

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

THE MAGNITUDES OF ATOMS.

BY THEODORE W. RICHARDS.

Received April 12, 1921.

Recently two interesting papers upon the diameters of atoms have been published, namely, those of W. L. Bragg¹ and A. Landé.² The former makes use of the method of X-ray reflection; whereas the latter depends upon Bohr's theory. In view of the fact that the results do not agree, it may be not uninteresting to point out that another much simpler and less recondite method of obtaining approximate estimates of diameters of some of the atoms in question under varying circumstances has been available for several years. This method, although it is probably no more uncertain than either of the methods mentioned above does not seem to have attracted general attention.

In a paper³ summing conclusions concerning atomic volumes, I pointed out that from the study of the contractions which occur when elements combine, together with the compressibilities of those elements, it is possible to draw a plausible inference as to the bulk which the elements occupy when combined. A graph (which had as its main object the proof that the magnitude of the contraction is dependent in part upon the magnitude of the compressibility of the factors) was given, depicting the compressibilities of the metals of the alkalis compared with the contraction occurring during the formation of their chlorides. This graph is represented in the uppermost curve of the accompanying diagram (Fig. 1) which now gives also corresponding curves for bromides and iodides.

"An interesting corollary suggested by this diagram is to be found in the extrapolation of the curve toward the left. The point where the abscissa becomes zero indicates the hypothetical contraction which would take place if an imaginary incompressible element were combined with chlorine by an affinity about equal to that of the others, to form a compound similar to lithium chloride." Since, in this case, the contraction of 12.5 cc. must be due to the 25.1 cc. of chlorine alone, we may suppose that in each of the actual cases of the alkali chlorides the contraction must be about the same, and that in each case the chlorine occupies about $25.1 - 12.5 = 12.6$ cc. From this assumption and the actual total contractions, the hypothetical bulk which each atom must oc-

¹ W. L. Bragg, *Phil. Mag.*, [VI] **40**, 169 (1920).

² A. Landé, *Z. Physik*, **1**, 191 (1920); *C. A.*, **14**, 2124 (1920). A discussion of allied questions took place recently in the Bunsen Gesellschaft, *Z. Physik*, **2**, 309 (1921); *Z. Elektrochem.*, **26**, 502 (1920).

³ T. W. Richards, *THIS JOURNAL*, **36**, 2417 (1914).

copy in its chloride was computed. The numerical estimates are based, as has been said, upon the assumption that the chlorine is equally compressed by the several affinities of the alkali metals. The assumption is partially justified by the fact that the heats of formation of the sev-

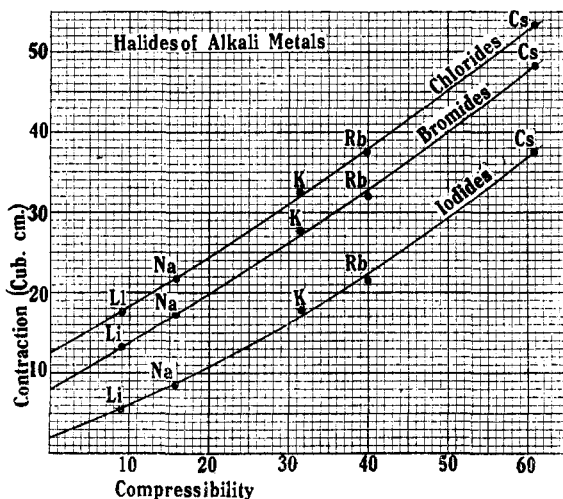


Fig. 1.

Fig. 1.—Graphs depicting the compressibilities of the alkali metals compared with the contraction during the formation of their halides. Contraction in cc. per mol is plotted ordinately; compressibilities of the elements are plotted as abscissas.

eral chlorides are nearly the same, and by the further fact that in such cases heat of formation is not very different from free energy change. Because the possible error of a cubic centimeter or two would make very little difference in the atomic diameters, however, these values will nevertheless be adequate for the present purpose.⁴ The probability is, that the affinity of the alkali metal increases somewhat as the atomic weight increases, which would make the volume of the chlorine somewhat less than 12.6 cc., especially in the cases of the heavier metals. Hence the values given below for the metals are minimal values.

