

THE RADII OF ATOMS AND IONS

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ATOMIC SHAPES AND RADII

A few years ago when atoms were thought of as being tiny solid baseballs, the term *radius* had a very definite meaning. In these days the picture of an atom is much more complex. We are given our choice of a static atom founded mainly on data obtained from solids and liquids, or of a Bohr atom founded mainly on data obtained from the spectra of elements in the gaseous state. In terms of the static atom picture, the word "radius" would be applicable to a circumscribed sphere passing through all the electrons in the outmost shell. In the Bohr picture, we might apply the word "radius" to the distance from the nucleus to the most distant part of the largest electronic orbit. Neither of these "radii" are quite consistent with the data of crystallography as determined by the diffraction of x-rays.

The atoms of an element pack together in a crystal as though they were solid objects in contact with each other. If models are made of the crystals of the elements, using balls to represent the atoms, it is found in general that each ball is surrounded by others which are symmetrically placed around it and which lie in direct contact with it. Within the limits set by the compressibility of the element and its thermal expansion, each atom seems to occupy a definite domain which, under ordinary conditions, may not be entered by any other atom. Such a state of affairs is hardly to be expected from the current pictures of atomic structure, yet such are the experimental facts of X-ray crystallography. It is as though each atom were completely surrounded by a "field of force" which set it apart from its neighbors. The region occupied by this "field of force" is the crystallographer's "atomic domain." It is with the shapes

and sizes of these domains that the crystallographer has to do, for they give him a definite mechanistic picture of how the atoms of the elements may be expected to act under various conditions. From the crystallographic point of view, these shapes and sizes are the effective shapes and dimensions of the atoms themselves.

Many elements crystallize in the face-centered cubic lattice (see fig. 1). Since a face-centered cube is one of the two alternative closest packings for spheres, it is assumed that such atoms have a spherical shape (1) (2), i.e., that their atomic domain is a sphere. Such elements are, Cu, Ag, Au, Ca, Al, Ce, Pb, Th, gamma Fe, Co, Ni, Rh, Pd, Ir, and Pt. It will be noticed that

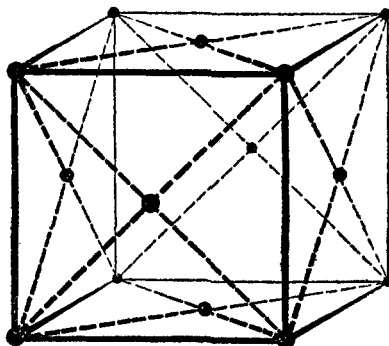


FIG. 1. FACE CENTERED CUBIC LATTICE

all the most ductile metals and all the best conductors of electricity are included in this group (2) (3). Each atom is surrounded by six others, symmetrically placed around it and apparently in contact with it. A line joining the center of any atom with the center of any one of the six which touch it will lie along the face diagonal of a unit-cube of the crystal lattice. The distance between the two centers is the distance of closest approach of the atoms. Half of this distance is therefore the radius of the atomic domain, or, as it is more often called, the "packing radius" of the atom; it is $\frac{1}{4}\sqrt{2}$ times the edge of the unit-cube of the crystal. The higher the purity of the metal used in the experiment, the more accurate is the measurement of

the edge of the unit-cube. The radii of metals having spherical atoms are given in table 1, using data from metals of the highest purity obtainable.

The other alternative closest packing for spheres is the triangular close-packed lattice (see fig. 2) when the axial ratio is 1.633. Co and Ce are the only elements known which are able to crystallize in this form with an axial ratio of exactly 1.633. Both of these elements are also found with the face-centered cubic structure. The other elements which crystallize in the triangular close-packed lattice have axial ratios ranging from 1.58 to 1.89. It is therefore assumed that the atoms of Co

TABLE I
Radii of spherical atoms

ELEMENT	PURITY	RADIUS	ELEMENT	PURITY	RADIUS
(1) Cu...	99.99%	1.276×10^{-8} cm.	(3) γ Fe.	?	1.27×10^{-8} cm.
(1) Ag...	99.999	1.442	(2) Co...	Electrolytic	1.257
(1) Au...	99.999	1.437	(1) Ni...	99.55	1.237
			(2) Rh...	?	1.350
(2) Ca....	?	1.97	(2) Pd...	?	1.397
			(4) Ir...	?	1.352
(1) Al....	99.97	1.430	(1) Pt...	99.995	1.383
			(1)	Davey	
(2) Ce....	?	1.82	(2)	Hull	
(1) Pb....	99.96	1.740	(3)	Westgren	
(1) Th...	?	1.77	(4)	Wykoff	

and Ce are spherical and that the other atoms which crystallize with this type of structure are spheroidal (2). Since the axial ratios of Be, Mg, Ti, Zr, Ru, and Os are less than 1.633, their atoms are considered to be oblate spheroids. Zn and Cd are assumed to be prolate spheroids. All these atoms are therefore given two radii which are half the major and minor axes of the spheroid.¹

The equatorial radius is half the distance of closest approach in the direction of the hexagonal (X and Y) axes of the crystal.

