ART. XXVI.—*Upon the Atomic Volumes of the Elements*; by FRANK WIGGLESWORTH CLARKE, S.B.

IN a recent paper in this Journal I called attention to some remarkable relations which seem to exist between the atomic volumes of certain elements in the liquid condition. Since that time I have found similar relations between the same elements in the solid state, and also between the atomic volumes of some other solid elements of which no liquid compounds are known.

A few relations between the atomic volumes of different metals have previously been observed. Chief of these we find the equality of the atomic volumes of the metals of the iron group, the similar equality connecting the platinum metals, the equality between silver and gold, and that between molybdenum and tungsten. But, as far as I have been able to learn, nothing seems to have been done toward studying the more remarkable multiple relations which connect the members of certain natural groups with each other.

None of the specific gravities cited in this paper are due to my own determinations. I have simply collected the most reliable data which I have been able to find upon specific gravity, and thence calculated the atomic volumes of the elements. But in every case I shall try to give the authority to whom the experimental observations are due.

The alkaline metals most appropriately come first in order. For the first four only have we any data, since cæsium has not been isolated. The specific gravities are as follows. Lithium 0·589, Bunsen; sodium 0·972, and potassium, 0·865, Gay Lussac and Thenard; rubidium 1·52, Bunsen. Upon dividing the atomic weights of the four metals by these specific gravities we get as their atomic volumes respectively the numbers 11·9, 23·7, 45·1, and 56·2. It will at once be seen that the three highest of these values are very nearly multiples by whole numbers of the lowest. If we assume that in reality an exact multiple relation connects the members of this group, and then, adding together the atomic volumes actually found for them, we take an average in order to get the multiples with the least possible alteration of our data, we obtain for these four metals the values 11·4, 22·8, 45·6, and 57·0. These stand to each other as 1 : 2 : 4 : 5, and vary but very slightly from the numbers actually found, and, moreover, correspond to these trifling alterations in the specific gravities, respectively, ·025, ·037, ·010, and ·022. Is it not safe to assume that under strictly comparable circumstances this apparent multiple relation would prove to be exact?

The oxygen group, oxygen, sulphur, selenium, and tellurium, affords a still more remarkable series of values. The atomic volume of oxygen in its solid compounds, varies according to the nature of the combination. For this element in the solid state Kopp has deduced three values,—2·6, 5·2, and 10·4. Kopp himself has called attention to the fact that these stand to each other as 1 : 2 : 4.* For this element in liquid compounds the same observer deduced the values 7·8 and 12·2. If we compare these with the values for solid oxygen we shall find that the four lowest numbers stand exactly in the ratio of 1 : 2 : 3 : 4, and that an alteration of 0·8 in the highest, making it 13·0 instead of 12·2, will place it also as a fifth multiple of the lowest. I cannot but think it probable that Kopp himself must have noticed this relation, although I find no mention of it in any paper of his that I have seen. The atomic volume of sulphur varies, both with its crystalline form, and with the state of combination. The specific gravity of the octahedral modification, according to Marchand and Scheerer, is 2·045. This gives us for its atomic volume the number 15·6, precisely three times the second value for oxygen. In the liquid condition also, it will be remembered that the lower value for sulphur, 23·4, is three times the lower value for oxygen.

Many metallic sulphids possess atomic volumes very nearly the sums of those of the free sulphur and the metal. The native sulphids, syepoorite, CoS, millerite, NiS, and troilite, FeS, however, seem to vary from this rule. Their atomic volumes, deduced from the specific gravities given in "Dana's Mineralogy," are respectively 16·9, 17·6, and 18·4. But here it must be borne in mind that the native minerals are not absolutely pure, and that the specific gravity of each mineral often varies considerably. Since the metals in these three sulphids have equal atomic volumes, and since their corresponding compounds in most cases have equal values also, it seems safe to assume that these minerals in an absolutely pure condition, would possess also equal atomic volumes. The mean of the three numbers above given is 17·6. If we subtract from this the value of the metal, 6·9, we get 10·7, as the atomic volume of the sulphur, a number varying but 0·3 from twice the second number for oxygen. As we pass on we shall meet farther confirmations of this apparent multiple relation. In the liquid state sulphur has three atomic volumes, two of which,

* Buff, Kopp and Zamminer. "Lehrbuch der Physicalischen und Theoretischen Chemie."

