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

IF we divide the weight of a given bulk of any liquid at 0° by the weight of an equal bulk of its vapor at the same temperature, it is plain that the quotient will represent the number of volumes of vapor formed by one volume of the liquid, supposing both to exist at the above named temperature.

These quotients I term the *vapor volumes* of liquids. It is true that but few liquids can form vapor at 0°, and therefore these vapor volumes are fictitious quantities: yet, nevertheless, real or imaginary, exceedingly interesting results may be obtained by comparing them.

Of the relations existing between the vapor volumes of different liquids, I shall have but little to say in this paper, except in so far as they have been instrumental in determining atomic volumes. However, I will state as briefly as possible the leading results I have obtained by their comparison, but, as I am still at work upon the subject, I shall not enter into details.

In any homologous series of liquid compounds, the first member of the series possesses a higher vapor volume than the second, the second higher than the third, and so on indefinitely. I have yet found no exception to this rule, although I have calculated the vapor volumes of more than 400 different liquids. Furthermore, the difference between the vapor volumes of the first and second members of a series is greater than the difference between those of the second and third, and this again, greater than the difference between the third and fourth, and so on. The only exceptions I have found to this rule lie among compounds which stand so high in their respective series that the differences between their vapor volumes are very small, and consequently a very slight error in determining the specific gravities of the liquids is enough to account for the trifling variations from the rule. Even these exceptions are rare.

The first of these rules may be carried still farther. If we calculate the number of volumes of vapor actually formed at the boiling point by one volume of liquid at 0°, we shall find that the first member of a series forms more vapor than the second, the second more than the third, and so on as far as I have had data from which to calculate.

Hence it seems that the usual increase in the boiling points as we ascend in a series, is not sufficient to counterbalance the decrease in the vapor volumes. Since, however, the differences between the vapor volumes are constantly diminishing as we ascend in any series, it seems almost certain that there must be a point at which the increase in the boiling points will overcome the decrease in the vapor volumes, and therefore the amounts of vapor formed by the members of the series at their boiling points must begin to increase with every step upward. I have as yet found no such point, however, in any series upon which I have calculated.

In any series of substitution compounds, as a rule, the vapor volumes diminish as the atomic weights increase.

Chlorid of arsenic has a lower vapor volume than the fluorid. Bromids have lower vapor volumes than the corresponding chlorids, and iodids still lower than bromids. Sulphids, also, have lower vapor volumes than the corresponding oxyds.

Last of all I give the rule upon which most of my work upon atomic volumes is based. Whenever two compounds have equal vapor volumes, their atomic volumes also are equal, or nearly so, and, as a general rule, the greater the vapor volume the less the atomic volume, and *vice versa.* There is not an actual inverse ratio between the vapor volumes of liquids and their atomic volumes although a casual glance at the numbers would seem to suggest one. It must be remembered that the vapor volumes are calculated from the specific gravities of liquids at 0°, while the atomic volumes are referred to the boiling points, and therefore an exact inverse ratio would be very improbable.

Although as yet I have found no relations between the vapor volumes of liquids which would enable me to calculate their specific gravities at 0° from their composition, still the relations which I have found seem to me to indicate decidedly the existence of definite relations between the atomic volumes of liquids, their boiling points, and their rates of expansion.

We now come to the subject named at the head of this paper,—the atomic volumes of liquids. In 1855 Kopp published several articles upon this subject.* In them he described a method of calculating the atomic volumes of liquid compounds, showing that the atomic volume of any compound equalled the sum of the atomic volumes of the elements composing it, just as its atomic weight equalled the sum of the atomic weights of its constituent parts. For a large number of compounds he actually determined the atomic volumes, and thence deduced those of the elements contained in them; but, as he employed the old atomic weights, the numbers he gave for oxygen, sulphur, and carbon, have since been doubled. With this correction the list stands as follows. Hydrogen 5·5, chlorine

* "Annalen der Chemie und Pharmacie," xcvi, 153 and 303, xcvii, 374, xcviii, 367.

22·8, bromine 27·8, iodine 37·5. Oxygen, in the radical 12·2, out of the radical 7·8. Sulphur, out of the radical 22·6, in the radical 28·6. Nitrogen, in compounds of the ammonia type 2·3, in hyponitric acid 8·6, and in cyanogen 17. Carbon 11. Besides these he also determined experimentally the atomic volumes of the following compounds, some of which are amended to suit the new atomic weights.