¹ Hull (2) lists, instead, the two distances of closest approach of atoms. One of these is the same as the equatorial radius. The other is intermediate between this and the axial radius.

The other, which we will call the axial radius, is the radius of the spheroid along the orthogonal (Z) axis of the crystal. Radii of this sort for the spheroidal atoms are listed in table 2.

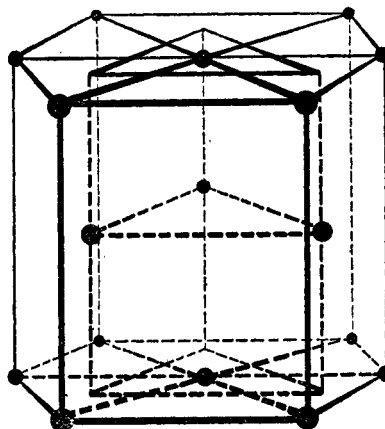


FIG. 2. TRIANGULAR CLOSE-PACKED LATTICE

TABLE 2
Radii of spheroidal atoms

ELEMENT	EQUATORIAL RADIUS	AXIAL RADIUS	SOURCE OF DATA
Be.....	1.141	1.106	McKeehan
Mg.....	1.597	1.593	Meier
Zn.....	1.329	1.515	Pierce, Anderson and Van Dyck
Cd.....	1.480	1.714	Hull
Ti.....	1.478	1.439	Patterson
Zr.....	1.61	1.57	Hull
Ru.....	1.343	1.307	Hull
Os.....	1.357	1.322	Hull

Li, Na, K, V, Ta, Cr, Mo, W, and alpha Fe crystallize with the body-centered lattice (see fig. 3). It is a characteristic of this lattice that each atom is symmetrically surrounded by eight other atoms. This is the closest packing for equal numbers of spheres of equal radius having opposite electric charges,

but the ordinary physical and chemical properties of these metals hardly justify a picture of half the atoms positively charged and half negatively charged. Crystals of alpha iron, and presumably of the other elements having the same structure, are quite permeable in the cold to atomic hydrogen, but not to molecular hydrogen (4). The crystal must therefore have tunnels running through it which are big enough for atomic hydrogen to pass through, but which are just too small for molecular hydrogen (effective "radius" 1.2×10^{-8} cm.) (5) to pass through at room temperature.²

Since the eight points of contact may be symbolized by the corners of a cube, Hull (2) assumed the shape of these atoms

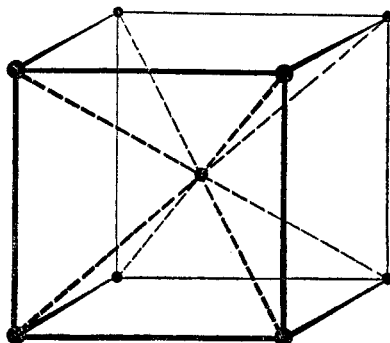


FIG. 3. BODY-CENTERED CUBIC LATTICE

to be cubic. Such an atomic shape gives tunnels of square cross section in the crystal. In alpha iron these tunnels are 1.427×10^{-8} cm. on a side. A dumb bell shaped molecule of hydrogen, 2.4×10^{-8} cm. long would be unable to fit along the diagonal of the cross section of this tunnel (2.02×10^{-8} cm.) at room temperature. Therefore no molecular hydrogen can pass very far through an iron crystal without becoming wedged in unless the temperature is such (red heat) that the tunnels become occasionally large enough by reason of the motion of the iron atoms. The diffusion of atomic carbon during the heat treatment of steel can be explained by these same tunnels

² The body-centered cubic structure is the closest packing for octahedra, but a closely packed structure would lack the tunnels.

(6). The diffusion of atomic carbon in Mo and W may be similarly pictured (7).

Following the precedent set by Hull, the dimensions of cubic atoms are measured in the direction of the distance of closest approach. This is along the body diagonal of the atom, and may be considered to represent the radius of the circumscribed sphere. Data are given in table 3.

TABLE 3
Equivalent radii of cubical atoms

ELEMENT	EQUIVALENT RADIUS	ELEMENT	EQUIVALENT RADIUS
(1) Li.....	1.51×10^{-8} cm.	(3) Cr.....	1.248×10^{-8} cm.
(1) Na.....	1.86	(4) Mo.....	1.361
(2) K.....	2.25	(4) W.....	1.366
(1) V.....	1.32	(4) Fe.....	1.236
(1) Ta.....	1.416		

- (1) Hull.
 (2) McKeehan.
 (3) Patterson.
 (4) Davey.

TABLE 4
Equivalent radii of tetrahedral atoms

ELEMENT	EQUIVALENT RADIUS
(1) C.....	0.77×10^{-8} cm.
(2) Si.....	1.174
(3) Ge.....	1.22
(4) Sn gray.....	1.40

- (1) Bragg.
 (2) Küstner and Remy.
 (3) Hull.
 (4) Bijl and Kolkmeier.

