CXXXIX.—*Molecular Volumes at Absolute Zero. Part III. Zero Volumes, Parachors, and Molecular Diameters.*

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IN Parts I and II of this series (J., 1927, 1780, 1786) no reference was made to the work of Biltz in the same field (*Nachr. Ges. Wiss. Göttingen*, 1926, 45; *Annalen*, 1927, **453**, 259). The first of these communications appeared in a journal not readily accessible in this country, and the second, which deals with additive relations in organic compounds, was published only a few months before the author's work was submitted for publication.

In these papers, Biltz has extended to organic substances the studies of limiting molecular volumes in the liquid and the solid state on which he has been engaged for some years. His zero volumes are obtained from a variety of different sources, *viz.*, extrapolation of liquid densities, densities in the solid state, and limiting molecular volumes deduced from the *X*-ray analysis of crystals; the values obtained by these methods usually agree within a few units %. For compounds, Biltz finds an additive relationship of the form $V_0 = \Sigma(nv_0/m)$, in which V_0 is the zero volume of the compound, and v_0, the zero volume of any one constituent free element obtained directly from its density, etc., is multiplied by the appropriate coefficient n/m, where n and m are small whole numbers. In many cases $n/m = 1$, *e.g.*, for carbon and the halogens; for hydrogen $n/m = \frac{1}{2}$, *i.e.*, this element in its compounds is assigned half the molecular volume it is found to occupy in the elementary condition. Similarly, for carbonyl oxygen $n/m = 1$, and for hydroxylic oxygen $n/m = \frac{1}{3}$.

This method of treating zero volumes differs in many respects from that adopted by the author (*loc. cit.*). Nevertheless, the atomic and structural constants deduced by the two methods show a fairly close agreement, as may be seen from the examples shown below.

	V_0 (Biltz).	V_0 (Sugden).		V_0 (Biltz).	V_0 (Sugden).
C	3·4	1·1	O (carbonyl)......	10·7	13·0
H	5·8	6·7	O (hydroxyl) ...	3·6	3·0
CH_2.........	15·0	14·5	O (ethers)	3·6	5·0
Cl	16·5	19·3	N (amines)	0·0	0·0
Br	19·5	22·1	Double bond ...	4·0	8·0
I	24·3	28·3	Triple bond	12·0	15·5

Furthermore, the zero volumes of compounds deduced from the densities of liquids or solids, or from crystal analysis, have been shown by Biltz to agree closely, and can be predicted with a fair degree of accuracy by using either series of constants.

It is therefore of interest to examine the relationship between zero volumes (and, in addition, parachors and critical volumes) and the actual dimensions of the molecules. The latter quantity is somewhat difficult to define with certainty, but probably the best measure of the diameter of a molecule is provided by the modern work on the viscosity of gases. The mathematical theory of Chapman (*Phil. Trans.*, 1916, *A*, **216**, 347) leads to the formula

$$\pi\sigma^2 = \frac{0{\cdot}491(1+\varepsilon)m\overline{V}}{\sqrt{2}\eta(1+C/T)} \quad . \quad . \quad . \quad . \qquad (1)$$

Here η is the viscosity of the gas at an absolute temperature T, m is the mass of the molecule, σ its diameter, and $\overline{V}$ its mean velocity (which varies as $\sqrt{T}$); ε is usually very small and can be neglected, and C is Sutherland's constant. Provided that Sutherland's law (*Phil. Mag.*, 1893, **36**, 507) holds, this formula gives a value for σ which is independent of temperature.

It will be seen from the formula that η is inversely proportional to the cross-sectional area of the molecule, and it is undoubtedly better to follow the procedure of Rankine (*ibid.*, 1921, **42**, 601, 615) and discuss collision areas rather than molecular diameters. In the present problem, however, molecular volumes have to be compared with the viscosity data, so some hypothesis about the shape of the molecule has to be made. In Table I, the molecules are regarded as spheres and the diameters of these spheres are compared. For the inert gases this procedure is probably accurate, but some uncertainty is introduced into the values for more complex molecules.

The volume occupied by an assemblage of N closely packed spheres of diameter σ is $V = N\sigma^3/\sqrt{2}$, hence $\sigma = \sqrt[3]{\sqrt{2}V/N} = 1{\cdot}326 \times 10^{-8}\sqrt[3]{V}$ cm., if V is the volume (in c.c.) of 1 g.-mol. In the liquid state we may assume a random distribution of molecules, so that the value of σ obtained in this way gives the average distance between the centres of adjacent molecules. In Table I the column headed σ_η

gives the molecular diameter (in Ångström units) calculated from the gas viscosity by formula (1). The data for the last five substances are taken from Hertzfeld (" Handbuch der Physik," Springer, Berlin, 1926, **22**, 409); for the others the values of σ_η are calculated from the observations of Rankine (*loc. cit.*). The columns headed σ_0, σ_p, and σ_c give the mean distances between the molecules respectively at absolute zero, as calculated from the author's zero volumes, at unit surface tension, as calculated from the parachor, and at the critical temperature. The last three columns give the ratio of these mean distances to σ_η.

