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THE RADII OF THE ALKALI AND HALOGEN IONS AND OF THE ATOMS OF INERT GASES

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Abstract

Packing radii of the alkali and halogen ions in crystal lattices.-An analysis of recent results for the distances of closest approach of the ions in the lattices of all the alkali halides indicates (1) that these ions pack as though they were nearly spherical in shape; (2) that the heavier ions have packing radii which are nearly constant, i.e. independent of the ions with which they are combined; and (3) that the radii of K^+ , Rb^+ , and Cs^+ are approximately equal to those of the negative ions with the same number of electrons, Cl-, Br-, and I-, respectively, the approximation being closer the greater the atomic number. Assuming the radii of Cs⁺ and I⁻ to be equal, and that the first two conclusions above hold rigidly, the radii of the ions are computed to be as follows, in units of 10-8cm: for Cs+ and I-, 1.974; Rb+, 1.679; Br-, 1.737; K+, 1.548; Cl-, 1.589; Na+, 1.1 to 1.2; Fl-, 1.0 to 1.2. These values are in general agreement with the average of the ionic radii computed by Landé (from crystal data), Richards (from compressibility), and Saha (from ionization potentials), but differ considerably from Bragg's results from x-ray data. The above conclusions are shown to be in qualitative agreement with the Lewis-Langmuir theory.

Packing radii of the inert gases computed from x-ray data on the assumption that for each gas the radius is the mean of those for the alkali and halogen ions with the same number of electrons, come out: for Xe, 1.97; Kr, 1.71; Ar, 1.57; Ne, 1.15. These are only from .0 to .27 units higher than the values obtained by Rankine from viscosity measurements. Assuming these radii, the *atomic volume per electron* comes out approximately constant for Xe, Kr and Ne, though somewhat low for Ar.

X-RAY diffraction patterns of crystals not only give the arrangement of atoms in space, but also give in centimeters the distance between the centers of adjacent atoms. These measurements are quite independent of any hypothesis as to the structure of the atoms or of the mechanism of their state of chemical combination.

The results of such measurements on the alkali halides have already been published¹ in detail. A summary is given in Table I for purposes of

¹ Davey, Phys. Rev. 21, 143 (1923).

reference in this paper. The data in this table show two peculiarities. The first has to do with the type of diffraction pattern; the second with certain *differences* in the distance of closest approach. It is the purpose of this paper to discuss these two peculiarities, and to apply the results of the discussion to a determination of the radii of the alkali and halogen ions, and the atoms of the inert gases.

It will be noticed that in the cases of CsI, RbBr and KCl and for these alone, the diffraction pattern and the crystal structure are the same. This means that the component atoms, alkali and halogen, have prac-

SC – simple cubic, BCC – Body-centered cubic, FCC – Face-centered cubic							
Salt	Diffraction pattern	Crystal structure	Side of unit cube	Distance of closest approach			
CsI CsBr CsCl CsF	BCC SC SC FCC	BCC BCC BCC SC	4.558 A 4.287 4.118 3.004	$\begin{array}{c} 3.947 \pm .004 \ \mathrm{A} \\ 3.713 \pm .004 \\ 3.566 \pm .004 \\ 3.004 \pm .003 \end{array}$			
RbI RbBr RbCl RbF(?)	FCC SC FCC SC	SC SC SC BCC	3.655 3.418 3.267 3.663	$\begin{array}{c} 3.655\pm.004\\ 3.418\pm.003\\ 3.267\pm.003\\ 3.172\pm.003 \end{array}$			
KI KBr KCl KF	FCC FCC SC FCC	SC SC SC SC SC	3.525 3.285 3.138 2.664	$\begin{array}{c} 3.525\pm.004\\ 3.285\pm.003\\ 3.138\pm.003\\ 2.664\pm.003 \end{array}$			
NaI NaBr NaCl NaF	FCC FCC FCC FCC	SC SC SC SC	3.231 2.968 2.814 2.310	$\begin{array}{c} 3.231 \pm .003 \\ 2.968 \pm .003 \\ 2.814 \pm .003 \\ 2.310 \pm .002 \end{array}$			
LiI LiBr LiCl LiF	FCC FCC FCC FCC FCC	SC SC SC SC	3.537 2.745 2.566 2.007	$\begin{array}{c} *3.537 \pm .005 \\ 2.745 \pm .003 \\ 2.566 \pm .003 \\ 2.007 \pm .004 \end{array}$			