The crystal structure of C, Si, Ge, and grey Sn are such that the atomic domains are pictured as being tetrahedra (see fig. 4) for each atom is equally distant from each of four others. This is in harmony with the mass of chemical evidence for the tetrahedral shape of C and Si. In order that the word "radius" may have any meaning in the case of tetrahedra, the dimensions of these atoms are expressed in terms of the radius of the in-

scribed sphere. This makes the "equivalent radius" equal to half the distance of closest approach. Data are given in table 4.

Frozen Hg, As, Sb and Bi, crystallize as rhombohedra, which may be regarded as being slightly distorted simple cubes. Their

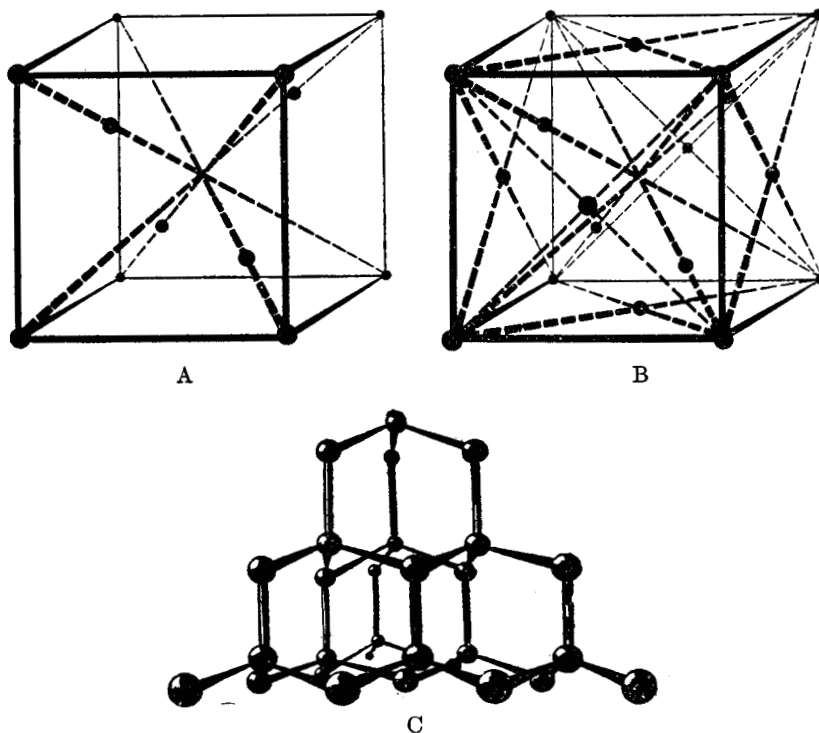


FIG. 4. DIAMOND CUBIC LATTICE

A, the superposition of figure 4A on figure 1 gives figure 4B.

B, diamond cubic lattice oriented so that one cubic axis is vertical.

C, diamond cubic lattice oriented so that the body-diagonal of the cube is vertical.

atomic domains may therefore be pictured as being distorted cubes. Their dimensions are at present unimportant.

The whole body of data on the shapes and sizes of atoms is summarized in table 5.

Although shapes and sizes were originally assigned to atoms by crystallographers in order to give a mechanistic picture of

TABLE 5

"SHAPES" AND "EQUIVALENT RADII" OF ATOMS.

GROUP 0.	GROUP 1. E ₂ O	GROUP 2. E O	GROUP 3. E ₂ O ₃	GROUP 4. E O ₂ E H ₄	GROUP 5. E ₂ O ₃ E H ₃	GROUP 6. E O ₃ E H ₂	GROUP 7. E ₂ O ₇ E H	GROUP 8.
H _c	H 1.2 L 1.51	B 1.106 E 1.141	B	Δ .77	N	O	F	
N _c A _r	N 1.86 K 2.25	M 1.593 C 1.597 G 1.97	A 1.430 S	Δ 1.174 T 1.439 E 1.478	P 2.64	S 1.248	C	F 1.236 B 1.27 C 1.257 G 1.237
K _r	1.276 C R	1.515 C 1.329 Z S	G	1.218 Δ E 1.57 1.61	C	S 1.361	B	R 1.307 C 1.343 P 1.350 E 1.397
X _c	1.442 A C	1.714 A 1.480 C B	I L	1.40 Δ C 1.82	S	T	I	
		RARE EARTHS			T 2.833	W 1.366	R	G 1.322 B 1.357 I 1.352 P 1.385
1.437 A		H	T	1.740 P	E			
RADIOACTIVE ELEMENTS								
								1.77 B

TABLE 6

Compressibilities of the alkali metals

ELEMENT	COMPRESSIBILITY (CALCULATED)	COMPRESSIBILITY (EXPERIMENTAL)
Li.....	7.4×10^{-12}	8.8×10^{-12}
Na.....	16.7	15.4
K.....	38.4	31.2
Rb.....	52.6	40.0
Cs.....	71.4	62.5

