CCXXXIV.—*Molecular Volumes at Absolute Zero. Part II. Zero Volumes and Chemical Composition.*

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IT has been shown (preceding paper) that the influence of temperature on the density of a liquid is represented accurately by the equation

$$D - d = D_0(1 - T/T_c)^{3/10} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where D and d are the densities of the liquid and its saturated vapour, respectively, at a temperature T, and T_c is the critical temperature. The constant D_0 is the density the liquid would have at absolute zero if equation (1) still held; this assumption is probably not far from the truth, since the coefficient of expansion decreases continually as the temperature falls and is already small at the freezing point. In general, equation (1) gives values for D_0 which are about 20% greater than the density at 0°, so that if sufficiently accurate density data over a wide range of temperatures are available, the extrapolation seems to be justifiable.

By dividing this constant into the molecular weight one obtains the " zero volume," V_0, *i.e.*, the molecular volume of a supercooled liquid at absolute zero; this appears to be a very significant constant, for the form of equation (1) shows that zero volumes are proportional to the molecular volumes for a series of liquids at the same reduced temperature, *i.e.*, they are corresponding volumes. It has also been shown in Part I that zero volumes are nearly proportional to critical volumes in a number of cases in which the latter constant has been determined with accuracy.

It will now be shown that zero volumes are an additive function of chemical composition, and can be predicted with considerable accuracy for a large number of substances by adding together suitable constants for the atoms and structures present in the molecule. In the tables, the zero volumes of 284 substances are recorded and compared with the values obtained by adding the constants given in Table II. For 236 substances, or 82% of the number studied, the difference between the extrapolated and the calculated values does not exceed 2%.

The method by which D_0 is calculated from a range of density observations is outlined in Part I (p. 1781). It is obvious that the accuracy of the value found will depend on the accuracy and temperature range of the data employed. For most of the substances studied, densities accurate to 1 part in 1000 parts over a range of 40° or more have been used, and it is estimated that the maximum error in the calculation of D_0 is considerably less than ½%. In a few cases, the available observations covered a smaller temperature range, and the values of V_0 found may therefore be burdened with a larger error of calculation; these are indicated in the tables by parentheses.

(2) *Evaluation of Constants.*

The first evidence that zero volumes are simply related to chemical composition is given by the fact that position isomerides give nearly the same value for this constant. Some examples are quoted in Table I, and others will be found in the tables which follow.

TABLE I.

Position Isomerides.

$C_2H_4O_2$.	V_0.	C_8H_{10}.	V_0.
Methyl formate	46·7	Ethylbenzene	(99·3)
Acetic acid	46·7	*o*-Xylene	(98·9)
		m- ,,	(99·1)
$C_9H_{18}O_2$.		*p*- ,,	(100·7)
Ethyl *n*-heptoate	149·6		
d-β-Butyl *n*-valerate	150·8	$C_8H_{10}O$.	
d-β-Hexyl propionate	149·7	Phenetole	105·5
d-β-Heptyl acetate	150·5	*m*-Tolyl methyl ether	(103·9)
		p- ,, ,, ,,	(104·0)

It was next found that several homologous series (hydrocarbons, alkyl halides, ethers, esters. ketones, aldehydes, and amines) gave very nearly a constant difference in zero volumes for a difference in composition of CH_2; the values found for this constant ranged from 14·2 to 14·9 in different series with a weighted mean of $CH_2 = 14·5$. From this value, the constant for hydrogen was obtained by subtracting nCH_2 from a series of observations for the paraffins C_nH_{2n+2}, the mean value being $H = 6·7$, whence $C = 1·1$. These fundamental constants were then employed to evaluate the constants for other elements and structures.

It soon became apparent that the analysis of zero volumes could be carried out with the same simplicity as is met with in the case of the parachors (Sugden, J., 1924, **125**, 1177). With one or two exceptions (see p. 1796), the same constant serves for a particular atom in all its compounds, and the same constant for a particular structure, no matter what elements are taking part in it. Thus a double bond has the same value in ethylene derivatives, ketones, esters, and benzene derivatives; the last can all be expressed satisfactorily on the basis of the Kekulé formula. The most probable values for a number of atomic and structural constants are collected in Table II.

A clear distinction is also shown between the two types of double bond which have already been differentiated by means of the parachor (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525). This

TABLE II.

Atomic and Structural Constants.

