystallize in those structures in which each ion is surrounded by as many of the opposite sign as possible.²

In the case of a uni-univalent or a bi-bivalent salt, for instance, the most probable structure from this viewpoint is the body-centered cubic or cesium chloride arrangement (Fig. 1) in which each ion is surrounded by eight others of unlike charge. The fact that other structures not only exist but are more common than this, shows that some other factor or factors must be taken into account. The two which at once suggest themselves are the relative sizes of ions and their shapes, that is, the distributions of the outer electrons. Of these, it will be assumed in this paper that the former is the more important; the latter will for the present be entirely neglected.

Ionic Radii

In comparing ionic sizes, it will be assumed with Bragg,³ Davey⁴ and

¹ *Note by Editor.*—The material contained in this article was originally submitted by Dr. Cuy before his death on May 25, 1925, in the form of seven articles received between November 18, 1924, and March 12, 1925. One of these, dealing primarily with the relative stabilities of the hydrates and ammoniates of the alkaline-earth halides, was by Cuy and Francis J. Norton.

As in their original form these articles were not considered suitable for publication; they have, at the Editor's request, been condensed into the present single article by Dr. M. L. Huggins.

² Although the idea involved in the foregoing is not explicitly stated by Cuy in his original articles, it seems to be involved in his assumptions, for example, that where both the cesium chloride and sodium chloride types of structure are geometrically possible, the former will be assumed.—M. L. H.

³ W. L. Bragg, *Phil. Mag.*, **40**, 169 (1920).

⁴ Davey, *Phys. Rev.*, **22**, 211 (1923).

others that the "spheres of influence" of ions are mutually tangent to each other in crystals and that the "sphere of influence" of an ion of a given kind is practically the same in different crystals. These assumptions enable one to calculate the differences between the radii of these spheres for ions of different elements by comparing the inter-atomic distances in corresponding compounds. To calculate the absolute radii values, a procedure will be adopted differing but slightly from that of Davey.

He assumes as the starting point for his ionic radii calculations that the Cs^+ and I^- spheres are of the same size, the radius of either being taken as half the inter-atomic distance in crystals of cesium iodide. However, since the nuclear charge of cesium is two units greater than that of iodine, one would expect the radius of the former to be somewhat smaller than

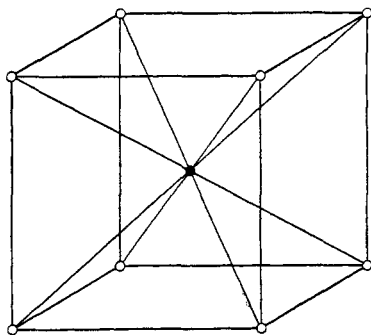


Fig. 1.—The arrangement of atomic centers in the unit cube of the body-centered cubic or CsCl structure. This also shows the arrangement around each Ca center in a crystal of CaF_2 .

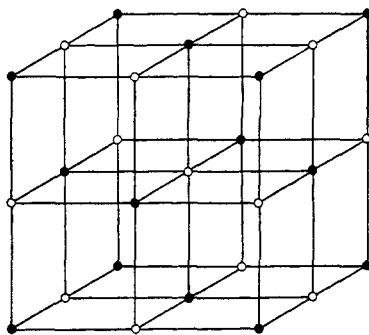


Fig. 2.—The unit cube of the NaCl structure.

that of the latter. In this paper a difference between them of about 5% will be assumed.⁵ The resulting radii and the inter-atomic-distance data on which they are based are given in Tables I and II. As may be seen from Table II, the radii calculated for a given ion from different compounds do not always agree with one another. Moreover, in some instances there is considerable disagreement between the different experimental inter-atomic-distance values. For these reasons, the calculations in this paper based on such radii—particularly the radii of the non-rare-gas type of ions—must be considered as quite rough and tentative. Variations of the radii of ions listed in Table I will for simplicity be ignored, but where an ion is given two or more radii in Table II, that radius (or radius range, where the data for the same compound disagree) will be used

⁵ Cuy offers no justification for this figure other than the results described in this paper. Furthermore, he ignores the fact that his assumed F^- radius is less than that of Na^+ .—M. L. H.

which was calculated from the inter-atomic-distance figures for the particular compound being considered.⁶

TABLE I

A COMPARISON OF INTER-ATOMIC DISTANCES (LOWER FIGURES) WITH THE SUMS OF THE RADII ASSUMED IN THIS PAPER (UPPER FIGURES)^a

	Assumed radius (A)	F ⁻	Cl ⁻	Br ⁻	I ⁻	O ⁻⁻	S ⁻⁻	Se ⁻⁻	Te ⁻⁻
		1.10	1.61	1.76	2.00	1.15	1.58	1.72	1.82
Li ⁺	0.98	2.08	2.59	2.74	2.98	2.13	2.56		
		2.01	2.57	2.75	3.01	2.00	2.47		
Na ⁺	1.21	2.31	2.82	2.97	3.21		2.79		
		2.31	2.81	2.97	3.23		2.83		
K ⁺	1.53	2.63	3.14	3.29	3.53				
		2.66	3.14	3.29	3.53				
Rb ⁺	1.67		3.28	3.43	3.67				
			3.29	3.43	3.66				
Cs ⁺	1.95	3.05	3.56	3.71	3.95				
		3.00	3.57	3.71	3.95				
Tl ⁺	1.70		3.31	3.46					
			{ 3.32;	{ 3.44;					
			{ 3.33	{ 3.45					
Be ⁺⁺	0.50					1.65			
						{ 1.64;			
						1.65			
Mg ⁺⁺	.95					2.10	2.53		
						{ 2.09-	2.54		
						2.11			
Ca ⁺⁺	1.26	2.36				2.41	2.84	2.98	
		{ 2.34;				{ 2.37;		2.96	
		2.36;				{ 2.39;	{ 2.80;		
		2.37;				2.42	2.84		
		2.38							
Sr ⁺⁺	1.42	2.52	3.03			2.57	3.00	3.14	
		2.53	3.03			2.55	2.93	3.12	
Ba ⁺⁺	1.59	2.69				2.74	3.17	3.31	
		2.68				{ 2.74;	3.17	3.31	
						2.75			
Pb ⁺⁺	1.36						2.94	3.08	3.18
							{ 2.92;	{ 3.07;	3.17
							2.97	3.08	