TABLE 7

Compressibilities of polyvalent elements

ELEMENT	VALENC	CALCULATED COMPRESSIBILITY (THOMSON)	EXPERIMENTAL COMPRESSIBILITY
Ca.....	2	5.2×10^{-12}	5.5×10^{-12}
Al.....	3	1.08	0.75
C.....	4	0.178	0.16

crystal formation, these shapes and sizes have a widespread theoretical application. From them may be calculated the compressibilities of the elements, their photo-electric properties, and their relative ionizing potentials (8) (9) (10). Tables 6 and 7 compare the calculated values for the compressibility with the experimental values for the alkali metals and for Ca, Al and C. A discussion of the derivation of the equations by which the results were calculated (9) would be out of place here. It will be sufficient to state that for body-centered cubic metals (i.e., for "cubic" atoms), the compressibility is

$$\frac{1}{k} = \frac{9}{8.06} \cdot \frac{\left(\frac{4R}{\sqrt{3}}\right)^4}{e^2} = 31.7 \frac{R^4}{e^2}$$

where e is the charge on an electron in electrostatic units and R is the "equivalent radius" of the cubic atom. Table 8 compares the calculated and experimental photo-electric properties of alkali metals. The longest wave-length of light which will cause a photo-electric effect in an alkali metal may be calculated by the quantum relation from the work in volts required to liberate an electron from an atom. This work for cubic atoms is given by the equation (9).

$$\begin{aligned} W &= -0.15 \times 4.03 e^2 \frac{\sqrt{3}}{4 R} \\ &= -0.262 \frac{e^2}{R} \end{aligned}$$

Experimental data on the longest useful wave-length are available only for Li and Na. Data are, however, available for four alkali metals on the wave-length of light, which can produce the maximum photo-electric effect. It is to be expected that these wave-lengths will be proportional to the maximum wave-lengths mentioned above. That this is so is shown in table 9. Table 10 shows that the atomic radius should be roughly inversely proportional to the ionizing potential. This is in accordance with theory (8) (9).

The atomic radii of simple atoms follow a periodic law which is consistent with the Mendelejeff Table (11). Elements which, upon chemical combination, tend to revert to the Ni, Pd, or Pt type of atoms (12) are supposed to have a relatively complex

TABLE 8
Maximum wave length which will produce a photo electric effect

ELEMENT	CALCULATED MINIMUM VOLTAGE TO LIBERATE ELECTRON	MAXIMUM λ FOR PHOTO-ELECTRIC EFFECT CALCULATED FROM QUANTUM RELATION	MAXIMUM λ FOR PHOTO-ELECTRIC EFFECT FROM EXPERIMENT	RATIO
Li.....	2.46	5000	4500	1.11
Na.....	2.03	6100	5500	1.11

$$W = \frac{hc}{\lambda} = 0.262 \frac{e^2}{R}$$

TABLE 9
Wave length which will produce a maximum photo electric effect

ELEMENT	CALCULATED MINIMUM VOLTAGE TO LIBERATE AN ELECTRON	CALCULATED MAXIMUM λ FOR PHOTO-ELECTRIC EFFECT	EXPERIMENTAL λ FOR MAXIMUM PHOTO-ELECTRIC EFFECT	RATIO
Li.....	2.46	5000×10^{-8} cm.	2800	0.56
Na.....	2.03	6100	3400	0.56
K.....	1.63	7600	4400	0.58
Rb.....	1.53	8100	4800	0.59

$$W_1 = \frac{hc}{\lambda} = 0.262 c \frac{e^2}{R}$$

TABLE 10
Relation between ionizing potential and atomic radius

ELEMENT	PACKING RADIUS OF ATOMS	IONIZING POTENTIAL	$R \times (I.P.)$
Li.....	1.51	5.37	8.1
Na.....	1.86	5.13	9.5
K.....	2.25	4.1	9.2
Cl.....	1.08	8.2	8.9

outer structure. They are the elements in the first five groups of Periods, 5, 7, and 9 of the periodic table. For brevity such atoms will be called "complex" atoms. The other atoms, which tend to revert upon combination to the inert-gas type of atom

will be called "simple" atoms. Excluding from consideration the first two periods of the table (i.e., H, and the period from He through F), the new law is as follows: "The ratio of the radii of any two simple atoms belonging to the same vertical column in the periodic table is the same as the ratio of the radii of any other two simple atoms on the same horizontal lines of the table provided that these atoms also belong to a common vertical column." When the atoms concerned are spheroidal, the ratio may be taken between their equatorial radii or between their axial radii. The law is illustrated in table 11. By it rough predictions may be made of the radii of the atoms of elements,