23·4 and 28·6, are cited in my last paper.* The first of these is three times the lower value for liquid oxygen, and of course is also a multiple of 2·6, which seems to be the starting point for this series. The second is also an exact multiple of 2·6. In two observations Buff obtained for the atomic volume of sulphuric anhydrid at its boiling point, the numbers 44·18 and 44·19. Regarding this compound as $(SO_2)O$, and taking Kopp's determination of the higher value for liquid oxygen, he deduced from these numbers as the atomic volume of hexvalent sulphur in its liquid compounds, the value 12·0. If, however, we take as the higher value of oxygen the altered number 13·0, we shall get as the value of sulphur in $(SO_2)O$ the number 10·39, which agrees closely with the 10·4 above suggested for sulphur in the solid sulphids of iron, cobalt and nickel.

The approximate equality between the atomic volumes of solid sulphur and selenium has often been noticed, and in my last paper I showed that a similar equality probably existed in the liquid condition. The specific gravity of crystalline selenium, according to Hittorf, is 4·808. This gives us as its atomic volume, 16·5, which exceeds by 0·9 the value for octahedral sulphur. An exact equality between sulphur and selenium, however, seems to me doubtful, since I have repeatedly noticed that, *as a rule*, the atomic volumes of selenids slightly exceed those of the corresponding sulphids, and also that the selenates have values slightly in excess of the sulphates. Yet there are striking exceptions to this, and the point is by no means decided.

Like the sulphids, many selenids have atomic volumes equal to the sum of those of the selenium and the metal. For the proto-selenid of iron we have no data, but the artificial selenids of cobalt and nickel, CoSe and NiSe according to Little, have the specific gravities 7 65 and 8·46, whence we obtain for their atomic volumes the numbers 18·2 and 16·9, or a mean of 17·5. This is very near the mean obtained for the sulphids, and gives us as another value for selenium, the number 10·6, only 0·2 greater than the double multiple of oxygen.

The sp. gr. of tellurium, according to Löwe, is 6·18, and hence we get as the atomic volume of this element, the value 20·7. 20·8 is exactly four times the second value for oxygen.

We now see that in the solid condition the atomic volumes of these four elements are to each other very nearly in the relation of 1 : 3 : 3 : 4, and since the first three preserve the

* My paper in the March No. of this Journal was sent to press before I had seen Buff's calculation of the atomic volume of hexvalent sulphur. See Buff's "Grundlehren der Theoretischen Chemie"

same relation in the liquid state, we must naturally expect that the fourth, (for which we have no data in its liquid compounds) will follow the same rule also. But this, although so extremely probable, remains to be proved. Other theoretical reasons might be adduced in support of the idea, but I prefer leaving the question for experiment to settle. In order to show more clearly the remarkable relations connecting the different atomic volumes of this group, I have arranged the values for these elements, both in the solid and liquid state, in the following tabular form. The independent numbers are those determined by theory, those in parentheses being the values actually determined.* This is in order to show the extent of alteration when change has been necessary.

Oxygen,	2·6	5·2	7·8	10·4	13·0 (12·2)	---	---	---	---
Sulphur,	--	--	--	10·4 (10·7)		15·6	---	23·4 (22·6)	28·6
Selenium,	--	--	--	10·4 (10·6)		15·6 (16·5)		23·4 (23·2)	---
Tellurium,	--	--	--	---	---	---	20·8 (20·7)		---

Of these thirteen numbers six need no alteration, and the amount of change in the other seven, varies from a minimum of 0·1 to a maximum of 0·9. Moreover, from 2·6 up to 28·6, but two multiples of the lowest are wanting, and if we place, from theoretical reasons given above, the atomic volume of liquid tellurium at 31·2, this relation becomes still more noteworthy.

It is worth while in this connection to observe the remarkable multiple relation connecting the atomic weights of this group.

Between the different allotropic conditions of sulphur and selenium I find no numerical relations whatever. The atomic volume of prismatic sulphur I find to be from 16·3 to 16·7, and that of amorphous selenium to be 18·6. These values find no place in the series above given.