^a The inter-atomic-distance values for the alkali halides are those given by Davey [*Chem. Rev.*, 2, 349 (1926)]. References to the crystal-structure determinations upon which the other inter-atomic-distance data in this and the following table are based, may be found in Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 1924, or in "International Critical Tables," McGraw-Hill Book Co., New York, 1926, vol. 1.

⁶ In Cuy's original papers, only a single value for the radius of each kind of ion was used, except Cu⁺ and Ag⁺, which were each given two values. The approximate and tentative nature of these radii was, however, emphasized.—M. L. H.

TABLE II
INTER-ATOMIC DISTANCES IN VARIOUS CRYSTALS, WITH THE RADII ASSUMED FOR THE
COMPONENT ATOMS^a

Crystal	Assumed radii (A)	Inter-atomic distance (A)
NH ₄ Cl (CsCl type)	NH ₄ ⁺ , 1.73-1.75; Cl ⁻ , 1.61	3.34; 3.35; 3.36
NH ₄ Cl (NaCl type)	NH ₄ ⁺ , 1.66; Cl ⁻ , 1.61	3.27 (250°C.)
NH ₄ Br (CsCl type)	NH ₄ ⁺ , 1.69-1.76; Br ⁻ , 1.76	3.45; 3.50; 3.52
NH ₄ Br (NaCl type)	NH ₄ ⁺ , 1.69; Br ⁻ , 1.76	3.45 (250°C.)
NH ₄ I (NaCl type)	NH ₄ ⁺ , 1.60; I ⁻ , 2.00	3.60
CuCl	Cu ⁺ , 0.71-0.77; Cl ⁻ , 1.61	2.32; 2.38
CuBr	Cu ⁺ , 0.73-0.76; Br ⁻ , 1.76	2.49; 2.52
CuI	Cu ⁺ , 0.61-0.64; I ⁻ , 2.00	2.61; 2.63; 2.64
Cu ₂ O	Cu ⁺ , 0.69-0.71; O ⁻ , 1.15	1.84-1.86
Cu ₂ Se	Cu ⁺ , 0.77; Se ⁻ , 1.72	2.49
AgCl	Ag ⁺ , 1.16; Cl ⁻ , 1.61	2.76; 2.77*; 2.78
AgBr	Ag ⁺ , 1.12; Br ⁻ , 1.76	2.88*; 2.89
AgI	Ag ⁺ , 0.81; I ⁻ , 2.00	2.81*; 2.83
Ag ₂ O	Ag ⁺ , 0.88-0.91; O ⁻ , 1.15	2.03; 2.04; 2.06
ZnO	Zn ⁺⁺ , 0.81-0.83; O ⁻ , 1.15	1.96; 1.98
ZnS	Zn ⁺⁺ , 0.75-0.77; S ⁻ , 1.58	2.33; 2.34; 2.35
ZnSe	Zn ⁺⁺ , 0.73; Se ⁻ , 1.72	2.45
CdO	Cd ⁺⁺ , 1.21; O ⁻ , 1.15	2.36
CdS	Cd ⁺⁺ , 0.94-0.96; S ⁻ , 1.58	2.52; 2.54
CdI ₂	Cd ⁺⁺ , 1.00; I ⁻ , 2.00	3.00
HgS	Hg ⁺⁺ , 0.95-0.96; S ⁻ , 1.58	2.53; 2.54
HgI ₂	Hg ⁺⁺ , 0.78; I ⁻ , 2.00	2.78
MnO	Mn ⁺⁺ , 1.05; O ⁻ , 1.15	2.20
MnS	Mn ⁺⁺ , 1.03; S ⁻ , 1.58	2.61
MnS ₂	Mn ⁺⁺ , 1.01; S, 1.58	2.59
FeS ₂	Fe ⁺⁺ , 0.67; S, 1.58	2.25
NiO	Ni ⁺⁺ , 0.93; O ⁻ , 1.15	2.07; 2.08*
CeO ₂	Ce ⁺⁺⁺⁺ , 1.19; O ⁻ , 1.15	2.34
ThO ₂	Th ⁺⁺⁺⁺ , 1.28; O ⁻ , 1.15	2.43
UO ₂	U ⁺⁺⁺⁺ , 1.22; O ⁻ , 1.15	2.37
SiO ₂ , α-quartz	Si ⁺⁺⁺⁺ , 0.44; O ⁻ , 1.15	1.59
SiO ₂ , β-quartz	Si ⁺⁺⁺⁺ , 0.47; O ⁻ , 1.15	1.62
SiO ₂ , β-cristobalite	Si ⁺⁺⁺⁺ , 0.39; O ⁻ , 1.15	1.54
Mg ₂ Si	Mg ⁺⁺ , 0.95; Si ⁻⁻⁻⁻ , 1.82	2.77
Mg ₂ Sn	Mg ⁺⁺ , 0.95; Sn ⁻⁻⁻⁻ , 1.98	2.92; 2.94
Mg ₂ Pb	Mg ⁺⁺ , 0.95; Pb ⁻⁻⁻⁻ , 1.98	2.93
MoS ₂	Mo ⁺⁺⁺⁺ , 0.83; S ⁻ , 1.58	2.41

^a The radii (Col. 2) are so chosen as to make their sums equal the experimental inter-atomic distances (Col. 3). In a few instances only one inter-atomic-distance determination (marked with a star) has been used in calculating the radii, the others being considered less accurate.