PCl_3 93·9, PBr_3 108·6, $AsCl_3$ 94·8, $SbCl_3$ 100·7, $SbBr_3$ 116·8, $SiCl_4$ 122·1, $SiBr_4$ 144·2, $SnCl_4$ 131·4, $TiCl_4$ 126·0.

Kopp suggested at the time, that probably phosphorus and arsenic had equal atomic volumes, and added to them silicon also, whose chlorid, regarded as $SiCl_3$, gave the number 91·6. Silicon now, however, stands apart. Tin and titanium also he regarded as having equal atomic volumes, but changing the atomic weight of silicon has brought that element near these two, so that the atomic volume of titanium agrees better with that of silicon than with that of tin.

As I shall show hereafter, tin stands by itself, having an atomic volume different from either silicon or titanium. Moreover, the fact that the atomic weights of silicon and titanium are nearer together than those of titanium and tin, goes to show that if titanium be classed with either, it should be with silicon.

As I previously stated, whenever two liquids have equal vapor volumes their atomic volumes also are equal, or nearly so.

For instance, the various isomeric ethers formed by the homologues of formic acid with the methyl series of hydrocarbons, (ethyl acetate, formate, &c.,) have both equal atomic volumes and vapor volumes, and so on with all strictly isomeric bodies. Again, to cite an example of liquids diverse in their natures, benzol, butyronitrile, and bromid of ethylene, all have the vapor volume 257. Their atomic volumes, calculated by Kopp's method, are respectively 99, 99·5, and 99·6. I could cite many other examples, but it is not necessary. There are exceptions, however, though they are not common.

Suppose now we wish to determine the atomic volume of any element in its liquid compounds,—boron, for example. The terbromid of boron has the vapor volume 239. Acetic anhydrid has the vapor volume 238. Therefore the atomic volumes of these two compounds must be nearly equal. The atomic volume of the anhydrid is 109·2, calculated by Kopp's process. Regarding this as also the atomic volume of the bromid, and subtracting from it that of the three atoms of bromine, we have left as the atomic volume of boron, the number 25·8. Triethyl boron, $C_6H_{15}B$, has the vapor volume 157, equal to that of œnanthic acid. The calculated atomic volume of the acid is 174. This, then, is also the atomic volume of triethyl boron, and, subtracting from it the atomic volume of C_6H_{15}, we have left for that of boron the number 25·5, closely agreeing with the result obtained from the bromid. But we do not get such close agreements in all cases, and therefore in order to obtain accurate results, we must compare the numbers obtained from several of the liquid compounds of the element in question, and regard the average of them all as nearest correct. Before going farther in this direction, however, let us compare the vapor volumes of a number of similar compounds of boron, phosphorus, and arsenic.

The chlorids of these three elements have respectively the vapor volumes 257, 262, and 252. The bromids of boron and phosphorus have respectively 239 and 241. Triethyl boron, triethyl phosphine, and triethyl arsine have the vapor volumes 157, 154, and 159, and triethyl phosphate and triethyl arsenate have 132 and 130.

Kopp, from the chlorids, found the atomic volumes of phosphorus and arsenic to be probably equal. The comparison of these vapor volumes confirms this view, and adds boron as also possessing the same atomic volume as phosphorus and arsenic.

To make this still more certain I have calculated the atomic volumes of these elements from the vapor volumes of their compounds, in the manner already described.

For boron I have made calculations from eleven compounds, —the chlorid, bromid, triethyl boron, trimethyl, triethyl, triamyl, and monamyl borates, ethyl diamyl, amyl diethyl, and methyl diethyl borates, and tetraphenyl diborate. In these compounds I obtained respectively as the atomic volume of boron in its liquid compounds, the numbers 30·9, 25·8, 25·5, 26·0, 24·1, 26·1, 19·7, 25·3, 31·9, 24·1, and 19·9. The average is 25·4.

Although there are very great variations between these different numbers, it will be seen hereafter that the averages obtained by this method agree closely with the numbers found by actual experiment.

The atomic volume of phosphorus I have calculated in a similar manner in eleven of its liquid compounds, exclusive of the chlorid and bromid. I include Kopp's numbers for these last, however, for the sake of completeness in making up the average.

The list of compounds then stands as follows. The chlorid, bromid, oxychlorid, oxybromid and oxybromochlorid of phosphorus, triethyl phosphine, triethyl phosphite, diamyl phosphoric acid, triethyl phosphate, tetrethyl pyrophosphate, and the ethyl, butyl, and amyl chlorophosphites. In these, giving

Kopp's numbers for the first two, the atomic volume of phosphorus is found respectively as follows: 25·5, 25·2, 26·2, 25·8, 22·4, 25·5, 26·1, 23·2, 29·3, 32·3, 27·1, 27·1, and 19·7. The average of these, 25·8, agrees very closely with Kopp's numbers, and varies only 0·4 from the average obtained for boron.