The nitrogen group affords another remarkable series of relations. In the liquid state, it will be remembered, nitrogen has three values, 2·15, 8·6, and 17·2, all multiples of the lowest. Then came boron, phosphorus, vanadium, and arsenic, with a common value, three times the second number for nitrogen. In the solid state, however, we find a variation from this. For nitrogen itself we have few suitable data, and I have made no elaborate calculations concerning it; yet as far as I have examined, it seems to possess several values. One of these is easily found. Kopp determined the atomic volume of NO_3 in nitrates, as 28·6: and if we subtract from

* In the numbers which required no alteration, parentheses seemed unnecessary.

this three times the most common value for oxygen, or 15·6, we have left, as the atomic volume of the nitrogen, the number 13·0. The specific gravity of crystalline red phosphorus, ("metallic phosphorus") according to Hittorf is 2·34, and hence, as its atomic volume, we get 13·2. Bettendorf found the specific gravity of crystalline arsenic to be 5·727, which gives us the atomic volume 13·1. For free vanadium we have no data, but the oxyd V_2O_2 has the specific gravity 3·64, (Schafarik) and hence the atomic volume 37·1. From this, subtracting the value of the oxygen, giving the latter element its second value, we obtain as the atomic volume of vanadium the number 13·3.

It must be borne in mind that both in this case, and with the radical NO_3, it is a pure assumption to give oxygen its second value, instead of its first or third, yet the assumption seems warranted by the results. From these numbers we see that in the solid state, some at least of the atomic volumes of nitrogen, phosphorus, vanadium, and arsenic, are equal, the mean being 13·15. 12·9 (a change of 0·25) is precisely half the atomic volume of the three latter elements in the liquid state, and a multiple by 6 of the lowest value for nitrogen. In connection with the apparent equality between phosphorus and arsenic, the fact is perhaps worth recalling that the alkaline phosphates and arsenates with 12 aq. were found by Playfair and Joule to have equal atomic volumes.

Antimony was found by Dexter to have a specific gravity from 6·707 to 6·718. This gives its atomic volume as 18·1. If we make this 0·9 less, or 17·2, it becomes precisely half the value for this metal in its liquid compounds. Bismuth, according to Marchand and Scheerer, has a specific gravity of 9·799. Its atomic volume, then, is 21·43. 21·5 is exactly 10 times the lowest value of nitrogen. In the liquid state its atomic volume is a matter of uncertainty, since the specific gravity of only one volatile compound of bismuth has been taken. In my last paper I suggested that perhaps this metal in its liquid compounds might have the same value as antimony, although farther investigations might place it higher. If now, we assume that bismuth, like phosphorus, vanadium, arsenic, and antimony has in the solid state an atomic volume half that which it possesses in liquid compounds, we shall get as the atomic volume of liquid bismuth, the number 42·86, or more probably, 43·0, which is a multiple of the second value of liquid nitrogen. This seems highly probable, yet cannot be regarded as settled. Nevertheless, it will be seen that the values actually found for the metals arsenic, antimony, and bismuth, are to each other very nearly as 3 : 4 : 5.

The atomic volume of ordinary phosphorus is from 16·9 to 17·0, and that of the amorphous red variety from 13·9 to 14·5. That of amorphous arsenic is 15·9. These numbers seem to bear no distinct relations to the others.

In its liquid compounds the atomic volume of boron is equal to that of phosphorus and arsenic, but this relation does not hold true for the solid element. The specific gravity of the diamond modification is given in Graham-Otto's "Lehrbuch" as 2·68, whence we get 4·1 as the atomic volume. If we place this element in the nitrogen group, as its atomic volume in the liquid state would induce us, it is worth while to notice that its value here is very nearly twice the lowest number for nitrogen, and one-sixth (if the alteration be made) of its value in liquid compounds.

Passing now to the carbon group, we still find close multiple relations existing. The sp. gr. of the purest graphite is 2·25 (Brodie) and hence its atomic volume is found to be 5·3. If we alter this to 5·5, we have just half the value of carbon in its liquid compounds. In the "Handwörterbuch" the specific gravity of graphitoidal silicon is given as 2·49, and from this we get 11·2 as its atomic volume. This is 0·2 greater than a multiple by two of the altered value for graphite.