⁴There is no need at present of attempting the analysis of the other questions which might affect such an estimate. In this latter category comes the question as to how nearly free energy change (which means the work which may be done in excess of that involved in the atomic compression) represents the force of affinity, and also the question as to the effect of the differing atomic volumes of the metals, which involve at the same time different bulks to be compressed and different surfaces exposed to pressure—circumstances partially counterbalancing one another. The heats of formation of the 5 alkali chlorides are respectively 392, 399, 431, 462, and 479 kilojoules.

On comparing the result for chlorides with those for bromides and iodides, it becomes evident that whereas the extrapolated value for the contraction of chlorides in forming alkali chlorides is about 12.6 cc., that of bromine on forming the alkali bromides is only about 8 cc. and that of iodine only about 2 cc. These latter figures (which likewise represent minimal values) are reasonable, since bromine in the elementary state is undoubtedly already much more compressed than chlorine. The so-called "atomic volumes" of bromine and iodine being respectively 25.6 and 25.7 cc., the bulks which these elements occupy in the bromides and iodides of the alkali metals can hardly exceed 17.6 and 23.7 cc. per gram atom respectively. Subtracting these values from the well-known molecular volumes of the halides we obtain the following values for the bulk of the metals in these compounds. As already said, all the figures for the metals being minimal values should probably be increased somewhat with increasing molecular weights; hence the table gives conservative evidence which can hardly fail to avoid exaggerating the differences to be emphasized.

TABLE I.—ATOMIC VOLUMES OF HALOGENS AND ALKALI METALS IN COMBINATION. (Cc. per gram Atom.^a)

	In chlorides.	In bromides.	In iodides.
Halogen.....	12.60	17.60	23.70
Lithium.....	7.90	7.47	9.26
Sodium.....	14.45	14.53	17.21
Potassium.....	24.92	25.70	29.46
Rubidium.....	30.61	31.77	36.12
Cesium.....	29.74	30.39	33.90

^a The second decimal place is not significant with regard to the individual values, but is significant with regard to their sums, which are simply the "molecular volumes" of the salts. The densities (20°/4°) used in these calculations were as follows: for the 5 alkali metals, respectively, 0.534; 0.9712; 0.8621; 1.532; and 1.882; for the 3 halogens, respectively 1.412; 3.120; and 4.94; for the 5 chlorides respectively, 2.068; 2.161; 1.987; 2.798; and 3.974; for the 5 bromides respectively, 3.464; 3.203; 2.749; 3.349; and 4.433; for the 5 iodides respectively 4.061; 3.665; 3.123; 3.550; and 4.509. See T. W. Richards and F. N. Brink, *THIS JOURNAL*, **29**, 117 (1907); G. P. Baxter, *Am. Chem. J.*, **31**, 558 (1904); Baxter and Wallace, *THIS JOURNAL*, **38**, 265 (1916). If Dewar's lower value for iodine were taken, the values for the bulk of the metals in the iodides would be somewhat reduced, but would still be much larger than the bulk in the bromides. (*Chem. News*, **91**, 216 (1905)). The compressibilities recorded in Fig. 1 are those of Richards and Stull, *Carnegie Inst. Pub.*, **7** (1903), and **76** (1907).

This table is striking in its evidence (wholly consistent except in the case of lithium bromide), that the metals are in a less compressed state in the bromides than in the chlorides and in a still less compressed state in the iodides. Such an outcome is only reasonable, considering the undoubted difference in the affinities of the halogens for the alkali metals, and granting that affinity and cohesion produce pressure and are

thus capable of diminishing the volume of the atoms and molecules upon which they act.