 TABLE I

 Crystallographic data on alkali halides

 SC = simple cubic; BCC = Body-centered cubic; FCC = Face-centered cubic

* This is quite different from the value of $3.03 \pm .01$ reported by Posenjak and Wyckoff (J. Wash. Acad. Sci. 12, 248, 1922). The difference may be due to the method of preparation of the sample. Since Wyckoff's value gives a calculated density more nearly equal to that obtained by ordinary methods, it is reasonable to suppose that his specimen corresponded more nearly to the ordinary state of Li F than my sample did. His value will therefore be used in the calculation of this article.

tically equal diffracting power. The diffracting power is so nearly equal that in the case of KCl additional lines due to incomplete interference could not be found even with prolonged exposures on a photographic film. Now in each of these cases, the atomic numbers differ by only two, so that the positive alkali ions Cs⁺, Rb⁺ and K⁺ have the same number of electrons as the corresponding negative halogen ions, I⁻, Br⁻ and Cl⁻. This equality of diffracting power can be readily explained by making two assumptions, (1) that the elements are present in these compounds, not as neutral atoms, but as electrically charged ions; (2) that the arrangement of electrons in space is the same in Cs^+ as in I^- , in Rb^+ as in Br^- and in K^+ as in Cl⁻. The first of these assumptions is consistent with the fact that these compounds are insulators when cold, but become ionic conductors when heated sufficiently. It receives additional support from the refractive equivalents of atoms and ions.² The second assumption is necessary in order that groups of equal numbers of electrons may act as equal diffracting centers. It implies equality (or at least approximate equality) in the volumes of Cs⁺ and I⁻, Rb⁺ and Br⁻, and K⁺ and Cl⁻. Although Na⁺ and F⁻ have equal numbers of electrons, their diffracting powers are not quite equal. This is to be expected, because the percentage difference in the nuclear charges is rather great so that the electrons in Na⁺ would be expected to occupy a smaller volume than those in F⁻. This seems to point to the conclusion that the other pairs of ions mentioned above do not have exactly equal volumes, even though the difference in the space-density of electrons cannot be detected from the type of diffraction pattern. If such is the case, the approximation to equality in volume should be closest in Cs⁺ and I⁻ where the percentage difference in the nuclear charge is least. The same reasons which would make one expect F^- to be a little larger than Na^+ would lead to the conclusion that Cl⁻ and Br⁻ should be very slightly larger than K⁺ and Rb⁺ respectively.

Table II gives the difference in the "distance of closest approach" D of oppositely charged ions in the alkali halides. It will be noticed that within the limits of error, \pm .007,

 $D(\mathrm{CsI}) - D(\mathrm{RbI}) = D(\mathrm{CsBr}) - D(\mathrm{RbBr}) = D(\mathrm{CsCl}) - D(\mathrm{RbCl})$ and

$$D(CsI) - D(KI) = D(CsBr) - D(KBr) = D(CsCl) - D(KCl)$$

hence

 $D(\mathrm{CsI}) - D(\mathrm{CsBr}) = D(\mathrm{RbI}) - D(\mathrm{RbBr}) = D~(\mathrm{KI}) - D(\mathrm{KBr})$ and

D(CsI) - D(CsCl) = D(RbI) = D(RbCl) = D(KI) - D(KCl)

These results suggest strongly that each of these ions, Cs^+ , Rb^+ , K^+ , I^- , Br^- , and Cl^- has a dimension, possibly the radius of its "sphere of influence," which we may call its "packing radius" or more simply its "radius," which does not depend on the ion with which it is combined, and that the distance of closest approach is merely the sum of the radii

² J. A. Wasastjerna, Oefvers Finska, Vet. Soc. **63** A, 18, (1921); Chem. Abstr. **16**, 3028 (1922).

of the component ions. This is a very surprising result. It is not true for the lightest elements, Na, F, and Li, and this suggests that still more accurate data would show it to be only an approximation for the heavier elements, the approximation being closer the higher the atomic number.