A Relation between Structure Type and the Ratio of the Ionic Radii

If we assume that the "spheres of influence" of two ions cannot overlap and that the "sphere of influence" of each positive ion in a crystal is just tangent to that of each of the surrounding negative ions and *vice versa*,

a maximum value for the ratio of the radii of the two ions (R_L/R_S) is calculable for each of the four simple types of structure which compounds of the general formula AB have been found to possess. (See Fig. 6.) Assuming further that where two or more structures are geometrically possible in accord with this relationship, the most probable structure is that in which each ion is surrounded by most of the other kind, we arrive at the following prediction for AB salts:

- CsCl type (I), if $1 < R_L/R_S < 1.365$
 NaCl type (II), if $1.365 < R_L/R_S < 2.41$
 ZnS (III) or ZnO (IV) type, if $2.41 < R_L/R_S$

It may be seen from the second and third columns of Tables III and IV that, although these relationships do not strictly hold true, the CsCl type crystals (I) have fairly low ionic-radii ratios, while the ZnS and ZnO types (III and IV) are assumed in general where the ratio is largest.

TABLE III

A COMPARISON OF THE STRUCTURE TYPES AND THE STABILITIES OF HYDRATES AND AMMONIATES WITH THE RATIOS OF THE IONIC RADII FOR VARIOUS A^+B^- TYPE COMPOUNDS

Compound	R_L/R_S	Structure type	Decomposition temp. of hydrate, °C. ^a	Differential heat of formation of ammoniate, cal. ^b
NH ₄ Br	1.00-1.04	I	...	
CsI	1.03	I	...	
NH ₄ Cl	1.03	II	...	
NH ₄ Br	1.04	II	...	
TlBr	1.04	I	...	
RbCl	1.04	II
KCl	1.05	II
RbBr	1.05	II	...	(3) 7.1
TlCl	1.06	I	...	
NH ₄ Cl	1.07-1.09	I	...	
NaF	1.10	II	...	
CsBr	1.11	I	...	
LiF	1.12	II	...	
KBr	1.15	II	...	(4) 7.15
TlI	1.18	I	...	
RbI	1.20	II	...	(6) 7.5
CsCl	1.21	I	...	
NH ₄ I	1.25	(I) II	...	
KI	1.31	II	...	(4) 7.65
NaCl	1.33	II	(2) 0	(5) 7.8
AgCl	1.39	II		(1) 11.11
KF	1.39	II	(2) ?	
NaBr	1.46	II	(2) 51	(5 ¹ / ₄) 8.45
RbF	1.52	?	(¹ / ₃) ?	
AgBr	1.57	II		(1) 10.65

^a Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 5th ed., 1923.

^b Biltz, *Z. anorg. Chem.*, 130, 93 (1923).

TABLE III (Concluded)

Compound	R_L/R_S	Structure type	Decomposition temp. of hydrate, °C. ¹²	Differential heat of formation of ammoniate, cal. ¹³
LiCl	1.64	II	(1) 98	(1) 12.4; (4) 8.8
NaI	1.65	II	(2) 65	(4 ^{1/2}) 9.4
CsF	1.77	II	(² / ₃) ?	
LiBr	1.80	II	(1) 159	(1) 13.6; (4) 10.2
LiI	2.04	II	(1) 300	(1) 16.0; (4) 11.6
CuCl	2.09-2.27	III		(1) 16.73
CuBr	2.32-2.41	III		(1) 14.64
AgI	2.47	III, IV		(¹ / ₂) 11.56
CuI	3.12-3.28	III		(¹ / ₂) 15.22

TABLE IV

A COMPARISON OF STRUCTURE TYPES WITH IONIC-RADII RATIOS FOR A⁺⁺B⁻⁻ TYPE COMPOUNDS

Compound	R_L/R_S	Structure type	Compound	R_L/R_S	Structure type
BaS	1.01	II	CaSe	1.36	II
CdO	1.05	II	BaO	1.38	II
BaSe	1.08	II	ZnO	1.39-1.42	IV
MnO	1.10	II	MnS	1.53	II
CaO	1.10	II	HgS	1.65-1.66	III
SrS	1.11	II	CdS	1.65-1.68	IV
MgO	1.21	II	MgS	1.66	II
SrSe	1.21	II	ZnS	2.06-2.11	III, IV
SrO	1.23	II	BeO	2.30	IV
NiO	1.24	II	ZnSe	2.36	III, IV?
CaS	1.25	II	BeS	3.16	III

A few AB compounds have been found to crystallize with structures other than the four mentioned. As limitations on the ionic-radii ratios

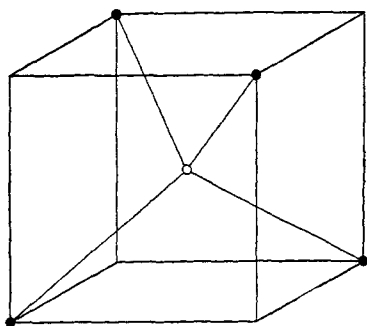


Fig. 3.—Illustrating the arrangement around each atomic center in the ZnS and ZnO structures, and around each F center in a crystal of CaF₂.