TABLE 11
Ratio of atomic radii

Ar/Ne = 1.57/1.26 = 1.25	Kr/Ar = 1.71/1.57 = 1.09
K/Na = 2.25/1.86 = 1.21	(1) Zr/Ti = 1.62/1.48 = 1.09
Ca/Mg = 1.96/1.61 = 1.22	(2) Zr/Ti = 1.59/1.45 = 1.10
(1) Ti/Si = 1.48/1.17 = 1.26	Mo/Cr = 1.36/1.25 = 1.09
(2) Ti/Si = 1.45/1.17 = 1.24	(1) Ru/Fe = 1.34/1.23 = 1.09
	(2) Ru/Fe = 1.32/1.23 = 1.07
	Rh/Co = 1.35/1.26 = 1.07
	Ta/V = 1.42/1.32 = 1.08
	W/Cr = 1.36/1.25 = 1.09
(1) Os/Fe = 1.36/1.23 = 1.11	
(2) Os/Fe = 1.33/1.23 = 1.08	
Ir/Co = 1.35/1.26 = 1.07	
Pt/Ni = 1.39/1.25 = 1.11	

whose crystal structure has not yet been determined. This is brought out in figure 5.

The application of atomic shapes and radii to the study of diffusion was touched on incidentally during the discussion of cubic atoms. It would make an interesting thesis for some graduate student to study the diffusion of atomic hydrogen through single crystals of all the body-centered cubic metals. Atomic dimensions are not generally useful in studying the diffusion of one metal through another, because this usually involves a consideration of the shapes and sizes of *ions* rather than of *atoms* (3). Further discussion of this point will be deferred until after the sizes of ions have been taken up.

IONIC SHAPES AND SIZES

There are, in general, two ways by which two elements may be held together in chemical combination. One is by the direct transfer of valence electrons from the atoms of one element to

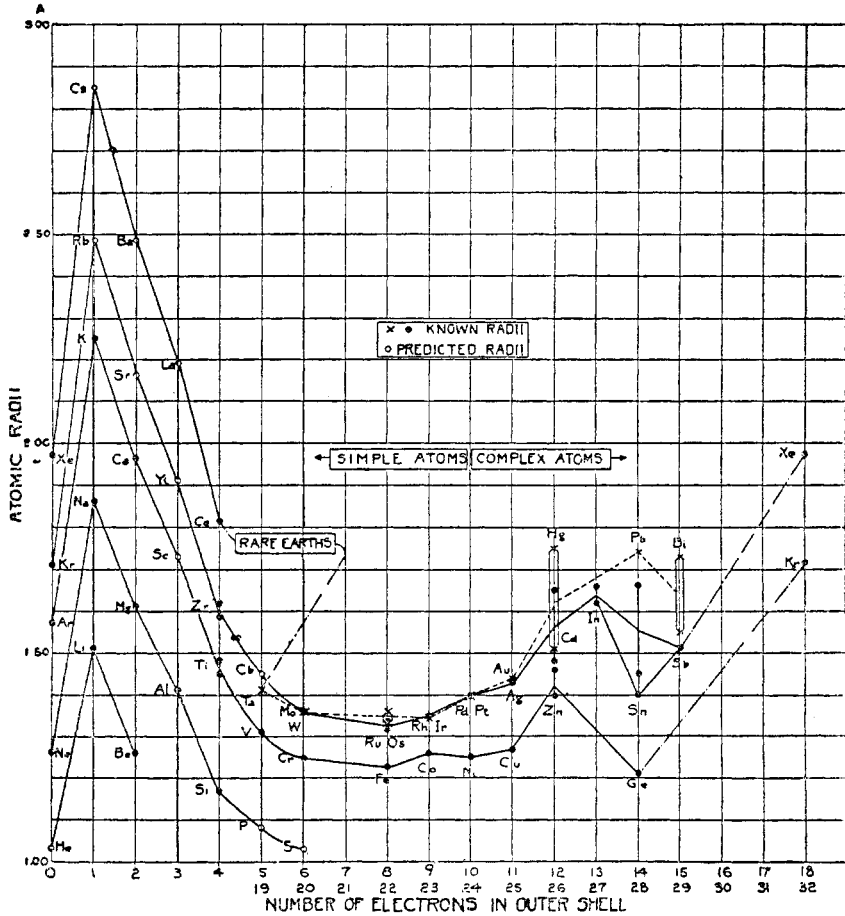


FIG. 5. PERIODIC LAW OF RADII

the atoms of the other element. The other is by the sharing of certain electrons by the atoms of both the elements. The first method produces "ionic" compounds in which the crystal of the solid is made up not of *atoms* but of *ions*. When crystals

of this sort are dissolved in water, the resulting solutions are electrically conducting. When these crystals are fused, they conduct by ionic conduction and the compound may be decomposed by electrolysis. All simple inorganic salts and all oxides and sulphides of metals with a valence of one or two are supposed to be of this sort. It is a characteristic of these compounds that they crystallize in such a way that each ion of one element is surrounded by ions of the other element, symmetrically placed and equally spaced.³ The second method produces "non-ionic" compounds. These include the oxides of elements with a valence of three or more, many organic crystals, and such radicals as NO_3^- , CO_3^{--} , SO_4^{--} , etc.