If the molecules of a supercooled liquid are in contact with one another at absolute zero, then σ_0/σ_η should be approximately unity. There are, however, many reasons for supposing that the field of force around a molecule, which at small distances produces attraction, changes to one giving a force of repulsion when two molecules approach each other very closely. When thermal agitation ceases at 0° Abs., the molecules are probably distributed at such distances that there is neither attraction nor repulsion between them. On the other hand, the value of σ_η gives the closest approach of two rapidly moving molecules in a gaseous collision; hence σ_0/σ_η would be expected to be rather greater than unity. It will be seen that most of the substances give a value for this ratio of 1·2—1·3. Hydrogen and helium give much higher values, but this is only to be expected since the van der Waals attractive force for these gases is small. This is shown by many of their properties, *e.g.*, their low boiling points and critical temperatures; they also show a marked deviation from Sutherland's law at lower temperatures.

TABLE I.

Substance.	V_0.	$[P]$.	V_c.	σ_η.	σ_0.	σ_p.	σ_c.	σ_0/σ_η.	σ_p/σ_η.	σ_c/σ_η.
He	22·3	20·2	57·6	1·94	3·73	3·61	5·12	1·92	1·86	2·64
Ne	12·8	25·1	41·8	2·32	3·10	3·88	4·60	1·34	1·67	1·98
A	22·4	53·8	75·2	2·90	3·74	5·01	5·73	1·29	1·73	1·97
Xe	33·0	—	112·7	3·44	4·25	—	6·41	1·24	—	1·86
H_2	22·0	35·1	46·9	2·18	3·72	4·34	4·78	1·71	1·99	2·19
Cl_2	38·6	111·5	123·7	4·12	4·48	6·38	6·61	1·09	1·55	1·60
Br_2	44·2	132·1	135·7	4·04	4·69	6·75	6·81	1·16	1·67	1·69
HCl	26·0	67·8	89·5	2·93	3·93	5·41	5·93	1·34	1·85	2·02
HBr	28·8	85·4	—	3·12	4·07	5·84	—	1·30	1·87	—
HI	35·0	105·3	—	3·43	4·34	6·26	—	1·26	1·83	—
NH_3	19·1	63·8	71·9	2·85	3·63	5·30	5·51	1·27	1·86	1·95
C_2H_4	37·4	99·5	—	3·71	4·43	6·14	—	1·20	1·66	—
C_6H_6	70·9	206·3	256·1	4·20	5·49	7·84	8·42	1·31	1·87	2·01
Ethyl acetate	76·1	217·5	286·3	4·37	5·62	7·98	8·74	1·29	1·83	2·00
iso-Pentane	86·1	229·2	307·0	4·87	5·86	8·12	8·95	1·20	1·67	1·84
Propyl acetate	91·3	256·0	345·3	4·67	7·52	8·42	9·31	1·28	1·80	1·99
							Mean	1·32	1·78	1·98

When the ratio σ_p/σ_η is considered, it will be seen that hydrogen falls into line with the other substances. The values oscillate about a mean of 1·78; the deviations may be ascribed chiefly to the omission of a correction for the shape of the molecule, but in some cases, notably with chlorine, may be due to uncertainties in the viscosity data. It is evident that, by comparing molecular volumes at equal surface tensions, the effect of the intermolecular field is largely eliminated, and a closer parallelism with the dimensions of molecules calculated from gas viscosities is obtained.

The ratio σ_c/σ_η calculated from the critical volume again shows high values for hydrogen and helium. For the remaining substances, the mean distance between the centres of adjacent molecules is about twice their diameter, *i.e.*, the " edges " of such molecules are separated by about one diameter. For liquids at the ordinary temperature the molecules will approach one another still more closely and cannot therefore be treated as point centres of force. It is this fact which is the chief difficulty in the way of an adequate theory of capillarity.

In general, it is to be expected that zero volumes and critical volumes will not be capable of accurate analysis as an additive function, but will show deviations for those substances of which the molecules have peculiar intermolecular fields. On the other hand, parachors, in which the influence of this field is largely eliminated, should approach more closely to the requirements of an ideal additive function. As an extreme example, the constants found for elementary hydrogen and for hydrogen in organic compounds may be quoted—the zero volumes show a large difference but the parachors are nearly identical :

	V_0.	$[P]$.
H_2 (element)	22·0	35·1
2H (combined)	13·4	34·2

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