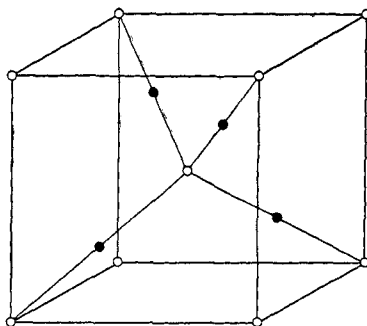


Fig. 4.—The unit cube of the Cu₂O structure. Cu centers are represented by dots, O centers by circles.

cannot be calculated in these cases, without assuming arbitrary parameter values, they have been omitted from the tables. AB compounds con-

taining trivalent or quadrivalent atoms are also omitted because the use of ionic radii in such cases would seem doubtful.

Of the various types of structure so far found for compounds of the general formula AB_2 (excluding those containing such double ions as S_2^{--}), limitations on the ratio of the ionic radii, based on the assumptions that ions of opposite charge just touch and ions of the same charge do not interpenetrate, can be placed only on three—those possessed by calcium fluoride, cuprous oxide and β -cristobalite (SiO_2) (see Figs. 1, 3, 4 and 5). The others all contain parameters, and without giving these parameters arbitrary values, no restrictions can be placed on the ionic-radii ratios. Moreover, except perhaps in anatase and rutile, the structures are in each case such as to indicate that the shapes or structures of the ions are of considerable importance in producing that structure; hence, these are not properly comparable with the arrangements found for calcium fluoride, cuprous oxide and β -cristobalite, in which each ion is symmetrically surrounded by ions of opposite charge.

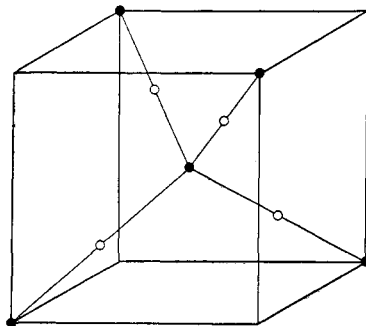


Fig. 5.—Illustrating the arrangement around each atomic center in β -cristobalite (SiO_2). Si centers are represented by dots, O centers by circles.

Calculating ionic-radii-ratio limits for these structures in the same manner as previously, the following are obtained.

CaF_2 (I)	$0.225 < R_B/R_A < 1.37$
Cu_2O (II)	$.225 < R_B/R_A < \infty$
SiO_2 , β -cristobalite (III)	$.225 < R_B/R_A < \infty$

In the CaF_2 structure each A ion (Ca^{++}) has eight B ions (F^-) around it, while each B ion is surrounded by four A ions. In the Cu_2O and β -cristobalite arrangements the A ions are each surrounded by four B ions, and the B ions each by two A ions. The assumption that each ion tends to surround itself by as many as possible of the other kind, together with the above ionic-radii limitations, leads to the prediction that AB_2 compounds of small ionic-radii ratios, R_B/R_A (the exact value 1.37 has, of course, little significance), will generally assume the CaF_2 type of structure (I), except where the ionic shapes or structures are of importance, while those having large radii ratios will prefer that of Cu_2O (II), that of β -cristobalite (III), or some other structure (IV).

The data collected in Cols. 2 and 3 of Table V are in good agreement with such a prediction, with the exception of those for cuprous oxide and for silver oxide. Their positions in the table may perhaps result from

TABLE V
A COMPARISON OF THE STRUCTURE TYPES AND THE STABILITIES OF AMMONIATES WITH
THE RATIOS OF THE IONIC RADII FOR AB₂ TYPE COMPOUNDS

Compound	R_B/R_A	Structure ^a type	Heat of de-ammonation
Cu ₂ Se	0.45	I	
Mg ₂ Sn	.48	I	
Mg ₂ Pb	.48	I	
Mg ₂ Si	.52	I	
Ag ₂ Te	.54	I	
Cu ₂ S	.55	I	
Ag ₂ Se	.57	I	
Cu ₂ O	.60-0.62	II	
Li ₂ S	.62	I	
Ag ₂ S	.66	I	
BaF ₂	.69	I	
SrF ₂	.77	I	
Na ₂ S	.77	I	
Ag ₂ O	.77-0.79	II	
Li ₂ O	.85	I	
CaF ₂	.87	I	
ThO ₂	.90	I	
UO ₂	.94	I	
CeO ₂	.97	I	
BaCl ₂	1.01	I ?	(8) 9.0 cal.
BaBr ₂	1.11	I ?	(1) 11.8
SrCl ₂	1.13	I	(1) 11.5
MgF ₂	1.16	IV	
SrBr ₂	1.24	I ?	(1) 16.8
BaI ₂	1.26	I ?	(2) 13.4
CaCl ₂	1.28	I ?	(1) 16.5
CaBr ₂	1.40	I ?	(1) 18.6
SrI ₂	1.41	I ?	(1) 18.3
MnCl ₂	1.56	I ?	
CaI ₂	1.59	I ?	(1) 19.5
MgCl ₂	1.69	IV	(1) 20.8
MgBr ₂	1.85	IV	(1) 21.7
MoS ₂	1.90	IV	
CdI ₂	2.00	IV	
MgI ₂	2.10	IV	(2) 22.7
SiO ₂ , β-quartz	2.45	IV	
HgI ₂	2.50-2.56	IV	
ZnI ₂	2.41-2.74	I ?	
SiO ₂ , α-quartz	2.61	IV	
SiO ₂ , α-cristobalite	2.95	III	

^a I? in Col. 3 denotes crystals known to be cubic and assumed to have the CaF₂ type of structure, although x-ray data are lacking.

the influence of the structure of the non-rare-gas ions of Cu⁺ and Ag⁺, already evidenced by lack of constancy in their radii.