The shape and size of an atom in the crystal of an element is, in general, quite different from that of the same element in combination, and the shape and dimensions in an ionic compound will necessarily be quite different from what they are in a non-ionic compound. If an element can have more than one valence, the ion will have a different size and shape for each valence. The radii of atoms when combined by sharing electrons are beyond the scope of this paper. Empirical estimates of these radii have been made and discussed in the well-known paper by W. L. Bragg (14). They are also discussed in the Bragg's book, "X-rays and Crystals Structure," 4th edition (Bell and Sons, 1924). There remains then to be discussed, the size and shape of the various ions.

No matter what picture we adopt of atomic structure, it is evident that the electrostatic forces inside of a "metallic" atom will be altered by the subtraction of each valence electron, with the result that the positive ion must be smaller than the neutral atom. The greater the number of valence electrons which are subtracted, the greater will be the change in the electrostatic forces and the smaller will the positive ion become. Similarly, a negative ion must be larger than the corresponding neutral atom, and the greater the valence of the element, the more

³ According to Pease (13), compounds such as Si C, Cu I, Ag I, etc., which crystallize in the diamond-cubic lattice are, in a sense, non-ionic in spite of the equal spacing and symmetrical locations.

will the negative ion swell beyond the size of the neutral atom. When an attempt is made to determine the absolute sizes of these ions from crystal structure data, it is at once found that

TABLE 12

*Difference between ionic radii*Differences in distances of closest approach in 10^{-8} cm.

	IODIDE	BROMIDE	CHLORIDE	FLUORIDE
Cs.....	3.947±0.004	3.713±0.004	3.566±0.004	
Rb.....	3.662±0.004	3.434±0.003	3.285±0.003	
Difference.....	0.285±0.008	0.279±0.007	0.281±0.007	
Cs.....	3.947±0.004	3.713±0.004	3.556±0.004	3.084±0.003
K.....	3.525±0.004	3.285±0.003	3.138±0.003	2.664±0.003
Difference.....	0.422±0.008	0.428±0.007	0.418±0.007	8.340±0.006
Cs.....	3.947±0.004	3.713±0.004	3.566±0.004	3.004±0.003
Na.....	3.231±0.01	2.968±0.003	2.814	2.310±0.002
Difference.....	0.716±0.007	0.745±0.007	0.752±0.004	0.694±9.005
Cs.....	3.947±0.004	3.713±0.004	3.566±0.004	3.004±0.003
Li.....	3.01±0.01	2.745±0.003	2.566±0.003	2.007±0.002
Difference.....	0.94±0.01	0.968±0.007	1.000±0.007	0.997±0.005

Differences in distances of closest approach in 10^{-8} cm.

	CAESIUM	RUBIDIUM	POTASSIUM	SODIUM	LITHIUM
I.....	3.947±0.004	3.662±0.004	3.525±0.004	3.231±0.003	3.01±.01
Br.....	3.713±0.004	3.434±0.004	3.285±0.003	2.968±0.003	2.745±0.003
Difference....	0.234±0.008	0.228±0.008	0.240±0.007	0.263±0.006	0.26
I.....	3.947±0.004	3.662±0.004	3.525±0.004	3.231±0.003	3.01±.01
Cl.....	3.566±0.004	3.285±0.003	3.138±0.003	2.814	2.566±0.003
Difference....	0.381±0.008	0.377±0.007	0.387±0.007	0.417±0.003	0.44
I.....	3.947±0.004		3.525±0.004	3.231±0.003	3.01±.01
F.....	3.004±0.003		2.664±0.003	2.310±0.002	2.007±0.002
Difference....	0.943±0.007		0.861±0.007	0.921±0.005	1.00

Rb salts, Havighurst, Mack and Blake.

LiI, Wyckoff and Posenjak.

All others, Davey.

the data give only $n - 1$ equations with which to determine n ionic radii. These $n - 1$ equations alone, therefore, will not enable us to calculate *radii*, but only *differences between radii*. These differences are listed in table 12 in terms of the best data available to date, using $\text{NaCl} = 2.814 \text{ \AA}$ as a standard. It will be noticed that, if we exclude Li^+ , Na^+ and F^- , these differences are constant for any two ions, to within the precision of the data. In other words, contrary to what might have been expected, the radii of these ions are at least approximately independent of their state of chemical combination. The fact that this is obviously untrue for Li^+ , Na^+ and F^- makes it seem likely that more precise data would show slight changes in the values for the other ions. In our present state of knowledge it is sufficient to say that Cs^+ , I^- , Rb^+ , Br^- , K^+ and Cl^- are so much more constant in size than Li^+ , Na^+ and F^- that we may consider them to act like rigid objects.