Atomic constants.	Atomic constants.	Structural constants.
H = 6·7	I = 28·3	Triple bond = 15·5
C = 1·1	P = 12·7	Double bond = 8·0
N = 3·6	S = 14·3	3-Membered ring = 4·8
O = 5·0	O (in alcohols) = 3·0	4-Membered ring = 3·2
F = 10·3	N (in amines) = 0·0	5-Membered ring = 1·8
Cl = 19·3		6-Membered ring = 0·6
Br = 22·1		Semipolar double bond = 0·0

is demonstrated by the data in Table III, in which the column headed ΣV_0 gives the sum of the atomic and structural constants for the substance considered except that for the linkage to be determined. By subtracting ΣV_0 from V_0 (obs.) the value shown in the last column for each type of double bond is obtained. It will be seen that, whilst a non-polar double bond gives a nearly constant increase of 8·0 c.c. in the zero volume, a semipolar double bond gives a constant which fluctuates about a value of zero.

TABLE III.

(i) Non-polar double bonds.

Substance.	Formula.	V_0 (obs.).	ΣV_0.	Double bond.
Ethylene	C_2H_4	37·4	29·0	8·4
Propylene	C_3H_6	51·7	43·5	8·2
Benzene	C_6H_6	71·2	47·4	7·9 × 3
Toluene	C_7H_8	86·7	61·9	8·3 × 3
Acetone	C_3H_6O	56·0	48·5	7·5
Acetylacetone	$C_5H_8O_2$	84·5	69·1	7·7 × 2
Methyl formate	$C_2H_4O_2$	56·7	39·0	7·7
Ethyl acetate	$C_4H_8O_2$	76·4	68·0	8·4

(ii) Semipolar double bonds.

Substance.	Formula.	V_0 (obs.).	ΣV_0.	Double bond.
Thionyl chloride	$SOCl_2$	58·0	58·1	−0·1
Sulphuryl chloride	SO_2Cl_2	62·6	63·1	−0·25 × 2
Methyl sulphate	$C_2H_6SO_4$	78·5	75·9	+1·3 × 2
Ethyl sulphite	$C_4H_{10}SO_3$	101·1	100·9	+0·2
Ethyl ethanesulphonate ...	,,	96·7	,,	−2·1 × 2
Ethyl sulphate	$C_4H_{10}SO_4$	107·3	103·9	+1·7 × 2
Nitrobenzene	$C_6H_5NO_2$	87·0	85·8	+1·2
Phosphorus oxychloride ...	$POCl_3$	73·4	75·4	−2·0
Ethyl phosphate	$C_6H_{15}PO_4$	140·5	139·6	+0·9
Phenyl phosphate	$C_{18}H_{15}PO_4$	(230·2)	226·8	+3·4
Nitric acid	HNO_3	32·7	33·3	−0·6
Sulphuric acid	H_2SO_4	47·1	47·7	−0·3 × 2
Perchloric acid	$HClO_4$	45·7	46·0	−0·1 × 3

It is noteworthy that the existence of the two types of double bond is now demonstrated by three independent lines of experimental evidence : (1) The different effect produced by these linkages on the parachor (Sugden, Reed, and Wilkins, *loc. cit.*), (2) the evidence from the optical activity of certain sulphur compounds which contain semipolar double bonds (Phillips, J., 1925,

127, 2552; 1926, 2079; this vol., p. 188), and (3) the effect of these two linkages upon the zero volume. The last of these methods has the advantage that it is applicable to associated liquids and shows (compare Table III) that free nitric, sulphuric, and perchloric acids contain, respectively, one, two, and three semipolar double bonds in accordance with the requirements of the octet theory of valency.

(3) *Normal Liquids.*

In this and the following section a comparison is made between the values of V_0 (obs.) derived from the density data and the predicted figure, V_0 (calc.), obtained by adding together the constants recorded in Table II. The column headed "Observer" gives initials only; full references are given on p. 1797.

Table IV gives the data for hydrocarbons.

TABLE IV.