Crystal structures have been determined for a number of AB₂ compounds

in which either A or B is a complex ion, such as $\text{Ni}(\text{NH}_3)_6^{++}$ or SnCl_6^{--} . In all cases the structure found is of the CaF_2 type (I). Calculating the radii of the complex ions by subtracting the radii of the simple ions from the distances between ion centers, and then computing the ratio R_B/R_A , the latter is found to vary from 0.55 to 0.79. These ratios are all low, in agreement with the theory.⁷

Crystalline Hydrates and Ammoniates

In considering now the relative stabilities of the crystalline hydrates and ammoniates of simple salts, we shall assume, as first approximations: (a) that the excess charge on an ion is uniformly distributed over the surface of a sphere of the size given in Table I or II;⁸ (b) that the greater the difference in ionic sizes the greater is the "stray field" or "residual affinity" within the crystal; and (c) that the greater this "residual affinity" or "stray field," the more stable the hydrates and ammoniates.

The basis for the second of these postulates may be readily visualized by a consideration of Fig. 6. The greater the difference in size, the greater the difference in surface-charge density and the greater the locally unneutralized charge on the side of the smaller ion adjacent to the larger; also, the greater the difference in size; the greater the repulsion is between the larger ions which are adjacent to each other.

The justification for the last postulate is merely that it seems reasonable and that the results to be presented seem to favor such an assumption

⁷ Cuy calculates a "radius" for $\text{Ni}(\text{NH}_3)_6^{++}$ by adding his assumed value of the Ni^{++} radius to assumed values for the nitrogen and hydrogen diameters; the "radius" of SnCl_6^{--} he obtains by adding the Sn^{++++} radius to the Cl^- "diameter;" and similarly for other complex ions. Comparing the ratios of the ionic radii so calculated for a large number of compounds with the crystallographic information in regard to whether the substances are hexagonal or cubic, it is concluded that in general a large ratio (R_B/R_A) results in a hexagonal structure, while a small ratio causes the compound to have a cubic structure, assumed to be that of calcium fluoride. Even if such a relationship exists, it seems to the writer that it cannot be considered as evidence for or against Cuy's theory until more is known concerning the nature of the hexagonal structure.—M. L. H.

⁸ This first postulate involves the idea that the positions of electrons are very little affected by adjacent atoms, together with the assumption that a kernel of charge ($+m$) surrounded by a spherical shell of charge ($n-m$) has the same effect (on an external charge) as a single spherical shell of the same size but having a charge of ($+n$).—M. L. H.

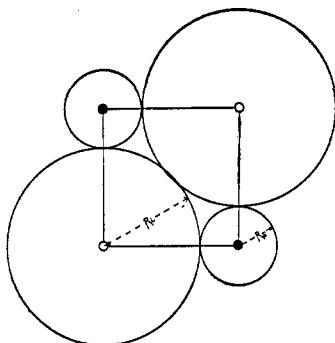


Fig. 6.—Illustrating the maximum ionic radius ratio, R_L/R_S , in a crystal of the NaCl type.

rather than that of Jones,⁹ who postulates a parallelism between hydration in solution and in the crystalline state.¹⁰

In Col. 4 of Table III are collected the available data on the decomposition temperatures (incongruent melting points) of the lowest hydrates of the alkali halides. A dash in this column means that no hydrates are formed. The numbers in parentheses are the numbers of "molecules" of water per "molecule" of MX in the lowest hydrate. It is evident that only the compounds of relatively large ionic-radii ratio form hydrates. Furthermore, when these decomposition temperatures are plotted against the radii ratios (Fig. 7), all the points except two fall nearly on a straight line, in spite of the fact that the lowest hydrates contain different numbers of "molecules" of water per "molecule" of salt.

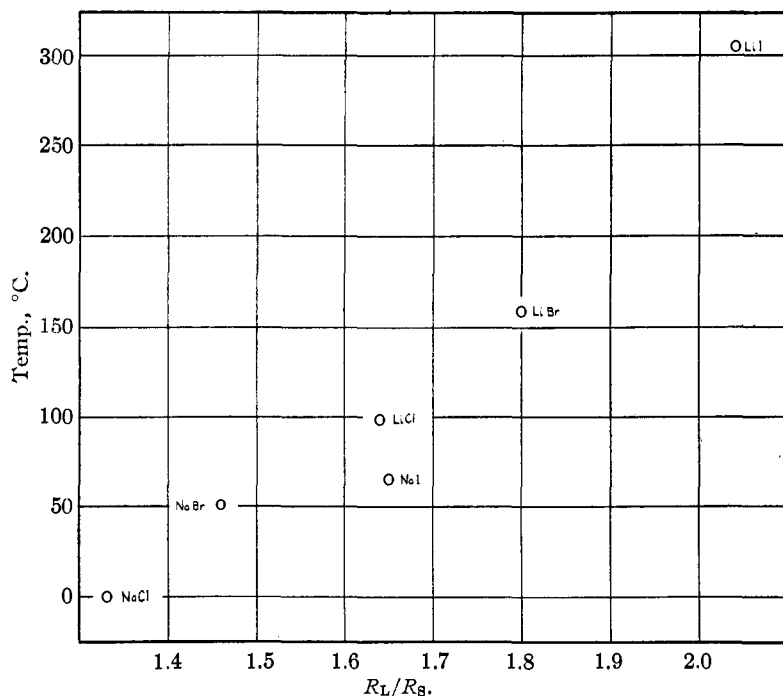


Fig. 7.—Decomposition temperatures of the lowest hydrates of the alkali halides versus ionic-radii ratios.