In order that we may advance from differences between radii to the radii themselves, it is necessary to make some plausible assumption which will furnish an additional equation. This assumption is furnished by the x-ray diffraction patterns themselves (15). When the diffraction patterns of the alkali halides are examined, it is found that Cs^+ and I^- have, as nearly as can be determined, equal diffracting power. Rb^+ and Br^- and K^+ and Cl^- respectively, also seem to have equal diffracting power. These three pairs are the only ones among the alkali halides for which this is so. A glance at the Periodic Table shows that each pair lies adjacent to an inert gas, and that each of the ions of each pair contains the same number of electrons as the adjacent neutral atom of the inert gas. The theory of diffraction leads us to believe that the only way in which equal numbers of electrons can show equal diffracting power is for them to be arranged similarly in atomic domains of equal volume. If our data on equality of diffracting power were quite reliable we would have three independent equations

$$\begin{aligned}\text{Radius of } \text{Cs}^+ &= \text{radius of } \text{I}^- \\ \text{Radius of } \text{Rb}^+ &= \text{radius of } \text{Br}^- \\ \text{Radius of } \text{K}^+ &= \text{radius of } \text{Cl}^-\end{aligned}$$

An actual trial shows that these equations are approximately true for they give fairly consistent values of ionic radii in spite of having two more equations than are needed. That they are not anything more than good approximations may be shown as follows. The periodic table would tempt us to make a fourth equation, similar to the other three, stating the equality of radii of Na^+ and F^- . But in this case the x-ray evidence clearly shows that the ten electrons in Na^+ do not have the same diffracting power as the ten in F^- , and that therefore their radii are probably different. This is not surprising when we remember that the ten in F^- are pulled inward by a nuclear charge of 9, while in Na^+ they are pulled in by a charge of 11. It would therefore seem as though the other pairs of ions were not quite of equal radius. This is confirmed by table 12, which shows that $\text{Cs}^+ - \text{Rb}^+$ is not quite equal to $\text{I}^- - \text{Br}^-$ and that $\text{Cs}^+ - \text{K}^+$ is not quite equal to $\text{I}^- - \text{Cl}^-$. Since the ions Cs^+ and I^- have the highest atomic numbers of any of the alkali and halogen ions, we will assume that the best approximation will be had by considering that their radii are equal to each other and therefore that each has a radius equal to one-half the distance of closest approach of Cs^+ and I^- in CsI . This assumption together with the differences listed in table 12 give us the ionic radii of table 13.

It will be interesting to compare these results with those of other investigators using other methods. Lande (16) assumes that since Li^+ contains only two electrons, it must be negligibly small in the presence of I^- in LiI . This should give an upper limit for the radius for I^- . By means of table 12, lower limits are obtained for the radii of the alkali ions, and upper limits for the halogen ions. The space-lattice constants used by Lande were considerably in error, so that his results have been recalculated for table 14. Richard's values (17) 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." His values have been recalculated using the data for CsCl which were used in table 12. Eve (18) has pointed out that the product of the ionization potential by this ionic radius is roughly a

constant. This has since been shown to have a theoretical basis (9). Saha (19) has used ionization potentials to calculate the ionic radii of metals according to this law. In comparing these radii with others, it should be remembered that they correspond

TABLE 13
Radii of the alkali and halogen ions

Cs ⁺	1.974×10^{-8} cm.	I ⁻	1.974×10^{-8} cm.
Rb ⁺	1.696	Br ⁻	1.740
K ⁺	1.548	Cl ⁻	1.589
Na ⁺		F ⁻	
in NaI.....	1.257	in CsF.....	1.030
in NaBr.....	1.231	in RbF.....	—
in NaCl.....	1.225	in KF.....	1.116
in NaF.....	<1.15	in NaF.....	>1.15
Li ⁺			
in LiI.....	1.03		
in LiBr.....	1.01		
in LiCl.....	0.98		
in LiF.....	<0.86 (?)		

TABLE 14
Comparison of radii obtained by different workers

	LANDÉ	RICHARDS	EVE AND SAHA	AVERAGE	DAVEY
Cs ⁺	1.81	2.2	1.9-	2.0	1.974
I ⁻	2.14	1.7		1.9	1.974
Rb ⁺	1.51	1.9	1.7	1.7	1.696
Br ⁻	1.90	1.5		1.7	1.740
K ⁺	1.38	1.6	1.7	1.6	1.548
Cl ⁻	1.76	1.4		1.6	1.589
Na ⁺	1.09	1.5	1.4	1.3	1.1-1.2
F ⁻	1.19				1.2-1.0

to relatively high temperatures, so that they probably approximate the upper limits for the radii of positive ions. Radii obtained by these three methods have been tabulated in table 14 to the same number of significant figures as given by the original authors. The radii derived above by the present writer may

therefore be more properly compared with the average of these other radii than with any one of them alone. This comparison is made in table 14.