That this method gives reasonable and consistent results is shown by a similar calculation involving the three halides of potassium. These, evolving respectively 431, 398 and 335 kilojoules in their formation show attendant volume changes of respectively —33.0, —27.7 and —18.0 cc. Extrapolating to zero compressibility both sets of values (plotted as above in relation to the compressibility of the halogen) to represent an imaginary incompressible halogen, we find that the heat of the formation of the imaginary halide of potassium would be 300 kj. and the attendant contraction (to be referred wholly to the potassium) about 14 cc. per mol. Assuming direct proportionality,⁵ the 431 kj. evolved when potassium chloride is formed should then correspond to about 20 cc. contraction of the potassium. We have seen that the contraction of the chlorine is to be considered as about 12.6. The sum of these two values 32.6, is very near the actual contraction, 33.0. Hence we may reasonably believe that the contraction has been rightly apportioned between the two component elements, and therefore that the volumes of the combined atoms are known with rather surprising exactness.

The figures in the table just given record the so-called "atomic volumes" of the metals in the several halides. From these figures, thanks to the remarkable investigations of Millikan and Perrin and others, we are able to compute at once the bulks occupied by the individual atoms and therefore the diameters which they must possess. Assuming that each gram-atom contains 6.062×10^{23} atoms, the following table is obtained for the bulk of the individual atoms in question under the varying circumstances.

TABLE II.—VOLUMES OF INDIVIDUAL ATOMS UNDER VARYING CIRCUMSTANCES.

Each Value is Multiplied by One Septillion (10^{24}) cc.

	In chlorides.	In bromides.	In iodides.
Halogen.....	20.8	29.0	39.1
Lithium.....	13.0	12.3	15.3
Sodium.....	24.3	24.4	28.4
Potassium.....	41.1	42.4	48.6
Rubidium.....	50.5	52.4	59.6
Cesium.....	49.0	50.1	55.9

Since in the halides, on account of the large volume changes and the intensity of compression, the atoms of the elements must be compressed

⁵ The true relationship is doubtless not one of exact proportionality, but in the absence of knowledge as to its nature this may be assumed as a first approximation. Of course a similar correction should be applied to the halogens as given in the table, each of which must really have different values in combination with the different metals. Here, however, the affinities concerned being more nearly equal for any given halogen, this correction seemed to be a work of supererogation.

into nearly cubical form⁶ (See Fig. 2), a close approximation to the distance between the faces of the atoms is to be obtained by simply tak-

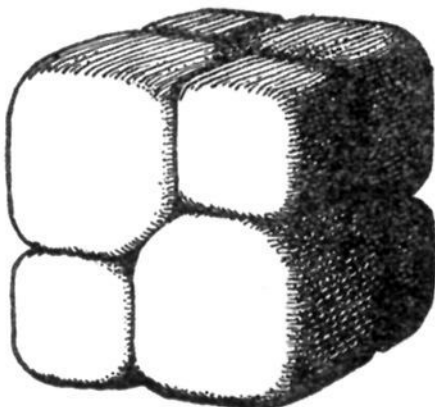


Fig. 2.

ing the cube roots of the volumes. This approximate distance in the case of chlorine is $20.6 \times 10^{-24} = 2.75 \times 10^{-8}$ cm. The following table records the results.

TABLE III.—THE CUBE ROOTS OF THE VOLUMES OF INDIVIDUAL ATOMS UNDER VARYING CIRCUMSTANCES.

(Each Value expressed in Ångstrom units.)

	In chlorides.	In bromides.	In iodides.
Chlorine.....	2.75
Bromine.....	3.09
Iodine.....	3.39
Lithium.....	2.35	2.35	2.48
Sodium.....	2.90	2.90	3.05
Potassium.....	3.45	3.49	3.65
Rubidium.....	3.70	3.74	3.91
Cesium.....	3.66	3.69	3.82

A clearer insight into the meaning of these figures may be gained from a glance at the diagram, which, representing the arrangement in space of the atoms of the alkali halides, has since been essentially confirmed by W. H. and W. L. Bragg, and may be considered as fairly certain.⁷ Incidentally attention may be called to the fact that the crystal must be built up of quadrimolecular units of this sort, not units with 3 atoms on each edge, since the latter unit (having 27 atoms in all) would have a surplus of one atom either of chlorine or metal.⁸ Whether or not such cubes unite evenly so as to cause the crystal to be a single molecule does not greatly concern us at present.