Hydrocarbons.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
1. Acetylene	C_2H_2	M. & W.	31·6	31·1	−1·6
"	"	Math.	32·0	"	−2·8
2. Ethylene	C_2H_4	M. & W.	37·4	37·0	−1·1
3. Ethane	C_2H_6	"	41·4	42·4	+2·4
4. Allylene	C_3H_4	"	44·3	45·6	+2·9
5. Propylene	C_3H_6	"	51·7	51·5	−0·4
6. Propane	C_3H_8	"	56·2	56·9	+1·3
7. *n*-Butane	C_4H_{10}	Wiss.	69·6	71·4	−2·6
8. *n*-Pentane	C_5H_{12}	Y.	83·9	85·9	+2·4
9. *iso*Pentane	"	"	86·1	"	−0·2
10. Benzene	C_6H_6	"	71·2	71·4	+0·3
"	"	P.	70·6	"	+1·2
11. Methyl*cyclo*pentane	C_6H_{12}	K.	(88·3)	88·8	+0·6
12. *cyclo*Hexane	"	J.	86·7	87·6	+1·0
"	"	Y.	86·0	"	+1·8
13. *n*-Hexane	C_6H_{14}	"	100·8	100·4	−0·4
14. Di*iso*propyl	"	"	99·9	" .	+0·5
15. Toluene	C_7H_8	"	86·7	85·9	−0·9
"	"	P.	86·2	"	−0·3
16. Methyl*cyclo*hexane	C_7H_{14}	K.	102·6	102·1	−0·5
17. *n*-Heptane	C_7H_{16}	Y.	115·7	114·9	−0·7
"	"	P.	116·2	"	−1·2
18. Ethylbenzene	C_8H_{10}	"	(99·3)	100·4	+1·1
19. *o*-Xylene	"	"	(98·9)	"	+1·5
20. *m*- "	"	"	(99·1)	"	+1·3
21. *p*- "	"	"	(100·7)	"	−0·3
22. 1 : 1-Dimethyl*cyclo*hexane	C_8H_{16}	K.	(117·4)	116·6	−0·7
23. *n*-Octane	C_8H_{18}	Y.	130·8	129·4	−1·0
24. Di*iso*butyl	"	"	130·9	"	−1·1
25. ψ-Cumene	C_9H_{12}	P.	113·4	114·9	+1·4
26. Cumene	"	"	(113·8)	"	+1·0
27. Mesitylene	C_9H_{12}	P.	115·0	114·9	−0·1
28. *n*-Propylbenzene	"	"	(113·8)	"	+1·0
29. *p*-Cymene	$C_{10}H_{14}$	"	(128·6)	129·4	+0·7
30. *iso*Butylbenzene	"	"	(126·8)	"	+2·1

It may be noted that the densities of di*iso*butyl quoted by Landolt–Bornstein (4th edn., 1912, p. 154) are wrongly transcribed from Young's paper; the figures given are the densities of *cyclo*hexane which appear on the adjoining page.

Tables V, VI, VII, and VIII are self-explanatory. Some marked

TABLE V.

Halogen Derivatives.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
31.	Carbon tetrachloride	CCl_4	Y.	77·4	78·3	+1·2
32.	Methylene iodide	CH_2I_2	P.	68·4	71·1	+3·9
33.	Acetylene tetrachloride	$C_2H_2Cl_4$	J.	87·7	92·8	+5·8
34.	,, tetrabromide	$C_2H_2Br_4$	,,	100·9	104·0	+3·1
35.	Ethylene dichloride	$C_2H_4Cl_2$	,,	62·8	67·6	+7·7
	,, ,,	,,	P.	62·8	,,	+7·7
36.	Ethyl iodide	C_2H_5I	,,	64·2	64·0	−0·3
37.	*n*-Propyl bromide	C_3H_7Br	,,	71·6	72·3	+1·0
38.	*p*-Dichlorobenzene	$C_6H_4Cl_2$	,,	96·8	96·6	−0·2
39.	Fluorobenzene	C_6H_5F	Y.	75·1	75·0	−0·1
40.	Chlorobenzene	C_6H_5Cl	,,	84·4	84·0	−0·4
	,,	,,	P.	83·2	,,	+1·0
41.	Bromobenzene	C_6H_5Br	,,	87·9	86·8	−1·3
	,,	,,	Y.	88·3	,,	−1·7
42.	Iodobenzene	C_6H_5I	,,	95·5	93·0	−2·6
	,,	,,	P.	94·1	,,	−1·2
43.	*p*-Fluorobromobenzene	C_6H_4FBr	J.	90·8	90·4	−0·4
44.	*p*-Chlorobromobenzene	C_6H_4ClBr	S.	99·1	99·4	+0·3
45.	*p*-Chloroiodobenzene	C_6H_4ClI	,,	102·9	105·6	+2·6
46.	*m*-Fluorotoluene	C_7H_7F	J.	90·2	89·5	−0·8
47.	*p*-Bromotoluene	C_7H_7Br	P.	102·3	101·3	−1·0
48.	*p*-Iodotoluene	C_7H_7I	S.	109·6	107·5	−1·9
49.	*n*-Octyl chloride	$C_8H_{17}Cl$	P.	140·4	142·0	+1·2
50.	*n*-Octyl bromide	$C_8H_{17}Br$	,,	144·7	144·8	+0·1
51.	*n*-Octyl iodide	$C_8H_{17}I$	,,	150·4	151·0	+0·4

TABLE VI.