For titanium in the free state I have been able to find no data, but in its compounds it approximates closely to silicon. Rock crystal has the sp. gr. 2·663 (Deville), and an atomic volume of 22·5.* Octahedrite, TiO_2, has a sp. gr. of 3·82—3·95, corresponding to an atomic volume of 21·5. If we assume that the atomic volumes of silicon and titanium are equal, and double the altered value for graphite, we shall find as the calculated atomic volume of rock crystal and of octahedrite, the number 21·4, (giving oxygen its second value.) Again, the native mineral enstatite, $MgSiO_3$, has a sp. gr. of 3·13, and an atomic volume of 31·9. The artificial titanate, $MgTiO_3$, obtained by Hautefeuille, has a sp. gr. of 3·91, and hence the atomic volume 31·2. If we also take into account the seeming equality between the atomic volumes of these elements in their liquid compounds, the conclusion concerning their values in the solid condition seems almost inevitable.

The specific gravity of tin, according to Miller, is 7·177. Hence its atomic volume is 16·4, which is only 0·1 less than three times the changed value for graphite. If now we take into review these four tetrad elements we see that with very trifling variations, their atomic volumes for the solid state are

* For specific gravities of minerals quoted in this paper, see the last edition of "Dana's Mineralogy."

to each other as 1 : 2 : 2 : 3. In the liquid state these elements have values standing to each other as 1 : 3 : 3 : 4, and therefore, although in the case of carbon a very simple connection appears between the two states of aggregation, with the higher members of the group the relations become complicated.

The specific gravity of the diamond is 3·55, according to Pelouze, and from this we get as its atomic volume the number 3·4. Although this seems to stand in no direct relation to the other values found in this group, still it affords a starting point for a number of metals, as I shall show hereafter. In connection with the carbon group the tetratomic metal zirconium is worth noticing. Its sp. gr. is given by Troost as 4·15. From this we get the atomic volume as 21·7, a value 0·3 less than four times that of graphite. This, however, may be accidental.

Another noteworthy series of relations appears between the atomic volumes of certain groups of metals. In this series the iron and zinc groups are connected, and possibly also the platinum group is involved. The equality between the atomic volumes of the members of the iron group has often been noticed, yet, for the sake of completeness, I have thought it advisable to recalculate their values. The specific gravities are as follows: Chromium 7·3, Bunsen; manganese 8·013, John; iron 7·844, Bröling; nickel 9·118, and cobalt 8·957, Rammelsberg; uranium 18·4, Peligot; copper 8·94, a mean of five determinations by Marchand and Scheerer. Deduced from these, their atomic volumes are respectively, 7·1, 6·7, 7·1, 6·7, 6·7, 6·5, 7·1, the average being 6·84.

The sp. gr. of magnesium is 1·743 (Bunsen), that of cadmium 8·6 (Graham-Otto's "Lehrbuch") and that of frozen mercury is given by Schulze as 14·391. Hence the atomic volumes of these three metals are respectively 13·8, 13·0, and 13·9, or, very probably, equal, the average being 13·6. Zinc, which we would naturally expect to find classed with magnesium and cadmium, varies, its sp. gr. being 7·03—7·2, (Bolley) and hence its atomic volume 9–9·2. Now it has been observed that the protosulphates of magnesium, zinc, iron, nickel, and cobalt, and also the double sulphates of magnesium and copper, magnesium and zinc, and magnesium and cadmium, all of which contain 7 aq, possess equal atomic volumes.* Now, since all of these compounds are formed upon precisely the same type, and since an element may possess different atomic volumes in different compounds, we should be inclined to suspect definite relations between the values of the different metals forming these salts. These metals in the free state represent three dif-

* See "Watts' Dictionary," vol. i, Art. "Atomic Volume."

ferent values, viz: 6·84 for the iron group, 9·0–9·2 for zinc, and 13·6 for the cadmium group, yet in these sulphates all appear to possess the same atomic volume. Now it is noteworthy that 13·6 is almost exactly twice 6·84, and zinc stands between in such a manner that the three values are to each other almost exactly as 3 : 4 : 6. Whatever may be the place of zinc in this series, whether accidental or not, it is certainly very remarkable that the metals cadmium and magnesium, forming sulphates isomorphous with those of iron, cobalt, and nickel, should possess an atomic volume almost precisely double that of the latter metals. This relation must be more than a mere coincidence.

