



VIII. On the specific volumes of oxides

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a great increase of dispersion. It was pointed out some years ago that the aromatic bodies have a great dispersive power*, and that "dispersion, as well as refraction, increases very rapidly with the number of atoms of carbon that are not combined with at least two of hydrogen or their equivalent."† Evidence of this is to be found both in the older and the more recent researches, whether in this country or on the Continent, and is always accumulating. Confining our attention to the figures given in this paper, it will be observed that in cases where the carbon is normal the specific dispersion is expressed by low figures (the highest of which is, in fact, acetone, ·0207); while in the isomeric allylic alcohol, which has a higher refraction, it rises at once to ·0275. The essential oils and their congeners, and such bodies as cresylic acetate, are above ·0300; while the purely aromatic compounds are all above ·0400.

2nd. Where isomeric bodies have the same or nearly the same specific refraction for the line A, they have the same also for the line H. The apparent deviations from this rule I am disposed to attribute to experimental error, and still more to impurity of substance. It is clear that in many cases of carbon compounds the presence of a differently constituted body would reveal itself by its influence upon dispersion more than upon refraction.

VIII. *On the Specific Volumes of Oxides.* By BOHUSLAV BRAUNER, *Ph.D.*, and JOHN I. WATTS, *Owens College*‡.

THE researches of Persoz, Karsten, Filhol, Kopp, Schröder, Löwig, Schafarik, Playfair and Joule, Baudrimont, Heimroth, and others have yielded a considerable supply of material relating to the specific volumes of many bodies, especially to those of the oxygen compounds; and by aid of these results many interesting theories can be conceived. It was, however, Kremer§ who first pointed out the regularities which the volumes of the oxides of the natural groups of elements exhibit. But after the demonstration of the Periodic Law by Mendelejeff this question considerably developed in importance, because the relations of the various members of the natural groups to one another were made more strikingly apparent. Mendelejeff himself|| points out the regularities which the specific volumes of the oxides exhibit in the different groups of the system; but he only followed this out in one

* Journ. Chem. Soc. 1870.

† Proc. Roy. Inst. March 1877

‡ Communicated by the Authors.

§ Pogg. Ann. cxxx. p. 77.

|| Ann. Chem. Pharm. Suppl. viii. p. 143; Chem. News, xl. p. 255, xli p. 49.

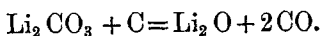
single series. He touches upon it, however, shortly, in his Russian 'Principles of Chemistry' (vol. ii. p. 857). We have not yet been able to consult his papers on this subject, published from 1858 to 1865 in the Russian 'Mining Journal.'

In Table I. we give an arrangement of all the oxides which are at present known, in which the number of oxygen atoms correspond to the numbers of Mendelejeff's groups. Some of these numbers have been obtained from estimations made by us by means of a very accurate method, which has been already described and used by one of us*.

TABLE I.—Specific Volumes of the Oxides.

Groups	I.	II.	III.	IV.	V.	VI.	VI.
Series.	$\frac{1}{2} R_2 O.$	$\frac{1}{2} R_2 O_2.$	$\frac{1}{2} R_2 O_3.$	$\frac{1}{2} R_2 O_4.$	$\frac{1}{2} R_2 O_5.$	$\frac{1}{2} R_2 O_6.$	$\frac{1}{2} R_2 O_7.$
1.	H 10						
2.	7 Li	8 Be 8	19 B	40? C	N	O	F
3.	11 Na 11	12 Mg 12	Al 13	Si 23	P 30	S 41	Cl
4.	17 K	18 Ca	18 Sc	20 Ti	26 V	37 Cr	Mn
5.	Cu 12	Zn 14	Ga (17)	— (23)	As 31	Se —	Br
6.	(21) Rb	22 Sr	23 Y	23 Zr	30 Nb	33 Mo	—
7.	Ag 14	Cd 16	In 19	Sn 22	Sb 42	Te —	I
8.	(25) Cs	28 Ba	25 La	26 Co			
9.					31 Ta	32 W	
10.					Pb 27	Bi 42	Ng?†
11.	Au (18)	Hg 19	Tl (23)	21 Th		56 U	
12.							