The atomic volume of arsenic I have deduced from the vapor volumes of three of its compounds exclusive of the chlorid. In the chlorid the element has the atomic volume 26·4, (Kopp) and in triethyl arsine, triethyl arsenite, and triethyl arsenate, I obtain the numbers 25·5, 26·7, and 29·2. The average of all four numbers is 26·9.

If now, regarding boron, phosphorus, and arsenic, as possessing the same atomic volume in their liquid compounds, we take the average of the numbers obtained from the twenty-eight compounds in which that atomic volume has been determined, we get the number 25·8. To these three elements we can probably add vanadium, which Roscoe has shown belongs in the same group. There is but one liquid compound of this metal for which I had data to calculate from,—the oxychlorid, Roscoe's "vanadyl trichlorid," $VOCl_3$. Calculating its vapor volume, and thence the atomic volume of vanadium, I obtained the number 27.4.

It will be seen that a number of compounds of boron, phosphorus, and arsenic gave higher results than this, and therefore, for a single compound, this number seems close enough to that found for the other three elements, to be classed with them. This view is somewhat strengthened by the fact that the atomic weight of vanadium is intermediate between those of phosphorus and arsenic.

For antimony, as already stated, Kopp determined the atomic volumes of the chlorid and bromid. Deducing the atomic volume of antimony from these, we get the numbers 32·3 and 33·4. In addition to these I have determined from their vapor volumes the atomic volumes of triethyl and triamyl stibine, and the chlorid and bromid of triethyl stibine. From these I obtain respectively as the atomic volume of antimony, the numbers 33·3, 32·1, 32·9, and 35·9. Adding in these with the numbers from the chlorid and bromid of the metal, we get 33·3 as the average.

In the case of bismuth there is but one liquid compound for which I had the necessary data. Triethyl bismuthine has the vapor volume 138, while triethyl stibine has the number 141. These are so near together that it seems probable that bismuth in its liquid compounds has the same atomic volume as antimony. But more data are needed to decide this point definitely.

In the case of silicon, thanks to the labors of Friedel, Crafts, and Ladenburg, materials were more abundant. Apart from the chlorid and bromid, whose atomic volumes were determined by Kopp, I have calculated the vapor volumes of sixteen liquid compounds of silicon, and thence the atomic volume of silicon itself. These compounds are tetramethyl, tetrethyl, and tetra-amyl silicates, diethyl, diethyl dimethyl, triethyl methyl, triamyl ethyl, diamyl diethyl, and trimethyl ethyl silicates, hexmethyl and hexethyl disilicates, ethylsilicic monochlorhydrin, dichlorhydrin, and trichlorhydrin and methylsilicic monochlorhydrin and dichlorhydrin. In these compounds I obtain respectively as the atomic volume of silicon, the numbers 31·0, 32·8, 33·0 30·3, 32·8, 32·2, 38·8, 35·2, 30·9, 30·3, 32·8, 36·3, 32·0, 39·0, 29·9, and 34·6. Taking also the numbers given by Kopp for the chlorid and bromid of silicon, amending them to suit the new notation and new atomic weight of silicon, and thence deducing the atomic volume desired, we get the numbers 33·0 and 30·9. Taking the average of these eighteen numbers we obtain 33·1 as the atomic volume of silicon in its liquid compounds. The atomic volume of titanium, as deduced from that of the chlorid, as determined by Kopp, is 34·8. Further investigation will probably show its atomic volume to be equal with that of silicon.

The atomic volume of the chlorid of tin, as determined by Kopp, and since doubled to suit the new notation, is 131·4. This gave for tin the number 40·2. The vapor volume of the same compound gave as the atomic volume of tin, the number 40·1. I have also calculated the vapor volume of the following nine compounds containing this metal. Stanntetrethyl, stanndimethyl diethyl, stanndiethyl, stannethyl trimethyl, the chlorid, bromid, and iodid of stanntriethyl, and the iodids of stanntrimethyl and stanndimethyl. From the vapor volumes of these liquids I have obtained respectively as the atomic volume of tin the numbers 46·5, 42·0, 39·3, 44·0, 37·7, 42·1, 41·0, 41·8, and 44·0. Including the number deduced from the chlorid of tin, we get as the average 41·8, the atomic volume of tin in its liquid compounds.