Another point to be noticed in regard to zinc and mercury is an exception to a rule which has seemed to hold true with the groups hitherto given. Between the atomic volumes possessed by these metals in the solid state, and their values in the liquid condition, no direct relation is manifest.

The platinum metals afford another remarkable instance of equality among atomic volumes, as has often been noticed. The specific gravities are as follows, according to Deville and Debray. Platinum 21·15, iridium 21·15, osmium 21·3–21·4, rhodium 12·1, ruthenium 11—11·4, palladium 11·4. Their atomic volumes are respectively 9·3, 9·3, 9·2–9·3, 8·5, 9·1–9·4, and 9·3. The average is 9·15, almost exactly the value for zinc, although this is probably a mere coincidence. A revision of the sp. gr. of rhodium will probably place it lower, and increase the atomic volume, so as to make the value for this group about 9·3.

Molybdenum and tungsten afford another well known examample of equality. The sp. gr. of the first is 8·64, (Bucholz,) and that of the second from 16·54—18·447, according to the state of aggregation and mode in which it was prepared, according to the observations (independent of each other) of Van Uslar and Zettnow. The atomic volume of molybdenum is therefore 11·2, and that of tungsten from 9·9–11·1. If instead of 11·1–11·2, we place the value for these metals at 11·4, we find that the latter number falls into a vacant place in the iron, zinc, and cadmium series, standing in that series so as to make the four values to each other as 3 : 4 : 5 : 6. This may be accidental, however.

The equality between silver and gold is also well known, the atomic volumes of these two metals being represented by the number 10·2.

A noteworthy relation to oxygen is found in the atomic volumes of the remarkably similar elements calcium, barium, strontium, and lead. The sp. gr. of calcium is 1·55 (Liés Bodart and Jobin), that of barium is 4·0 (Clarke), that of strontium 2·5418 (Matthiessen), and that of lead is 11·37 (Reich.) Hence the atomic volumes are respectively 25·8, 34·2, 34·3, and 18·2. These numbers approximate very closely to multiples of the lowest value for oxygen, 2·6. The number for lead requires no change whatever, that for calcium but 0·2, and those of barium and strontium but from 0·4–0·5, to produce the exact multiples. Whether this relation is accidental or not, it is impossible for me to say, but the coincidence is certainly remarkable.

Another similar relation we find between the atomic volume of the diamond, and those of certain metals which are often classed as tetratomic. The sp. gr. of glucinum is 2·1 (Debray), that of aluminum 2·56–2·65 (as given in the "Handwörterbuch), and that of thorium 7·657–7·795, (Chydenius). Hence their atomic volumes are respectively 6·7, 10·1–10·6, and 30·4–30·9. The atomic volume of the diamond is 3·4, that of glucinum wants but 0·1 of twice that, three times 3·4 is within the limits between which aluminum varies, and nine times 3·4, or 30·6, is within the limits for thorium. Cerium, according to Wöhler, has the sp. gr. 5·5, corresponding to an atomic volume of 16·7, which is 0·3 less than an exact multiple of that of the diamond. Perhaps this metal might be classed with the three above mentioned.

The remaining metals, as far as we have data, seem to find places in none of the previous series. Thallium, according to Crookes, has a sp. gr. of 11·81–11·91. Its atomic volume, then, is 17·2. Winkler gives the sp. gr. of indium as 7·421, which corresponds to an atomic volume of 10·2. For niobium, tantalum, lanthanum, didymium, yttrium, and erbium, we have no data whatever.

The sp. gr. of iodine is 4·947 (Handwörterbuch). This gives as its atomic volume the number 25·6, almost exactly two thirds of its value in its liquid compounds. The atomic volumes of bromine and fluorine in their solid compounds I have not been able to calculate in any satisfactory manner from the data at my command, since the values obtained did not agree with each other. The atomic volume of chlorine in solids, has been calculated by Kopp, who obtained two values; but between these and its value in the liquid state I have found no relations.