Preparation and Specific Gravity of Lithium Oxide.—The lithium oxide used for the sp. gr. determinations was prepared by strongly heating pure lithium carbonate with a slight excess of charcoal. Lithium oxide is formed according to the equation



This mode of preparation, however, is not to be recommended, because the $Li_2 O$ dissolves platinum. In our observations we estimated the sp. gr. of the insoluble residue, and made a correction for it.

Mean sp. gr. of $Li_2 O$ at $15^\circ C.$ (corrected for insoluble residue) = 2.102; sp. vol. = 7.12.

We attempted to prepare $Li_2 O$ in a pure state by heating the nitrate in a silver basin; but we obtained a very impure product containing $Li_2 CO_3$ and silver.

Specific Gravity of Bismuth Pentoxide.—A sample of hydrated $Bi_2 O_5$ was obtained from Mr. M. M. P. Muir, and heated to $120^\circ C.$ until it ceased to lose weight.

* Thorpe and Watts, Journ. Chem. Soc. Feb. 1880, p. 102.

† This place will be probably occupied by the metal Norvegium, $Ng = 214$, if it forms, besides the oxide $Ng_2 O_3$, a peroxide of the formula NgO_3 .

- I. Sp. gr. of $\text{Bi}_2\text{O}_3 = 5.917$.
 II. " " " " = 5.919.

Specific Gravity of Uranic Oxide.—One sample of UO_3 was prepared by heating the nitrate to 280° . A second one was prepared by heating the hydrated oxide to 300° .

Sp. gr. of sample No. 1 = 5.26 } Mean = 5.14 ; sp. vol. 56.03.
 " " " " 2 = 5.02 }

In explanation of Table I. it is to be borne in mind that the numbers refer to one atom of the metal in the form of oxide, in order to obtain comparable numbers. Many of the numbers are taken from the latest papers of Nilson and Petterson *, and are found to give values for specific volumes somewhat smaller than those derived from older observations.

We only give the above values as approximate ones, because the material to work upon does not allow of great accuracy; and we only take the first seven groups into consideration, because the specific gravities of oxides of the eighth, with the formula RO_4 , are not known.

A glance at the table shows us that the specific volume increases steadily along the horizontal as well as down the vertical lines. The difference between the even and the odd series is particularly well defined. Some of the "typical elements," especially Li, Be, Na, and Mg, can be used as representatives of both series. The specific volume of an oxide, where it is at present unknown, can be calculated from data obtained from the values surrounding it.

Of all the oxides which are at present known, that of lithium possesses the smallest specific volume, the metal having the least atomic weight. On the other hand, uranic oxide, UO_3 , has the largest atomic volume, uranium possessing the greatest atomic weight.

A remarkable increase of volume is exhibited by antimony and bismuth pentoxides. It should nevertheless be mentioned that Sb_2O_5 seems to exist in two allotropic forms, which possess quite different specific gravities. One has the sp. gr. 6.525 (Boullay), and the other 3.779 (Playfair and Joule) †. Accordingly the specific volume is either 25 or 42.

It appears likely that two similar modifications of other oxides exist—of bismuth, for example, and of uranium oxide, the second one possessing the specific volume about 30. Others of the numbers given are still uncertain, that for BaC for example. The values at present given for its sp. gr

* *Ber. deut. chem. Gesell.* xiii. p. 1459.

† Clarke, 'Constants of Nature,' No. I. Our other values are also mainly derived from this source.

extend from 4.0 to 5.456; and accordingly the atomic volume varies from 28.1 to 38.3. An oxide of barium of sp. gr. 6.4, giving sp. vol. 24, might be expected to exist.