In the case of zinc there were but three liquid compounds for which I was able to calculate the vapor volumes. These were zinc ethyl, zinc methyl, and zinc amyl. The atomic volume of zinc, deduced from their vapor volumes, I obtained respectively as 23·2, 24·2, and 23·2. The average is 23·6.

Of liquids containing selenium I have the vapor volumes of but two,—the oxychlorid, $SeOCl_2$, and monohydrated selenic acid. The latter of these, however, has never been obtained free from an excess of water, the strongest containing only about 97 per cent of monohydrate; and therefore its atomic volume, as deduced from its vapor volume, is undoubtedly a trifle too low. Be that as it may, however, in these two compounds I obtained as the atomic volume of selenium the numbers 24·7 and 21·8, the mean being 23·2. This is only 0·6 greater than the number given by Kopp as the lower atomic volume of sulphur, and, therefore, taking into account that sulphur and selenium in the solid condition have equal atomic volumes, it seems almost certain that the same equality holds true in their liquid compounds.

I determined the vapor volumes of two lead compounds, lead tetrethyl and lead triethyl, but, to my great surprise I obtained the same number for both. This is so anomalous that I am inclined to think either that there is an error in the numbers published as the specific gravities of these liquids, or else that their vapor densities do not follow the usual law. At all events I could get nothing reliable from them.

From the vapor volume of chlorochromic acid I determined its atomic volume, and thence that of chromium in liquid compounds, as 43·6. The vapor volume of the fluorid of arsenic gave me the means of ascertaining the atomic volume of fluorine, for which I obtained the number 10. But as each of these was determined from only one compound of the element, I place no great reliance upon either, regarding them merely as possible approximations to the truth.

In order to test more thoroughly this process of determining atomic volumes by means of vapor volumes, not being content with the coincidence of my numbers with those of Kopp in the cases of phosphorus, arsenic, antimony, silicon and tin, I calculated the atomic volumes of chlorine, bromine, and iodine by the same method. For chlorine, in an average of forty-one compounds, I obtained the number 22·9, Kopp's determination giving 22·8. Bromine, in an average of fourteen compounds, gave me 28·0, Kopp's number being 27·8; and iodine, calculated from nine of its liquid compounds gave the number 38·5, that of Kopp being 37·5. To this determination of the atomic volume of iodine I shall refer again hereafter.

In regard to phosphorus, arsenic, antimony, silicon, and tin, my determinations might be regarded by some as labor lost, after Kopp's examination of the chlorids and bromids. But, very frequently, the atomic volume of a single compound as calculated by Kopp's method, varies considerably from that actually found. Therefore, in order to determine accurately the atomic volume of any element in its liquid compounds it is necessary to ascertain the atomic volumes of a number of those compounds.

The examination of one, or even two or three compounds of any element may give a very different result from that which would be obtained from a larger number of determinations. For instance, Kopp's earlier experiments upon a small number of liquids gave him the number 4·7 as the atomic volume of carbon ($C=6$), but, upon examining a larger number of compounds he obtained the number 5·5. Doubling these to agree with the modern atomic weight of carbon, and we have a difference of 1·6. Therefore my results in the cases of the elements above named are useful as confirmatory of Kopp's. My determinations for boron, bismuth, vanadium, selenium, and zinc, however, are entirely new.

The atomic volume of mercury at its boiling point I have calculated directly from the metal itself, by the data furnished by Regnault. According to this chemist, the specific gravity of mercury at 0° is 13·5959, its boiling point is 350°, and one volume of the metal at 0° becomes at 350°, 1·065743 volumes. From these data I find the specific gravity of mercury at its boiling point to be 12·7572, and dividing the atomic weight by this number I get 15·68 as the atomic volume.

It will be seen here that I assume that mercury when free has the same atomic volume as when combined. This appears true for bromine, ammonia, cyanogen, and hyponitric acid, according to Kopp's determinations, and therefore it seems allowable to regard mercury as following the same rule. Possibly this metal may have more than one atomic volume, like oxygen, nitrogen, or sulphur ; in that case 15·68 is probably either one of them or their mean. If all elements possessing but one atomic volume in their liquid compounds follow after bromine, then we can calculate approximately their specific gravities at their boiling points. That of hydrogen would be 0·1818, and that of carbon 1·0909. This, however, is a mere matter of curiosity at present.