Ethers.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
52.	Ethylene oxide	C_2H_4O	M. & B.	37·7	38·8	+2·9
53.	Epichlorohydrin	C_3H_5OCl	J.	63·6	65·9	+3·6
	,,	,,	S. & W.	65·5	,,	+0·7
54.	Ethyl ether	$C_4H_{10}O$	Y.	77·1	76·4	−0·9
55.	Paraldehyde	$C_6H_{12}O_3$	P.	(106·4)	102·6	−3·6
56.	Acetal	$C_6H_{14}O_2$	W.	112·2	110·4	−1·7
57.	Anisole	C_7H_8O	P., Sch.	90·8	90·9	+0·1
58.	Phenetole	$C_8H_{10}O$	,,	105·5	105·4	−0·1
	,,	,,	B.	104·2	,,	+1·2
59.	*m*-Tolyl methyl ether	,,	P.	(103·9)	,,	+1·5
60.	*p*- ,, ,, ,,	,,	,,	(104·0)	,,	+1·4
61.	Veratrole	$C_8H_{10}O_2$	J.	106·1	110·4	+4·1
62.	Dimethylresorcinol	,,	P.	109·2	,,	+1·1
63.	Phenyl propyl ether	$C_9H_{12}O$	,,	(117·9)	119·9	+1·7
64.	Phenyl *iso*propyl ether	,,	,,	(117·5)	,,	+2·0
65.	Phenyl octyl ether	$C_{14}H_{22}O$	,,	(188·7)	192·4	+1·9

deviations occur in compounds containing several halogen atoms, *e.g.*, ethylene dichloride (No. 35) and acetylene tetrachloride (No. 33). Since, however, carbon tetrachloride gives a satisfactory agreement, it is probable that these discrepancies are due to errors of observation. The long series of esters in Table VIII gives a test of accuracy of the additive properties of V_0 over a large range of molecular weight, and affords, in general, excellent support for the views now advanced.

TABLE VII.

Aldehydes and Ketones.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
66.	Acetone	C_3H_6O	B.	56·0	56·5	+0·9
67.	Methyl ethyl ketone	C_4H_8O	T. & J.	71·8	71·0	−1·1
68.	Furfural	$C_5H_4O_2$	W.	68·5	68·1	−0·6
	"	"	J.	68·7	"	−0·9
69.	Acetylacetone	$C_5H_8O_2$	"	84·5	85·1	+0·7
70.	Methyl propyl ketone	$C_5H_{10}O$	T. & J.	85·2	85·5	+0·4
71.	Diethyl ketone	"	"	84·3	"	+1·4
72.	Ethyl acetoacetate	$C_6H_{10}O_3$	P.	103·8	104·6	+0·8
73.	Benzaldehyde	C_7H_6O	"	85·3	85·5	+0·3
74.	Dimethylacetylacetone	$C_7H_{12}O_2$	"	111·6	114·1	+2·3
75.	Dipropyl ketone	$C_7H_{14}O$	"	113·9	114·5	+0·5
76.	Acetophenone	C_8H_8O	"	97·8	100·0	+2·2
77.	Benzylideneacetone	$C_{10}H_{10}O$	"	123·8	123·6	−0·2
78.	Benzophenone	$C_{13}H_{10}O$	"	141·3	143·5	+1·6

TABLE VIII.

Esters.

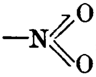
	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
79.	Methyl formate	$C_2H_4O_2$	Y.	46·7	47·0	+0·7
80.	Methyl acetate	$C_3H_6O_2$	"	61·1	61·5	+0·7
81.	Ethyl formate	"	"	61·9	"	−0·7
82.	Methyl propionate	$C_4H_8O_2$	"	75·5	76·0	+0·7
83.	Ethyl acetate	"	"	76·4	"	−0·5
	" "	"	W.	75·9	"	+0·1
84.	*n*-Propyl formate	"	Y.	76·7	"	−0·9
85.	Methyl *n*-butyrate	$C_5H_{10}O_2$	"	90·7	90·5	−0·2
86.	Methyl *iso*butyrate	"	"	90·6	"	−0·1
87.	Ethyl propionate	"	"	90·9	"	−0·4
88.	Propyl acetate	"	"	91·3	"	−0·9
89.	Ethyl carbonate	$C_5H_{10}O_3$	S. R. & W.	98·2	95·5	−2·7
90.	Methyl maleate	$C_6H_8O_4$	S. & Wh.	103·8	104·2	+0·4
91.	Methyl fumarate	"	"	107·5	"	−3·2
92.	*d*-β-Butyl acetate	$C_6H_{12}O_2$	P. & K.	106·1	105·0	−1·1
93.	Methyl citraconate	$C_7H_{10}O_4$	S. & Wh.	117·1	118·7	+1·4
94.	Methyl mesaconate	"	"	116·0	"	+2·3
95.	Ethyl *cyclo*butanecarboxylate	$C_7H_{12}O_2$	S. & W.	108·5	109·3	+0·7
96.	*d*-β-Butyl propionate	$C_7H_{14}O_2$	P. & K.	121·5	119·5	−1·7
97.	Methyl benzoate	$C_8H_8O_2$	P.	(104·3)	105·0	+0·7
98.	Phenyl acetate	"	"	104·8	"	+0·2
99.	*d*-β-Butyl *n*-butyrate	$C_8H_{16}O_2$	P. & K.	134·4	134·0	−0·3
100.	*d*-β-Hexyl acetate	"	"	135·5	"	−1·1