The crystal structure of CsI, is body-centered cubic. Since this is the closest packing for equal numbers of oppositely charged spheres of equal radius, it would appear that Cs^+ and I^- are spherical ions. This is confirmed by the fact that $\text{CsI} - \text{CsBr}$ in table 11 is, within experimental error, equal to $\text{RbI} - \text{RbBr}$ and to $\text{KI} - \text{KBr}$ in spite of the fact that the directions through the ions differ by about $54\frac{1}{2}$ degrees. The structures of the RbK and Na halides show that the shapes of Rb^+ , K^+ , Na^+ , Br^- , Cl^- , F^- , are to be regarded as spheres with six flat spots, or what amounts to the same thing, cubes with rounded corners (20). These shapes are consistent with that mass of chemical data which has given rise to the "static atom" picture of atomic and ionic structure (12). The radii in such cases are measured in the direction of the distance of closest approach.

We are tempted to consider the radii of the inert gases to be half way between the radii of the adjacent ions in the Periodic Table. These radii are larger than those found by Rankine (21) from viscosity measurements. The crystal structure of solid argon has lately been determined (22). The radius of argon calculated directly from the distance of closest approach is considerably larger than that obtained in terms of K^+ and Cl^- . This is not surprising, for a crystal of argon at 40°K would not be under as high a state of compression as the oppositely charged ions in an ionic salt like KCl .

It has already been mentioned that the radii of ions are related to their ionizing potentials. This is not the only use for a knowledge of ionic radii. It is an experimental fact that Ag , Na and Li ions can migrate through hot glass under the influence of an electric field (23). It is found that K ions cannot travel readily through such glass, and that any attempt to force them to do so cracks the glass (24). This makes it seem as though there were tunnels of some sort through the silica framework of the glass which were large enough for Na^+ to pass through, but too

small for K^+ . A study of the diffusion of other ions through hot glasses would yield valuable information. Theoretical metallurgy offers a large field for the application of ionic radii, for it now appears that solid solutions are usually ionic rather than atomic in their nature (3). Unfortunately the use of ionic radii is limited at present because of the lack of certainty of ionic magnitudes other than of the alkalis and the halogens. Using different assumptions Pease (13) and the present writer (25) have arrived at quite different values for Cu, Zn, and Ag, and there seem to be very few other data which will serve as criteria to distinguish between the two sets of values. Data on diffusion and on the compressibilities of these ions are urgently needed.

REFERENCES

- (1) BORN: *Verh. d. deutch. phys. Gesel.*, **20**, 230, (1918).
- (2) HULL: *Proc. Am. Inst. Elect. Eng.*, **38**, 1171, (1919); *Jour. Franklin Inst.*, **193**, 189, (1922).
- (3) DAVEY: *Trans. Am. Soc. Steel Treating*, **6**, 375, (1924).
- (4) FULLER: *Trans. Am. Electrochem. Soc.*, **32**, 247, (1917).
EDWARDS: *Jour. Iron and Steel Inst.*, **110**, (1924).
- (5) DUCHMAN: *Gen. Elect. Rev.*, **18**, 1042, (1915).
- (6) WESTGREN AND PHRAGMEN: *Jour. Iron and Steel Inst.*, **109**, 159, (1924).
- (7) Work on the diffusion of C in Mo and W will be published by S. Dushman and M. R. Andrews.
- (8) THOMSON: *The Electron in Chemistry*, Franklin Inst. (1923).
- (9) DAVEY: *Jour. Franklin Inst.*, **197**, 479, (1924).
- (10) BORN: *The Constitution of Matter*, E. P. Dutton and Co. (1923).
- (11) DAVEY: *Phys. Rev.*, **23**, 318, (1924).
- (12) LANGMUIR: *Jour. Am. Chem. Soc.*, **41**, 868, (1919).
- (13) PEASE: *Jour. Am. Chem. Soc.*, **44**, 769, 1497, (1922).
- (14) BRAGG, W. L.: *Phil. Mag.*, **40**, 169, (1920).
- (15) DAVEY: *Phys. Rev.*, **22**, 211, (1923).
- (16) LANDE: *Zeit. f. Phys.*, **1**, 191, (1920).
- (17) RICHARDS: *Jour. Am. Chem. Soc.*, **43**, 1584, (1921); **45**, 422, (1923).
- (18) EVE: *Nature*, **107**, 552, (1921).
- (19) SAHA: *Nature*, (1921).
- (20) DAVEY: *Phys. Rev.*, **17**, 402, (1921).
- (21) RANKINE: *Proc. Roy. Soc.*, **84**, 182, (1920); *Phil. Mag.*, **42**, 601, (1921).
- (22) SIMON AND SIMSON: *Zeit. f. Phys.*, **25**, 160, (1924).
- (23) KRAUS AND DARBY: *Jour. Am. Chem. Soc.*, **44**, 2783, (1922).
- (24) SCHUMACHER: *Jour. Am. Chem. Soc.*, **46**, 1772, (1924).
- (25) DAVEY: *Phys. Rev.*, **19**, 248, (1922).