Having now the atomic volumes of twenty elements in their liquid compounds at their boiling points, we may proceed to compare the numbers, and see if there are any definite relations between them. Of the relations found between the atomic volumes of compounds by Schröder and Kopp I shall have nothing to say, since more important relations between the elements seem to exist.

Hydrogen, having in liquids the atomic volume 5·5, is most readily substituted, atom for atom, by chlorine, bromine, iodine, and hyponitric acid. These have respectively, according to Kopp, the atomic volumes 22·8, 27·8 37·5, and 33.

The last of these is an exact multiple by a whole number of that of hydrogen, and the second varies but 0·3, the first by

0·8, and the third by 1·0 from multiples of the same. Now since Kopp does not claim rigid accuracy for his numbers, perhaps we may be justified in altering these to multiples of 5·5. Then for chlorine, bromine, and iodine we shall have the atomic volumes 22, 27·5, and 38·5. The last of these, it will be seen, is the same number which I deduced from the vapor volumes of nine compounds of iodine. The lower number was deduced from only three compounds,—the iodids of methyl, ethyl, and amyl, whose atomic volumes were determined by actual experiment. The atomic volume of iodid of methyl, according to Kopp, is from 65·4 to 68·3, that of iodid of ethyl from 85·9 to 86·4, and that of the amyl compound from 152·5 to 158·8. If now we calculate the atomic volumes of these three compounds, we shall find that if we regard iodine as having the atomic volume 37·5, we shall get a better agreement with the numbers found for the second of these compounds than if we ascribe to this element the value 38·5; but in the first and third cases, although the lower value for iodine agrees best with the lower of the two numbers between which the atomic volume of each compound varies, the value 38·5 agrees more nearly with them than between those numbers. In other words, we shall get a closer agreement with the results of experiment, if we ascribe to iodine the atomic volume 38·5, than if we give it the lower number obtained by Kopp.

The atomic volumes of seventeen organic liquids containing chlorine, have been determined by Kopp. When two values are given for one liquid I take the mean between them, and then I find upon calculating their atomic volumes, that the number 22 for chlorine agrees best with the determinations in seven cases, while Kopp's number affords a closer agreement with the numbers found for the remaining ten.

For bromine, out of five compounds whose atomic volumes have been actually determined, Kopp's number coincides best with the results found for four, while the altered number is nearer to the value obtained for the remaining one. Yet the alteration of Kopp's numbers is least in the case of bromine. Let us now examine some other groups of elements in a similar manner.

Since hyponitric acid, replacing as it does, hydrogen atom for atom, possesses an atomic volume an exact multiple of that of hydrogen, let us take this compound as our starting point for the nitrogen group. According to Kopp, nitrogen has three atomic volumes; in ammonia 2·3, in hyponitric acid 8·6, and in cyanogen, 17·0.

If now we alter the first to 2·15, and the third to 17·2, leaving the second (our starting point) as it is, then the second becomes exactly four times the first, and the third just twice the second. In other words, the higher atomic volumes of this element become multiples by whole numbers of the lower. This coincidence seems too remarkable to be accidental. For boron, phosphorus, vanadium, and arsenic, the number 25·8 was found as the atomic volume. This is exactly three times 8·6, our starting point for this group. The number obtained for antimony, 33·3, it will be seen lacks 1·1 of a multiple of 8·6. But of the six compounds of antimony from which I calculated, two contain chlorine, and two bromine.

In my calculation I employed Kopp's values for those elements. If, however, the altered numbers are the true atomic volumes of chlorine and bromine, then we must re-calculate the atomic volume of antimony. Doing this, using the altered values for chlorine and bromine, we obtain as the atomic volume of antimony, the number 34·2. If we take the atomic volumes actually found for the chlorid and bromid of antimony, and from them determine the value of antimony, using the new numbers for chlorine and bromine, we obtain a mean of 34·5. 34·4 is just four times 8·6 ! This seems to lend additional strength to the idea that the chlorine group of elements have atomic volumes which are multiples by whole numbers of that of hydrogen.

If, however, we re-calculate the atomic volume of antimony on the basis of new values for chlorine and bromine (iodine also, whenever necessary), we must do the same for boron and the elements classed with it. Doing this, we obtain the number 26·4, a variation of only 0·6 from the multiple of 8 6 previously found.

In making these corrections it must be borne in mind that whenever the atomic volume of an element is deduced from the vapor volume of a compound, if that vapor volume is compared with that of a compound containing either chlorine, bromine, or iodine, then the atomic volume of the latter must itself be corrected, before deducing from it that of the element in question.