⁶ T. W. Richards, *THIS JOURNAL*, **35**, 381 (1913); **36**, 1686 (1914).

⁷ Compare W. J. Sollas, *Proc. Roy. Soc.*, **63**, 273 (1898), who first proposed this arrangement, without, however, postulating atomic compression. See also T. W. Richards, *THIS JOURNAL*, **35**, 381 (1913).

⁸ Compare W. H. and W. L. Bragg, "X-rays and Crystal Structure," **1916**, p. 95.

A glance at the diagram shows that the data as given above in Table III need a slight correction, since they are computed for perfect cubes, and the "atomic domain" of the larger atom of her pita must have its cubic shape somewhat modified in order to attain perfect close packing. In other words, because of the basis of the calculation, it is necessary to account for *all* the molecular volume. This fact must cause the true distance between the atomic centers to be slightly greater than half the sum of any two of these cube roots—unless the two atomic volumes are identical, when half the sum of the roots gives the exact value. The true distance between the atomic centers may obviously be found by calculating the edge of the cube or crystal unit depicted in Fig. 2. Such a cube involves 4 molecules. The gram-molecular volume of CsCl is 42.34; hence of 4 CsCl, 169.36 cc. Dividing by 6.062×10^{23} and extracting the cube root of the result we have 6.53×10^{-8} cm., the exactly computed length of the edge of such a cube. The sum of the atomic diameters given in Table III is 6.40, a difference of 0.13 Ångstrom. This difference must be due to the modification of the larger of the two cubes at the inside edges, as shown in the diagram. Only in the cases of rubidium chloride and lithium iodide is any other deviation as great as this. Usually the effect is negligible.

Evidently, since the smaller cube of any pair is probably not essentially modified, its value may be taken as correctly given in the preceding table, and the distance between the faces of the larger atom may be computed as the difference between the total value and the smaller exact cube root from Table III. These distances may be called "atomic diameters" of which the corrected values are given in the table below, compared with the figures for the same elements obtained by Landé and Bragg respectively.

TABLE IV.—DIAMETERS (*d* OR *d'*) OF INDIVIDUAL ATOMS OF ALKALI METALS AND HALOGENS (IN ÅNGSTROM UNITS).

	Landé.	Bragg.	T. W. R. In chlorides.	T. W. R. In bromides.	T. W. R. In iodides.
Chlorine.....	3.3	2.1	2.8
Bromine.....	3.6	2.4	...	3.1	...
Iodine.....	4.1	2.8	3.4
Lithium.....	...	3.0	2.3	2.4	2.6
Sodium.....	2.2	3.5	2.9	2.9	3.1
Potassium.....	2.9	4.2	3.5	3.5	3.7
Rubidium.....	...	4.5	3.8	3.8	3.9
Cesium.....	3.2	4.7	3.8	3.7	3.8

It is striking that the newly recorded values all lie about half way between those of Landé and those of Bragg. Landé's results for the halogens are all much larger, and accordingly, his results for the metals all much smaller than the other estimates. One cannot help thinking that

Landé's estimates are in error, especially because his value for iodine, for example, corresponds with an "atomic volume" of this element in iodides of 38.8 cc., which means an *expansion* per 127 g. of iodine of over 13 cc. in the act of forming an iodide. All evidence upon the question of volume change in chemical reaction contradicts such a conclusion. Nevertheless it is interesting that Landé's figures, depending upon hypothetical assumptions, should be as close to the others as they are.

Bragg's results, depending much more closely upon experiment, are safer, but seem to demand a rather excessive contraction of halogen. For example, a gram-atom of chlorine in the act of combination, is made to contract from 25.1 cc. to 5.6 cc., which seems unlikely. Probably the method of calculation (which involved no consideration of the changing volume of an atom under varying affinity-pressures) must have caused this anomaly. While admitting that the atom (or its "sphere of influence") might change somewhat in size, he does not appear to have correlated different values in relation to the affinities concerned.