For hydrogen, the data at hand are quite complicated, not being in any connected series of compounds, and as far as I have been able to decide, it appears to have several values. However, in some of its solid compounds, hydrogen seems to possess the same atomic volume as in the liquid state, viz., 5·5. If we calculate the specific gravities of cerotene, $C_{27}H_{54}$, and melene, $C_{30}H_{60}$, upon the basis of this value for hydrogen, giving carbon the amended atomic volume of graphite, we shall get for the first the sp. gr. 0·846, and for the second 0·848. The specific gravities actually found for these bodies, as given in Weltzien's "Systematische Zusammenstellung," are respectively 0·861, and 0·890, a variation in the first case, of only 0·015, and in the second case of 0·042, from the calculated values.

Having thus compared the atomic volumes of many elements with each other, a question which now naturally arises, is, how far are the relations which have been found, significant, and how far are they accidental.

In work of this kind, great caution is necessary, for a slight prejudice in favor of the kinship of two elements might often lead one greatly astray. Thus, gold, silver, aluminum, and indium, possess almost exactly the same atomic volume, about 10·2, and yet no direct chemical relations are known to connect them, and they seem to belong to four different metallic groups.

Probably of a similar nature is the seeming relation between zinc and the platinum metals. Yet in spite of these dangers of error, some of the relations which are found between the atomic volumes of certain elements, cannot but be considered as deeply significant. The series of relations which I regard as fully made out, are the following: The multiple series of the alkaline metals; the series formed by oxygen, sulphur, selenium, and tellurium; the nitrogen series, and also that formed by carbon, silicon, tin, and titanium. The equal values for the platinum metals, and the similar case of the iron group. Of the series less thoroughly made out, or less easy to account for, I am inclined to regard that which connects the iron group with zinc and the cadmium group and possibly also with molybdenum and tungsten, as genuine. Also that series connecting the metals of the alkaline earth with oxygen. The series formed by the diamond, with glucinum and the kindred metals, and also the seeming relation between lead and oxygen, appear to me more questionable.

As a rule it will be seen that whenever an element possesses more than one atomic volume in its compounds, these different values are distinctly related to each other, and also to the value of that element in the free state. But between the different allotropic forms of an element, we find no distinct relations at all! If this be found to hold true, it will be plain that the different properties possessed by the same element in different compounds cannot be accounted for upon the supposition that in one compound the element exists in one allotropic form, and in another compound in another.

One of the most important points to which I have been led, seems to me to be the very direct and simple relations connecting the atomic volumes of an element in two different states of aggregation. In the oxygen series, the most common value for each element in the solid state is almost precisely two thirds of that which it has in the liquid condition. Phosphorus, arsenic, vanadium, antimony, and bismuth seem to have in the solid state, values just half those which they possess as liquids, and carbon seems to follow the same rule.

The exceptions found under zinc and mercury, however, must be borne in mind, showing as they do, that the law is not a general one. But how far these relations between solids and liquids holds true, seems to me a matter of great interest, as possibly affording a clue to some general law connecting the different states of aggregation.

One more point and I am done. In many cases, even when the relations between the elements have been plainest, it has been necessary to slightly alter the atomic volumes actually found, in order to bring them in accordance with theory. Some of these alterations have been wholly within the limits of experimental error, yet others are in this respect more doubtful. Now it has often been suggested that the atomic volumes of solids, like those of liquids, should be compared at similar temperatures, and under corresponding circumstances. For solids, the similar temperatures are supposed to be the melting points. Now in many of those cases in which I have altered the values actually found for elements, it would be wholly unjustifiable for me to ascribe the variations from theory to experimental error. And yet the multiple relations are often extremely plain, and by their occurrence in so many different series, they in a certain sense confirm each other. Therefore, taking all things into consideration, I am firmly convinced that whenever the atomic volumes of the elements are compared under strictly similar circumstances, then the relations between them will be found exact. In other words, the variations from theory are probably due to the fact that the specific gravities from which we calculate, were determined under dissimilar conditions. Concerning the cause of these relations between different elements, I shall hazard no conjectures. Not only are our data too incomplete, and unfit to form the basis of any theory, but it seems to me that until we know more of the nature of the elements themselves, it will be too early to attempt to frame any hypothesis whatever, concerning the cause of relations between them.