Passing now to the oxygen group, we have two atomic volumes given by Kopp for oxygen, 7·8 and 12·2. Between these two I have yet found no relation. But mercury, as calculated from the metal, has the atomic volume 15·68. 15·6 is just twice 7·8. Zinc, having according to my calculation the atomic volume 23·6, exceeds by only 0·2 a multiple of 7·8 by 3. For sulphur, Kopp gave the numbers 22·6 and 28·6. Between these two I have found no relation, but the lower one varies only 0·8 from three times 7·8. For selenium I obtained the number 23·2, only 0·2 less than the same multiple of 7·8. Hence it seems very probable that the true lower atomic volume for sulphur and selenium is 23·4.

I have found no relation, however, between the higher atomic volumes of oxygen and sulphur.

One more group remains, that of tetratomic elements. Of these, carbon, as determined by Kopp, has the atomic volume 11. For silicon I obtained the number 33·1, almost exactly three times 11. Altering this, as in the case of antimony, to agree with the altered atomic volumes for chlorine, bromine, and iodine, we get 33·7, still near enough to 33 to be regarded as following the usual rule.

In the case of tin we meet the first and only obstacle to this rule in the list of elements whose atomic volumes have been determined. For this metal I obtained by means of the vapor volumes of ten of its compounds, the atomic volume 41 8. Corrected for chlorine, bromine, and iodine, it stands 41·5, the nearest multiple of 11 to this being 44. Therefore either tin is an exception to the generality of cases, or else my determination of its atomic volume is incorrect.

For the chlorid of tin, the atomic volume found was 131·4. If we regard chlorine as possessing the atomic volume 22, then tin in this compound has the value 43·4. Also from the vapor volume of stanntrimethylethyl I obtained the number 44·0 as the atomic volume of tin. Therefore it is not unlikely that a more accurate investigation will decide the atomic volume of this metal in its liquid compounds to be 44, but for the present it must remain in doubt.

This comparison of the atomic volumes of these elements in their liquid compounds at their boiling points, makes it therefore extremely probable that the atomic volume of every element in the liquid condition is a multiple by a whole number of that of the element typifying its group. That is, the atomic volumes of monatomic elements are multiples of 5·5, those of diatomic elements, of 7·8, those of triads, of 8·6, and lastly those of tetrads, multiples of 11, and consequently also of 5·5. Tin may be an exception, but the only one in twenty elements. Whether this rule be absolutely true or not, however, it will be seen to be very near the truth, since in only one case, that of iodine, have I altered the number found by so high a quantity as 1·0, and that in many cases, a change of only from 0·1 to 0·3 was necessary.

Furthermore, the numbers 5·5, 7·8, and 8·6 are not numbers for which we would expect to get exact multiples, unless some definite law accounted for it. Coincidences in two or three cases might be ascribed to accident, but in nineteen cases, all probability is against such an idea. I should not venture to alter any of Kopp's numbers, had he claimed rigid accuracy for them, and the variations between his own earlier and later results for carbon, seem to render such alterations as I have made, more justifiable. His later numbers for oxygen, hydrogen, and carbon, having been deduced by comparing the atomic volumes of forty-five compounds containing them, it will be seen I have not changed at all. His numbers for chlorine, bromine, iodine, and sulphur, however, which I have altered the most, were obtained from a comparatively small number of compounds containing them.

If my alterations be accepted, and also my new determinations, then the list of the atomic volumes of elements in their liquid compounds at their boiling points will stand as follows. Hydrogen 5·5, chlorine 22·0, bromine 27·5, iodine 38·5, oxygen 7·8 and 12·2, sulphur 23·4 and 28·6, selenium 23·4, mercury 15·6, zinc 23·4, nitrogen 2·15, 8·6, and 17·2, boron, phosphorus, vanadium, and arsenic 25·8, antimony, and possibly also bismuth 34·4, carbon 11·0, silicon, and titanium 33·0, tin, doubtful, either 41·5 or 44·0, probably the latter.

Note.—For the benefit of any who may wish to consult the authorities upon the subject of atomic volumes, I will state that, apart from Kopp's original articles, previously referred to, the best summaries I have been able to find are in the following works. "Watts' Dictionary," vol. 1. article "Atomic Volume." Kekulé's "Lehrbuch der Organischen Chemie," vol. 1, and Buff, Kopp, and Zamminer's "Lehrbuch der Physikalischen und Theoretischen Chemie."