Quantitative data are available on the differential heats of formation of the ammoniates of many of the halides. We may take the heat of

⁹ H. C. Jones, "Elements of Physical Chemistry," Macmillan Co., New York, 3rd ed., 1907, p. 240.

¹⁰ Although lithium is said to be the most hydrated of the alkali ions in solution and cesium fluoride is the only cesium halide which separates from solution hydrated, lithium fluoride forms no hydrate whatsoever.

formation of the lowest ammoniate as a measure of its stability (or of the tendency of the salt to form ammoniates), although of course where the number of molecules of ammonia per molecule of salt is not the same in two cases, the figures are not strictly comparable. The heats of formation of the tetra-ammoniates of the lithium halides, the reaction concerned being $\text{LiX} \cdot 4\text{NH}_3 \rightleftharpoons \text{LiX} \cdot 3\text{NH}_3 + \text{NH}_3$, are also given. Plotting these heats of formation against ionic-radii ratios (Figs. 8 and 9), the agreement with the theory is seen to be quite good—better than could be expected, considering the nature of the assumptions and the neglect of

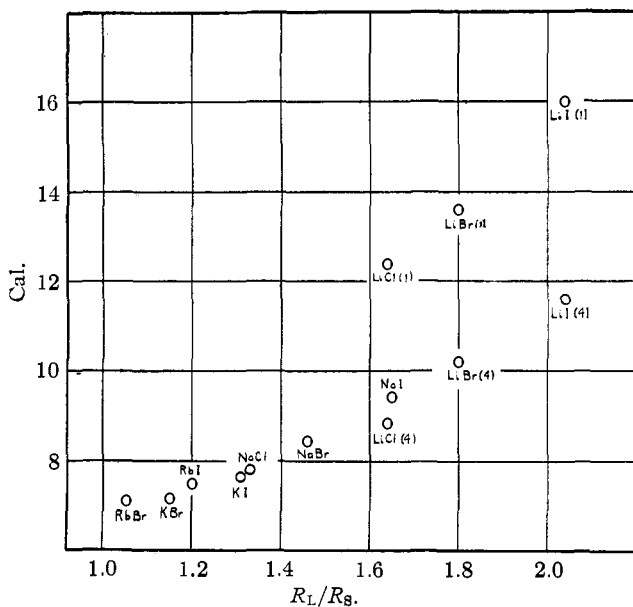


Fig. 8.—Differential heats of formation of ammoniates of alkali halides *versus* ionic-radii ratios.

different degrees of ammoniation, etc.—provided the figures for the copper and silver halides are discarded as not comparable and those for $\text{LiX} \cdot 4\text{NH}_3$ are used in preference to those for $\text{LiX} \cdot \text{NH}_3$.

The available data on the relative stabilities of the hydrates of the AB_2 compounds are too meager and unreliable to be of much use in the present discussion.

A Relation between Ionic Sizes and Temperature-Composition Diagrams of Certain Two-Component Systems

Under this heading will be considered certain systems, such as $\text{MX}-\text{M}'\text{X}$ or $\text{MX}-\text{MX}'$, where two salts have a common ion.

If the uncommon ions have practically identical sizes (as in the case of isotopes) we should expect the salts to form solid solutions in any pro-

portion, the melting point and other properties varying practically linearly with composition. With uncommon ions of slightly different sizes we should also expect solid solutions throughout the whole range of composition, but the melting-point curve should dip below the straight line joining the melting points of the pure components. If this dip is sufficiently great, a minimum will be observed. If the radii of the uncommon ions differ considerably in size, we should expect only partial miscibility or none at all, and the melting-point curve should show a eutectic. Finally, we

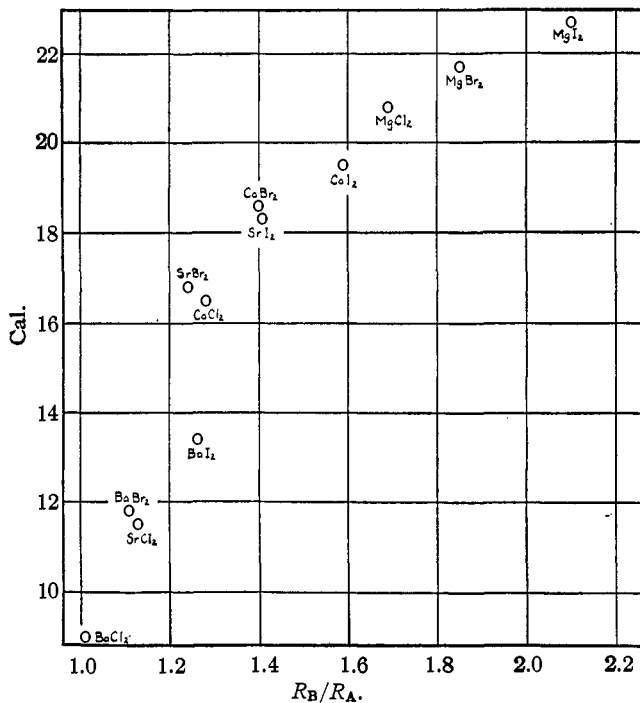


Fig. 9.—Differential heats of formation of ammoniates of alkaline-earth halides *versus* ionic-radii ratios.