It should be noted that the packing radii are the same when measured along the cube-diagonal (as in the case of the body-centered salts of Cs) as when measured along the cube-edge (as in the case of the simple-cubic salts of Rb and K). This indicates that the ions are approximately

Constancy of size of the large ions								
	Iodi	ide	Bromide	Chloride	Fluoride			
Cs	3.9	47	3.713	3.566	3.004			
Rb Diff	3.6	55	3.418	3.267	3.172			
Diii.	. 4	<i>94</i>	. 495	. 499	100			
Cs	3.9	47	3.713	3.566	3.004			
K D'ff	3.5	25	3.285	3.138	2.664			
<u>D</u> іп.	.4	-66	. 428	.428	. 340			
Cs	3.9	47	3.713	3.566	3.004			
Na	3.2	31	2.968	2.814	2.310			
Diff.	. 7	16	.745	.752	. 694			
Cs	3.9	47	3.713	3.566	3.004			
Li	3.5	37	2.745	2.566	2.007			
Diff.	.4	-10	.968	1.000	997			
	Caesium	Rubidium	n Potassium	Sodium	Lithium			
I	3.947	3.655	3.525	3.231	3.537			
Br	3.713	3.418	3.285	2.968	2.745			
Diff.	.234	.237	.240	. 263	. 792			
I	3.947	3.655	3.525	3.231	3.537			
Cl	3.566	3.267	3.138	2.814	2.566			
Diff.	. 381	. 388	. 387	.417	.971			
I	3.947	3.655	3.525	3.231	3.537			
Ē	3.004	3.172	2.664	2.310	2.007			
Diff.	.943	.483	. 861	.921	1.530			

TABLE	II
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spherical in shape. Other evidence for this conclusion has already been published³ in which it was shown that these ions pack as though they were cubes with rounded corners, i.e. spheres with six "flat spots." The ions which pack like compressible spheres are those whose electrons do not extend beyond what Langmuir⁴ has called the "IIa" layer. As soon as the "IIb" layer is filled the ions act like practically incompressible spheres.

³ Davey, Phys. Rev. 17, 402 (1921).

⁴ Langmuir, J. Am. Chem. Soc. 41, 870 (1919).

If we take the distance of closest approach of Cs⁺, Rb⁺, K⁺ to I⁻, Br⁻, Cl⁻ as being the sum of the radii of the ions, the experimental results give nine equations. These, together with the four equations given above, give five independent equations containing six unknown quantities. If we assume in addition that $R(Cs^+) = R(I^-)$, which must be very approximately true, as stated above, then we can determine all the radii. The results are given in Table III. It is seen that the radii of Rb^+ and

	TABLE III Radii of the alkali and halogen ions								
	Cs+ Rb+ K+	1.974 A 1.679 1.548	I– Br– Cl–	1.974 1.737 1.589	A				
in NaI NaBr NaCl NaF*	Na+ 1.257 A 1.231 1.225 <1.15	in CsF RbF KF NaF*	$\begin{array}{r} F^{-} \\ 1.030 \text{ A} \\ (1.493) \\ 1.116 \\ + > 1.15 \end{array}$		in LiI** in LiBr LiCl LiF	<	Li+ 1.06 A 1.008 0.977 0.86(?)		

* As a first approximation, the radii of Na+ and F- are 1.15 A. This is half the distance of closest approach in NaF. **The radius of Li+ in LiI is 1.563 A if my value is used instead of Wyckoff's.

 Br^- and of K^+ and Cl^- are very nearly equal, but that the negative ion is in each case about $\frac{1}{3}$ per cent larger than the positive ion. This is consistent with the prediction made in the first part of this paper. In the case of Na⁺, F⁻ and Li⁺, if we assume that the radii of the heavier ions are constant, the radii of the positive ions, Na⁺ and Li⁺, seem to decrease as the atomic number of the negative ions decreases. The radius of F^- increases as the atomic number of the positive ion decreases. The high value for F⁻ in RbF seems anomalous.