Bragg's statement⁹ that the cesium atom, when combined with a halogen, occupies less space than the rubidium atom, is verified by these new results. He points out that with oxygen compounds of cesium the reverse is the case. May not the reason for this apparent contradiction be simply that the affinity of cesium for the halogens is much greater than the affinity of cesium for oxygen? The heat of oxidation of a gram-atom of cesium is only 172 kj., whereas $\text{Cs} + \text{Cl}$ evolves 479 kj. In the case of a very compressible element like cesium this difference of affinity is quite enough to account for the apparent contradiction, and all the results fall thus into line.

The importance of change of volume under the influence of chemical affinity and cohesion, in any such calculations, cannot be over-estimated. The arguments in favor of it, based upon the comparative volumes of liquids and solids, are so convincing as to leave no doubt concerning the magnitude of the changes involved.¹⁰ They are not matters of theory, but the actual result of the comparison of accurately determined molecular volumes of elements and compounds. For example, 70.6 cc. of cesium combines with 25.1 cc. of liquid chlorine (95.7 cc. in all) to make only 42.34 cc. of cesium chloride. That such contractions are greater the greater the compressibilities of the elements concerned, is likewise clear, and so is the effect of the cohesion of the product.

The fact that the "atomic domain," or "sphere of influence," or "atomic playroom," or "practical bulk of the atom," (as this space has been variously called) thus changes, makes the assignment of any fixed volume to it under varying conditions illusory. The only reason why definite

⁹ W. L. Bragg, *Phil. Mag.*, [6] 40, 174 (1920).

¹⁰ T. W. Richards, *THIS JOURNAL*, 36, 2417 (1914).

bulks could be assigned as a first approximation to chlorine, bromine and iodine in the last three columns of Table III, is because the affinities of any one of these halogens for the different alkali metals are so nearly alike that the extent of chemical and cohesive compression of any one halogen must be nearly the same when in combination with each of the five metals. But even here this assumption cannot be absolutely correct although it serves as the basis of a conservative first approximation. Correction for this error would bring new results somewhat nearer to Bragg's, but apparently could not, in any probability, give volumes of the metallic atoms as large as he makes them.¹¹

There is nothing, in the present paper, inconsistent with the brilliant experimental results of the Professors Bragg. The only premise needed for the construction of a completely consistent scheme from all these varied data seems to be the recognition of the almost certainly ascertained conclusion that affinity and cohesion are capable of altering the "atomic domain," and that the compressibilities of the factors affect the outcome. Taking all these considerations together it is evident that there has been attained an insight into the actual magnitudes of the space demanded by atoms in crystals which was not dreamed possible twenty years ago.

The bearing of these conclusions upon the "valency volume" hypothesis of Pope and Barlow may be noted, but needs no discussion.¹²

Summary.

In brief it is pointed out that the contraction suffered during combination, taken in connection with the compressibilities of the elements combined, makes possible an approximate estimate of the bulk occupied by the several constituents in a compound.

Calculations are made for the diameters of the atoms of the halogen and the alkali metals, which diameters are found to lie about half-way between the results of Bragg and those of Landé.

Emphasis is placed upon the importance of considering the compressing effect of the affinities concerned, in making any comparison of atomic volume.

CAMBRIDGE 38, MASS.

¹¹ In a careful calculation (too complicated to be worth printing in this brief notice) in which maximum allowance was made for all reasonable corrections to these results, only one of them (CsI) was changed more than 0.1 Ångstrom. In this one case the "atomic volume" of the combined iodine found was only 19 cc. instead of 23.7, which makes the atomic diameter of this element 3.15 instead of 3.39 Ångstrom. This corrected value would make the diameter of the Cs atom 4.09 instead of 3.85. Most of the values given above were practically unchanged by this calculation.

¹² W. J. Pope and W. Barlow, *J. Chem. Soc.*, **89**, 1675 (1906); T. W. Richards, *THIS JOURNAL*, **35**, 381 (1913); **36**, 1686 (1914); W. J. Pope and W. Barlow, *ibid.*, **36**, 1575, 1695 (1914).