XXVIII.—*Observations on the Atomic Volumes and Boiling Points of analogous Organic Liquids.* By W. A. MILLER, M.D., F.R.S.,
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It is well known that Kopp,* from a series of researches and observations on the atomic volume and the boiling points of various organic liquids, some years ago, deduced the conclusion that analogous fluid compounds exhibit like differences in their equivalent volume. That the atomic volume of a hydrated acid, for example, is about 534 less than that of the corresponding ether, and about 300 less than that of the corresponding methyl compound; whilst between corresponding compounds of the ethyl and methyl series, there is a difference equal to about 234 in the atomic volumes of the two.

* *Annalen der Chemie*, 1841. Bd. 41, s. 79.

Between the boiling points of the hydrated acids and the ethers

he finds a difference of 45°

Between the acids and the methyl compounds 63°

And between the corresponding ethyl and methyl compounds . 18°

Later experiments and observations led him to the conclusion, that two members of the ethyl and methyl series of compounds, which differ in their empirical atomic formulæ by multiples of (2 CH), differ by equal multiples of 19° C. in their boiling points.*

He has further concluded, that the atomic volume of an element, in all fluid compounds, at corresponding temperatures, is the same, and that chemical equivalents of oxygen and hydrogen in fluid compounds, at corresponding temperatures, occupy equal bulks. Corresponding temperatures being understood to be those at which the tension of vapour of the two is equal. In default of observations on the equal tension of the vapours, Dr. Kopp has assumed as approximations to the truth—temperatures equidistant from the boiling point as “corresponding temperatures.”

In this country, the attention of chemists generally has lately been recalled to this theory by the appearance of a valuable report on the subject in the 1st volume of the Cavendish Society's publications, and the following remarks may, therefore, not be without interest. M. Pierre,† having recently published a series of most elaborate researches upon the expansion of a considerable number of liquids, both inorganic and organic, and having with great care determined their boiling points, and their specific gravities at 0° C., I was induced, in order to satisfy myself of the correctness of the generalizations of Kopp, to test them by the new data thus furnished. To my great surprise, however, and disappointment, I may add, I found the results very wide of those required, if the views entertained by Kopp be correct; and it may be worth while, in the present period of the discussion, simply to state them.

The laborious researches of M. Pierre have embraced no fewer than twenty-eight liquids, some inorganic, others organic compounds. Twelve of these will serve directly for the purposes of the present inquiry.

The following table includes the results observed by M. Pierre.

It may here be mentioned, that these experiments prove, as indeed Kopp had surmised it to be probable, that similar compounds do not expand equally at equal distances from the boiling point, and this

* *Annalen der Chemie*, Bd. 55, s. 177.

† *Annales de Chimie and de Physique* 3ème Série, Vol. xv. p. 325, xix. p. 193, xx. p. 5.

variation necessarily introduces some discrepancy between Kopp's calculated results and those furnished by experiment. The observations of Pierre, moreover, enable us to obviate this objection by calculating the atomic volume not at equal distances from the boiling point, but at the boiling point itself, *i. e.*, just as the cohesion of the liquid is about to yield. This calculation I have accordingly made.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Name.	Formula.	Equi- valent.	Boiling point C°.	1000 at 0° =	Sp. gr.		At boiling point.
				at boiling.	0° C.	At boil- ing.	Atomic volume.
Fousel oil . . .	$C_{10}H_{11}O, HO$	1100	131.8	1153	0.827	0.717	1534.5
Alcohol . . .	C_4H_5O, HO	575	78.3	1093	0.815	0.745	771.0
Wood-spirit . .	C_2H_3O, HO	400	66.3	1089	0.820	0.754	530.0
Iodide of ethyl .	C_4H_5, I	1942	70.	1088	1.975	1.815	1070.0
Iodide of methyl	C_2H_3, I	1767.0	43.8	1058	2.199	2.076	851.0
Bromide of ethyl	$C_4H_5Br.$	1340.8	40.7	1059	1.473	1.391	964
Brom. of methyl	$C_2H_3Br.$	1165.8	13.0	1019	1.664	1.633	714
Acetate of ethyl	$C_4H_5O, C_4H_3O_3$	1100	74.14	1110	0.907	0.817	1346
Acetate of methyl	$C_2H_3O, C_2H_3O_3$	925	59.5	1088	0.866	0.796	1162
Butyrate of ethyl	$C_4H_5O, C_8H_7O_3$	1450	119.0	1171	0.902	0.769	1884
Butyr. of methyl	$C_2H_3O, C_6H_5O_3$	1275	102.1	1147	1.029	0.897	1423
Formiate of ethyl	$C_4H_5O, C_2H_3O_3$	950	52.9	1079	0.935	0.866	1096
Ether	C_4H_5O	462.5	35.5	1057	0.735	0.694	665.8
Water	HO	112.5	100.0	1044		0.958	117.4

The headings of the columns of the preceding table will sufficiently explain their contents. Column 5 represents the bulk that 1,000 parts of the different liquids, measured at 0° C., attain when raised to the temperature at which they respectively boil. Column 7, the sp. grav. at the boiling point, being calculated from the data contained in 5 and 6.