Some interesting numbers are obtained if we calculate the volume which one atom of oxygen possesses in the various oxides. To commence with, we suppose that the metal does not alter in volume when it combines with oxygen, we subtract the specific volume of the metal from that of the oxide. We quote the values from Lothar Meyer's 'Modern Theory of Chemistry,' 4th edit. 1880, p. 141. To take an example,

$$\frac{1}{2} \text{Na}_2\text{O} = 11.1, \quad \text{Na} = 23.7, \quad 11.1 - 23.7 = -12.6 \text{ for } \frac{1}{2} \text{O},$$

or

$$-25.2 \text{ for O, and so on.}$$

The following Table contains the corresponding numbers when the elements are arranged according to the periodic law.

TABLE II.

Specific Volume of one Atom of Oxygen in the Oxides.

Groups	I.	II.	III.	IV.
Series.	R ₂ O.	R ₂ O ₂ .	R ₂ O ₃ .	R ₂ O ₄ .
1.	H			
2.	- 9.6 Li	+ 2.7 Be	+8 B	+21.2 C
3.	-25.2 Na -25.2	- 1.8 Mg -1.8	Al +1.4	Si + 5.7
4.	-55.4 K	- 7.2 Ca	(-0.7) Sc	(+3) Ti
5.	Cu +10.4	Zn +5.1	Ga (+2.9)	— (+5)
6.	(-70) Rb	-12.9 Sr	(-0.7) Y	+0.8 Zr
7.	Ag +7.6	Cd +5.5	In +2.5	Sn +3.2
8.	(-84) Cs	- 8.5 Ba	+1.7 La	+2.2 Ce
9.
10.	Au (+5)	Hg +4.7	Tl (+4)	Pb +3.7
11.
12.	-1.8 Th

Groups	V.	VI.	VII.
Series.	R ₂ O ₅ .	R ₂ O ₆ .	R ₂ O ₇ .
1.			
2.	N	O	F
3.	P +6.6	S +8.3	Cl
4.	+6.6 V	+ 9.3 Cr	Mn
5.	As +7.0	Se	Br
6.	+6.6 Nb	+ 7.2 Mo	—
7.	Sb +9.5	Te	I
8.			
9.			
10.	+4.8 Ta	+ 9.0 W	
11.	Bi +8.4	Ng ?	
12.	+14.3 U	

We deduce the following :—

1. In strong bases the oxygen possesses a negative volume.
2. In the oxides of the heavy metals and metalloids the volume of the oxygen is positive.
3. The earth-metals unite with oxygen without any appreciable change of volume; and on this account they form a connecting link between acids and bases.
4. The higher the specific volume of the metal in the oxide, the more negative is the specific volume of the oxygen combined with it; for instance

$$\text{Sp. vol. K} = 45.4,$$

$$\text{Sp. vol. O} = 55.4.$$

The lower the specific volume of the element, the more positive is the specific volume of the oxygen in the oxide; for example

$$\text{Sp. vol. C} = +3.6,$$

$$\text{Sp. vol. O} = +21.2.$$

Mendelejeff has published some very interesting observations of this kind in his Russian 'Principles of Chemistry,' pp. 856–859. He gives a very beautiful hypothesis of the mechanical theory of the act of combination. It is not, however, suitable to enter upon these discussions here.

When we observe the above arrangement in Table II, we notice the following :—The more strongly electro-positive the base which an element forms with oxygen, the greater is the negative value for the volume of the oxygen. It appears as if the negative maximum were reached with caesium. On the contrary, the maximum of positive values is probably attained in the vicinity of fluorine. From this one perceives that the value representing the atomic volume of the oxygen in the oxides can, to a certain extent, be looked upon as the amount of affinity of the metal for the oxygen.

In the same manner that, in the horizontal series of the periodic system, the electro-negative character increases with the atomic weight, the volume of the oxygen changes from negative to positive. The opposite appears to be the case in the vertical groups—at all events, as regards the even elements. In this matter new researches upon the metals and their oxides would be of considerable interest.

We cannot conclude without thanking Mr. M. M. Pattison Muir, of Caius College, Cambridge, for his great kindness in supplying us with the material to make our determinations of the specific gravity of bismuth pentoxide.