might look for compound formation if there is a large difference between the “densities of surface charge” of the competing ions, this difference producing complex ions in which all of the common ions are grouped around the uncommon ion having the larger surface-charge density. If the two competing ions have the same net charge, their “surface-charge densities” are inversely proportional to the squares of their radii, hence the greater the difference in radii, the greater the likelihood of compound formation.

It seems reasonable to assume, as a first approximation, that the size and other characteristics of the common ion have little or no effect on the type of temperature-composition diagram.

Summarizing the above predictions, if we arrange comparable salt pairs having a common ion in the order of the ratios of the radii of their uncommon ions, we should expect successively: (a) solid solutions with a roughly linear melting point-composition curve; (b) solid solutions, the melting point-composition curve showing a minimum; (c) eutectic formation, with partial miscibility or none at all; (d) compound formation, stable or unstable.

Table VI shows that in the $\text{MX}-\text{M}'\text{X}$ and $\text{MX}-\text{MX}'$ series (excluding Cu and Ag compounds from consideration) this order is quite closely followed. The degree of agreement for systems of the types $\text{MX}_2-\text{M}'\text{X}_2$ and $\text{MX}_2-\text{MX}'_2$ is shown in Tables VII and VIII.

Corresponding data for $\text{MX}-\text{M}'\text{X}_2$ and $\text{MX}-\text{MX}'_2$ systems are col-

TABLE VI

THE CORRELATION BETWEEN THE FORM OF THE TEMPERATURE-COMPOSITION DIAGRAM AND THE RATIO OF THE RADII OF THE UNCOMMON IONS, FOR $\text{MX}-\text{M}'\text{X}$ AND $\text{MX}-\text{MX}'$ SYSTEMS

Component ions	R_L/R_S	Type of T-X diagram	Component ions	R_L/R_S	Type of T-X diagram
Tl, Rb, Cl	1.02	a	K, Na, Br	1.26	b
Rb, K, Cl	1.09	a	K, Na, I	1.26	b
Br, Cl, Na	1.09	b	Cs, K, Cl	1.27	b
Br, Cl, K	1.09	b	Rb, Na, Cl	1.38	c
Br, Cl, Tl	1.09	b	Tl, Na, Cl	1.40	c
Tl, K, Cl	1.11	a	Cl, F, Na	1.46	c
I, Br, Na	1.14	b	Cl, F, K	1.46	c
I, Br, K	1.14	b	K, Li, Cl	1.56	c
I, Br, Tl	1.14	b	K, Li, Br	1.56	c
Cs, Tl, Cl	1.15	b	Br, F, Na	1.60	c
Cs, Rb, Cl	1.17	b	Br, F, K	1.60	c
Na, Li, Cl	1.23	b	Cs, Na, Cl	1.61	c
Na, Li, Br	1.23	b	Rb, Li, Cl	1.70	c
I, Cl, Na	1.24	c	Tl, Li, Cl	1.74	c
I, Cl, K	1.24	b	I, F, Na	1.82	c?
I, Cl, Tl	1.24	c	I, F, K	1.82	c?
K, Na, F	1.26	c	Cs, Li, Cl	1.99	d
K, Na, Cl	1.26	b			

TABLE VII

THE CORRELATION BETWEEN THE FORM OF THE TEMPERATURE-COMPOSITION DIAGRAM AND THE RATIO OF THE RADII OF THE UNCOMMON IONS, FOR $\text{MX}_2-\text{M}'\text{X}_2$ SYSTEMS

Component ions	R_L/R_S	Type of T-X diagram	Component ions	R_L/R_S	Type of T-X diagram
Sr, Pb, Cl	1.04	a	Ca, Mn, Cl	1.22	b
Mn, Mg, Cl	1.08	a	Ba, Ca, Cl	1.26	c
Pb, Ca, Cl	1.08	c	Pb, Mn, Cl	1.32	c
Ba, Sr, F	1.12	c	Ca, Mg, F	1.33	b
Ba, Sr, Cl	1.12	b	Ca, Mg, Cl	1.33	c
Sr, Ca, Cl	1.13	b	Sr, Mn, Cl	1.38	c
Ba, Pb, Cl	1.17	a	Ba, Mn, Cl	1.54	d

TABLE VIII

THE CORRELATION BETWEEN THE FORM OF THE TEMPERATURE-COMPOSITION DIAGRAM AND THE RATIO OF THE RADII OF THE UNCOMMON IONS, FOR MX_2 - MX_2' SYSTEMS

Component ions	R_L/R_S	Type of T-X diagram	Component ions	R_L/R_S	Type of T-X diagram
Ca, Br, Cl	1.09	b	Ba, Cl, F	1.46	d
Ba, Br, Cl	1.09	b	Pb, Cl, F	1.46	d
Pb, Br, Cl	1.09	a	Ca, Br, F	1.60	d
Pb, I, Br	1.14	c	Ba, Br, F	1.60	d
Ba, I, Cl	1.24	c	Pb, Br, F	1.60	d
Pb, I, Cl	1.24	c	Ca, I, F	1.82	d
Ca, Cl, F	1.46	d	Ba, I, F	1.82	d
Sr, Cl, F	1.46	d	Pb, I, F	1.82	d