The Xe atom has the same number of electrons as Cs⁺ and I⁻. Its nuclear charge lies between that of Cs^+ and that of I^- . It would therefore be expected to have approximately the same radius. In the same way the radius of the Kr atom should be the average of the radii of Rb+ and Br^- . The radius of Ar should be the average of K^+ and Cl^- , etc. Radii of the atoms of the inert gases, calculated in this way, are given in Table IV. It is also shown in Table IV that these radii are roughly

	Tabl	e IV	
Constancy	of volume	occubied	by electrons

Inert Gas	Atomic Number N	$N^{rac{1}{3}}$	Radius <i>R</i>	$N^{\frac{1}{3}}/R$
Ne	10	2.15	1.15	1.87
Ar	18	2.62	1.57	1.67
Kr	36	3.30	1.71	1.93
Xe	54	3.78	1.97	1.92

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proportional to the cube root of the atomic number. That is, *the volume* of the atom of an inert gas is roughly proportional to the number of electrons which it contains. This must mean that the average volume occupied by an electron in an inert gas is approximately a constant. Thus the same conclusion is reached from a study of the diffraction patterns of crystals that was reached by Langmuir⁴ from purely chemical considerations.

Table V gives the volume in cubic centimeters of the ions of the alkalies and halogens and of the atoms of the inert gases. The average volume occupied per electron is also given in each case. It is evident that the average volume per electron should be greater for the halogen ions than

	1 2		
Ion or atom	Electrons	Volume $(10^{-24}cc)$	Volume per electron $(10^{-25}cc)$
Cs+ Rb+ K+ Na+ Li+	54 36 18 10 2	32.5 20.0 15.6 6.4 to 8.3 2.6 to 5.0	6.03 5.56 8.67 6.4 to 8.3 13 to 25
I- Br- Cl- F-	54 36 18 10	32.522.117.04.6 to 6.4	$\begin{array}{r} 6.03 \\ 6.14 \\ 9.44 \\ 4.6 \text{ to } 6.4 \end{array}$
Xe Kr Ar Ne	54 36 18 10	32.521.016.36.7	6.03 5.83 9.06 6.7

TABLE V								
Volume	occupied b	v	electrons	in	ions	and	atoms	

for the alkali ions, because the attractive force of the nucleus is less. It is not at all certain, however, that these values for the volumes occupied by electrons represent anything more than an *average* for the atoms or ions in question.

In Table VI, the values of the radii of the alkali and halogen ions are compared with the results of other investigators using other methods.⁵ The results for the inert gases are compared with the results calculated by Rankine⁶ from the viscosity of the inert gases. Since each of these

⁵ Landé, Zeit. f. Phys. 1, 191, (1920); Richards, J. Am. Chem. Soc. 43, 1584, (1921); 45, 422, (1923); Eve, Nature, 107, 552 (1921); Davis, Nat. Acad. Sci. Proc. 8, 61, (1922); Saha, Nature, July 28, (1921); Bragg, Phil. Mag. 40, 169, (1920); Pease, J. Am. Chem. Soc. 44, 769-1497, (1922).
⁶ Rankine, Proc. Roy. Soc. 84, 182, (1910); Phil. Mag. 42, 601, (1921); Proc. Roy. Soc. 98, 360, (1922). methods is founded upon assumptions of one sort or another, it is worth while to examine them further.