TABLE II.

I.	II.	III.	IV.	V.
	Observed difference of		Calculated for each (C ₂ H ₂) difference of	
	Boiling point C°	Atomic volume.	Boiling point.	Atomic volume.
EO, HO — MeO, HO = C ₂ H ₂	..	..	12.0	241
EI — MeI = C ₂ H ₂	..	..	26.2	219
EBr — MeBr = C ₂ H ₂	..	..	27.7	250
EO, $\overline{\text{Ac}}$ — MeO, $\overline{\text{Ac}}$ = C ₂ H ₂	..	..	15.64	184
EO, $\overline{\text{Bu}}$ — MeO, $\overline{\text{Bu}}$ = C ₂ H ₂	..	..	16.9	461
EO, $\overline{\text{Ac}}$ — EO, $\overline{\text{Fo}}$ = C ₂ H ₂	..	..	21.24	250
MeO, $\overline{\text{Bu}}$ — EO, $\overline{\text{Ac}}$ = C ₂ H ₂	..	..	27.9	87
EO, $\overline{\text{Bu}}$ — EO, $\overline{\text{Ac}}$ = 2(C ₂ H ₂)	34.8	338	17.43	169
MeO, $\overline{\text{Bu}}$ — MeO, $\overline{\text{Ac}}$ = 2(C ₂ H ₂)	42.6	261	21.3	130.5
MeO, $\overline{\text{Bu}}$ — MeO, $\overline{\text{Fo}}$ = 2(C ₂ H ₂)	49.2	327	24.6	163.5
EO, $\overline{\text{Bu}}$ — EO, $\overline{\text{Fo}}$ = 3(C ₂ H ₂)	66.1	788	22.03	262.6
EO, $\overline{\text{Bu}}$ — MeO, $\overline{\text{Ac}}$ = 3(C ₂ H ₂)	59.5	722	19.8	240.7
AmO, HO — EO, HO = 3(C ₂ H ₂)	53.5	763	17.8	254.3
AmO, HO — MeO, HO = 4(C ₂ H ₂)	65.5	1004.5	16.3	251.1
MeO, $\overline{\text{Ac}}$ — EO, $\overline{\text{Fo}}$ 0	6.6	66	..	..

In this second table, the different compounds enumerated in the first are compared together, two and two. In the first seven cases, the difference between the compounds compared is 1 equivalent of the carbo-hydrogen (C₂ H₂). In the first five, the difference is in the basic portion of the compound; in the 6th, it is the acid member of each compound; and in the 7th, the difference is in the empirical formula; in the subsequent cases there are differences, of 2 (C₂ H₂), 3 (C₂ H₂), and 4 (C₂ H₂), in all varieties; the last two columns are calculated from the preceding two, by division of the numbers in columns 2 and 3, by the multiple of the carbo-hydrogen which these numbers represent.

In atomic volume the results do not very greatly differ from similar calculations made by Löwig upon the same subject, on data existing previous to the experiments of Pierre.

The difference between alcohol and wood-spirit is . . .	241
Between fousel oil and alcohol	254·3
„ fousel oil and wood-spirit	251·1

The equivalent volume of C_2H_2 , deduced from these combinations, will be therefore 249 as a mean.

And with this the conclusion derivable from the bromides
of ethyl and methyl = 250

And the acetate and formiate of methyl = 250
also agree.

That derivable from the butyrate and formiate of ethyl 262·6
and the butyrate of ethyl and acetate of methyl . . . = 240·7

does not greatly differ from the preceding, the mean being 251·6

But here all further agreement with Kopp's law ceases.

Compare the iodides of ethyl and methyl 219

Or the corresponding acetates 184

The butyrates corresponding 461

The butyrate and acetate of ethyl 169

Butyrate and acetate of methyl 130

Butyrate of methyl and formiate of ethyl 163

or even the formiate of ethyl with the acetate of methyl, two bodies possessing the same empirical formula: we have here a difference of 66 in the atomic volume of the two, instead of perfect coincidence.

It is unnecessary for me to continue further the comparison with other bodies, or deduce the atomic volume of water in combination, from different compounds. Löwig has already shown that Kopp's hypothesis of the equality in volume of oxygen and hydrogen does not correspond with facts, and the new data do not at all affect this general conclusion.

Before any general law can be deduced, with even tolerable hopes of success, a large number of careful and laborious experiments, such as those which have furnished materials for the preceding remarks, are indispensably requisite. The industry of chemists is daily, in some degree, filling up this void, and no one has attempted to remove this difficulty with greater earnestness than Kopp himself; but until this want is supplied, the foundation on which alone such speculations can be built, or on which the still more extended and elaborate calculations of Löwig can be based, is wanting. Numerous remarkable numerical coincidences, in compounds of analogous composition, show that some important quantitative connection between chemical composition and atomic volume exists; but the true law of that connection still remains to be discovered.

Simple inspection of the differences in the volume of the boiling points, where discrepancies exist even still greater than those observed between the atomic volume (differences both in excess and in deficiency far greater than can be attributed to errors of observation), shews the law of Kopp, regarding the boiling points, to be at variance with the facts observed.