TABLE IX

Component ions	$R_{bi}/\sqrt{2} R_{uni}$ or $\sqrt{2} R_{uni}/R_{bi}$	Type of T-X diagram	Component ions	$R_{bi}/\sqrt{2} R_{uni}$ or $\sqrt{2} R_{uni}/R_{bi}$	Type of T-X diagram
Li, Pb, Cl	1.02	c	Tl, Ba, Cl	1.51	c
Li, Sr, Cl	1.03	c	K, Sr, Cl	1.52	d
Li, Sr, Br	1.03	d	K, Sr, Br	1.52	d
Na, Ba, Cl	1.08	c	K, Pb, Cl	1.59	d
Na, Ba, Br	1.08	c	Na, Mn, Cl	1.67	d
Li, Ca, Cl	1.10	b (c, d)	Tl, Sr, Cl	1.69	d
Li, Ca, Br	1.10	c	K, Ca, Cl	1.72	d
Li, Ba, Cl	1.15	c	K, Ca, Br	1.72	d
Li, Ba, Br	1.15	c	Rb, Pb, Cl	1.74	d
Na, Sr, Cl	1.21	c	Tl, Pb, Cl	1.77	d
Na, Sr, Br	1.21	c	Na, Mg, Cl	1.80	d
Na, Pb, F	1.26	c ^a	Na, Mg, Br	1.80	c
Na, Pb, Cl	1.26	c	Tl, Ca, Cl	1.91	d
Li, Mn, Cl	1.35	b	Cl, O, Ca	1.98	d
F, O, Pb	1.35	c	Cl, O, Sr	1.98	d
Na, Ca, Cl	1.36	c	Cl, O, Ba	1.98	d
Na, Ca, Br	1.36	c, d	Cl, O, Pb	1.98	d
K, Ba, F	1.36	c	K, Mn, Cl	2.10	d
K, Ba, Cl	1.36	d	Br, O, Pb	2.16	d
K, Ba, Br	1.36	d	K, Mg, Cl	2.28	d
Cl, S, Pb	1.44	c	K, Mg, Br	2.28	d
Li, Mg, Cl	1.46	b	Tl, Mg, Cl	2.53	d
Li, Mg, Br	1.46	c			

^a Only partially investigated, up to about 20 mole % of MF_2 .

lected in Table IX. With such systems one would not expect the temperature-composition diagrams to be of either Type a or Type b, for it is difficult to see how a salt having two negative ions can continuously displace more and more of a salt having only one and, without an abrupt change, give a homogeneous crystal of any desired composition from pure univalent salt to pure bivalent salt. Nevertheless, as shown by the table, certain pairs of such salts, according to the literature, are completely miscible in all proportions (Type b).

If the ratio of the surface charge densities of the competing ions is the main factor in determining whether or not compounds are formed, as postulated above, the double charge on one of these ions must be taken into account. This may be done by using for our basis of comparison, not the ratio of the radii $(R_L)/(R_S)$, but $(R_{bi})/(\sqrt{2} R_{uni})$ or $(\sqrt{2} R_{uni})/(R_{bi})$, according to which fraction is greater than one.¹¹ It may be seen from the table that large ratios, calculated in this way, are usually accompanied by compound formation while small ratios give no compounds.

Summary

Using a set of ionic radii differing slightly from those of Davey, evidence has been presented to show that in general the following relationships hold.

1. For uni-univalent and bi-bivalent salts, the sequence of structure types, CsCl, NaCl, ZnS and ZnO, parallels the order of ionic-radii ratios, (R_{large}/R_{small}) , as predicted on the basis of the assumptions: (a) that the spheres of influence of adjacent oppositely charged ions are mutually tangent; (b) that the spheres of influence of like ions cannot interpenetrate; (c) that, the above limitations not interfering, that structure is assumed in which each ion is surrounded by as many as possible of the other kind.

2. For salts of the general formula AB_2 , the CaF_2 structure type is preferred except for large ratios (R_B/R_A) , as predicted on the basis of the same assumptions.

3. The greater the ratio (R_L/R_S) , the greater the tendency is to form hydrates and ammoniates and the greater the stability of those formed, as predicted from the assumptions (a) that hydrate and ammoniate formation parallels the magnitude of the stray field in the simple salt and (b) that this stray field is greater the greater the ionic-radii ratio.

4. The sequence of types of temperature-composition diagrams—(a), (b), (c), (d)—parallels the order of ionic-radii ratios, as predicted from similar considerations to the foregoing; (a) represents solid solutions, with a nearly linear melting-point curve; (b) represents solid solutions with a pronounced minimum in the melting-point curve; (c) represents a eutectic, with or without some solid solution formation; (d) represents compound formation.

¹¹ This procedure is necessary if we are to conform to Cuy's postulates. He ignores this, however, tabulating R_{bi}/R_{uni} . The change alters the positions of but five systems in the table, affecting the degree of agreement with the theory very little. Cuy also includes Cu, Ag, Zn and Cd compounds in his table, but in view of the uncertain radii of these ions and the fact that their electronic structures are probably of considerable importance in determining the types of temperature-composition diagram, they have been omitted. These omissions make the apparent agreement with the theory somewhat better.—M. L. H.