Landé assumes that since Li⁺ contains only two electrons, it must be negligibly small in the presence of I⁻ in LiI. If this assumption is correct, the radius of I⁻ can be at once calculated from the diagonal of the face of the unit cube of LiI. He then tabulates the values for the other ions as the average of the results calculated from the space-lattice constants in terms of the assumed value for iodine. These calculations implicitly assume the constancy of size of I⁻. This assumption receives support from Table II of this paper. The space-lattice constants used by Landé were considerably in error. His results have therefore been recalculated for Table VI. In this calculation the side of the unit cube of LiI is taken from Posenjak and Wyckoff's value as given in Table I, since their value gives a calculated density more nearly equal to the commonly accepted value. If my value is used instead, the radii of the negative ions become about 12 per cent larger than given in Table VI

TABLE VI

Comparison of atomic and ionic radii according to various workers

(1) Calculations of Landé; (2) Compressibility method of Richards; (3) Ionization potential method of Eve and Saha; (4) Average of (1), (2) and (3); (5) Viscosity method of Rankine; (6) Crystal structure method of the present article; (7) Crystal structure method of Bragg.

	(1) Landé	(2) Richards	(3) Eve & Saha	(4) Average (1)-(2)-(3)	(5) Rankine	(6) Davey	(7) Bragg
Cs Xe	1.81	2.2*	1.9-	2.0	1 75	1.974	2.37
I	2.14	1.7		1.9	1.75	1.974	1.40
Rb Kr	1.51	1.9	1.7	1.7	1.59	1.679 1.71	2.25
Br	1.90	1.5		1.7	2105	1.737	1.19
K Ar	1.38	1.6	1.7	1.6	1.43	1.548 1.57	2.07
Cl	1.76	1.4		1.6	1.10	1.589	1.05
Na Ne	1.09	1.5	1.4	1.3	1 17	1.1 - 1.2 1 15	1.77
F	1.19					1.2-1.0	0.67

* Calculated from CsCl by the writer, using Richards' method.

and the radii of the positive ions become correspondingly smaller. It is not clear that Landé is justified in assuming a negligible radius for Li⁺. It is evident, however, that his method must give the upper limits of the radii of the negative ions and the lower limits for the positive ions. These limits could probably be brought closer by using the lattice-constant of HI.

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Richards' values depend fundamentally upon his assumption that "the contractions which occur during the formation of the alkali halides are proportional to the compressibilities of the elements concerned." Richards' published value for the radius of Cs⁺ is incorrect, due to an error in the method of calculation and the assumption of an incorrect crystal lattice. The value has been recalculated in Table VI. His values of Cs⁺ and K⁺ do not give differences corresponding to the experimental values of (CsI-KI) or (CsBr-KBr) such as are given in Table II. His fundamental assumption must therefore be regarded as only a good first approximation. The rest of his values check these experimental differences as closely as the accuracy of his end results permits. His values of the halogen ions are all about 10 per cent lower than mine, while his values of the alkali ions are about 10 per cent higher. Richards finds from Bridgman's experimental data that the Na atom acts as though it had a relatively incompressible core whose volume is 30 per cent of the volume of the uncompressed atom. It is interesting to note that a similar conclusion can be drawn from the x-ray data. Of the various radii assigned to Na⁺ in Table III, the largest (that of Na⁺ in NaI) is taken as representing the radius under the smallest compressive force represented in the table, thus corresponding most nearly to the forces used experimentally by Bridgman. This radius is 1.25 A. The radius of the Na atom as determined from the distance of closest approach of atoms in the element⁷ is 1.86 A. The volume of Na⁺ is therefore .30 of the volume of the Na atom. The close agreement with Richards' value makes it look as though his "relatively incompressible portion" is really the ion. As may be seen from Table II, Na⁺ is only "relatively incompressible." It would be valuable if experimental data were available for the pressure volume relations of K, Rb, and Cs. Richards has attempted to fill the gap by extrapolating from the values of Na to those to be expected for K. His extrapolated value for the "incompressible" portion of K is .20 of the value of the atom. The radius of K⁺ given in Table IV in comparison with the radius of K^{8} gives a ratio of .33.

A. S. Eve⁵ has pointed out, using Bragg's estimate of atomic radii,⁵ that the product of the ionization potential by the atomic radius is roughly a constant. M. Saha⁵ has used the ionization potentials as a means of calculating atomic radii according to this law. Eve's law holds roughly true with the radii given in Table IV. There is, however, a systematic decrease in the size of the constant as the atomic number decreases. This is to be expected from the fact that the radii are measured at room tem-

⁷ A. W. Hull, Phys. Rev. 10, 661 (1917).

⁸ L. W. McKeehan, Proc. Nat. Acad. Sci. 8, 254 (1922).

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perature by the crystal method. The ionization method measures the radius at some higher temperature, probably comparable with that of the boiling point of the element. The correction is in the right direction to reduce the discrepancies in the value of Eve's constant as calculated from the radii given in Table IV. It should be noted that the ionization potentials of the inert gases give radii for the *ions* of the inert gases which are considerably smaller than those assigned for the *atoms* in Table V. This is in accord with theory. The radii as given in this paper do not support B. Davis'⁵ modification of Eve's theory in which he claims that the *difference* between the ionization and the radiation potentials, multiplied by the radius, should be a constant.

The best known estimate of radii from crystal data is that of W. L. Bragg.⁵ He makes no distinction between the radii of atoms, those of ions, and those of atoms in valence compounds, but apparently he has based all his calculations on "valence compounds." It is inevitable that he should obtain an apparent check between his calculated and observed values, for his number of equations does not exceed the number of his unknown quantities. The values that he gives for the alkalies and halogens do not, however, satisfy the assumption of this article that Cs⁺ and I⁻have equal radii nor the experimental facts on which that assumption is based. His radii for the alkalies are nearly twice those for the corresponding halogens. In view of the excellent confirmation shown above for the assumption of equality of size it is necessary to reject Bragg's values in so far as ions are concerned. This does not affect in any way the question of the validity of Bragg's radii for atoms which combine to form "valence" compounds.

R. N. Pease⁵ has lately estimated the "radii" of atoms in such diamondlike structures as SiC, CuI, AgI, etc., which he considers to be valence compounds, sharing electrons. He finds very good numerical justification for his assumptions. His *radii* for Cl, Br and I do not agree with those given here, nor is there any reason why they should agree if he is correct in assuming that the salts he has considered are "valence compounds."

A. O. Rankine⁶ calculated the radii of the atoms of inert gases from his viscosity measurements, using Chapman's formula. Table VI shows that the agreement is not very close. Rankine's results can be converted into mine by the following formula, $(R-0.35)\sqrt{2} = D$ where R stands for Rankine's value for a given radius and D stands for mine. This means that Chapman's formula could be at once modified empirically to give results which correspond with those from the crystal method. So far, I have been unable to find any theoretical reason for such a modi-

fication. It may be remarked that Rankine's value for Xe falls below the lower limit set by Landé's values, and that his radii do not show constancy of volume occupied by the electrons (see Table V).

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GENERAL ELECTRIC COMPANY, SCHENECTADY, NEW YORK, December 2, 1922.

Note added August 27, 1923. R. W. G. Wyckoff, in the Proc. Nat. Acad. Sci. 9, 33 (1923), finds a radius for chlorine of 1.081 A. He arrives at this figure by subtracting the distance between centers of Cs^+ and I^- in CsI from the corresponding distance in $CsCl_2I$. Now $CsCl_2I$ has the Cs and I arranged in a structure like Na⁺ and I^- in NaI except that the cube is distorted to a rhombohedron. The Cl atom is at the body-center of this distorted cube. Since the crystal as a whole is electrically neutral, there are three alternatives open: (1) Cs loses an electron to each of the three halogens, so that it has a valence of three; (2) the crystal is made up entirely of uncharged atoms; (3) the Cl is a neutral atom mechanically held in the center of a distorted simple cube of Cs⁺ and I⁻. Of these three, the last is the simplest and fits best the properties of CsCl₂I. If it is correct, Wyckoff's value is not the radius of Cl⁻ but of the neutral atom of chlorine. The following is evidence of the correctness of this conclusion. Cl⁻ should be larger than atomic Cl due to the presence of the extra electron, and atomic K should be larger than K⁺ in about the same proportion. Assuming that Wyckoff's value applies to atomic Cl we have,

 $C1/C1^{-}=1.08/1.59=.68;$ $K^{+}/K=1.55/2.25=.69.$