TABLE VIII (*contd.*)

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 calc.).	Diff., %.
101.	Ethyl 1-cyano*cyclo*butane-1-carboxylate...	$C_8H_{11}O_2N$	S. & W.	122·5	122·8	+0·3
102.	Ethyl benzoate	$C_9H_{10}O_2$	P.	(119·0)	119·5	+0·4
103.	Ethyl *cyclo*propane-1 : 1-dicarboxylate ...	$C_9H_{14}O_4$	S. & W.	145·4	144·5	−0·6
104.	Ethyl *cyclo*propane-1 : 2-dicarboxylate ...	„	„	146·0	„	−1·0
105.	Ethyl *n*-heptoate	$C_9H_{18}O_2$	P.	149·6	148·5	−0·7
106.	*d*-β-Butyl *n*-valerate	„	P. & K.	150·8	„	−1·5
107.	*d*-β-Hexyl propionate ...	„	„	149·7	„	−0·8
108.	*d*-β-Heptyl acetate	„	„	150·5	„	−1·3
109.	Methyl cinnamate	$C_{10}H_{10}O_2$	S. & Wh.	127·5	128·6	+0·9
110.	Methyl *allo*cinnamate ...	„	„	124·3	„	+3·6
111.	*n*-Propyl benzoate	$C_{10}H_{12}O_2$	P.	(133·5)	134·0	+0·4
112.	*iso*Propyl benzoate	„	„	(136·6)	„	−1·9
113.	Ethyl *o*-toluate	„	„	(131·7)	„	+1·7
114.	Ethyl *p*-toluate	„	„	(133·3)	„	+0·6
115.	Ethyl phenylacetate	„	„	(130·2)	„	+2·8
116.	Ethyl *o*-methoxybenzoate	$C_{10}H_{12}O_3$	„	(135·1)	139·0	+2·9
117.	Ethyl *m*-methoxybenzoate	„	„	(137·1)	„	+1·4
118.	Ethyl anisate	„	„	(136·7)	„	+1·7
119.	Ethyl *cyclo*butane-1 : 1-dicarboxylate	$C_{10}H_{16}O_4$	S. & W.	158·4	157·4	−0·7
120.	*d*-β-Butyl *n*-hexoate	$C_{10}H_{20}O_2$	P. & K.	164·8	163·0	−1·2
121.	*d*-β-Hexyl *n*-butyrate ...	„	„	161·2	„	+1·2
122.	*d*-β-Heptyl propionate ...	„	„	164·7	„	+1·1
123.	*d*-β-Octyl acetate	„	„	164·6	„	+1·0
124.	Methyl α-bromocinnamate	$C_{10}H_9O_2Br$	S. & Wh.	138·7	136·0	−2·0
125.	Methyl α-bromo*allo*cinnamate	„	„	140·4	„	−3·2
126.	Methyl β-bromocinnamate	„	„	139·5	„	−2·5
127.	Methyl β-bromo*allo*cinnamate	„	„	142·4	„	−4·7
128.	Ethyl cinnamate	$C_{11}H_{12}O_2$	P.	141·9	143·1	+0·8
129.	Ethyl benzoylacetate ...	$C_{11}H_{12}O_3$	„	145·6	148·1	+1·7
130.	Ethyl phenylpropionate	$C_{11}H_{14}O_2$	„	146·7	148·5	+1·2
131.	*n*-Butyl benzoate	„	„	(147·4)	„	+0·7
132.	*iso*Butyl benzoate	„	„	(148·5)	„	±0·0
133.	Ethyl *p*-*iso*propylbenzoate	„	„	(149·5)	„	−0·7
134.	Ethyl caronate	$C_{11}H_{18}O_4$	S. & W.	171·4	173·5	+1·2
135.	*d*-β-Butyl *n*-heptoate ...	$C_{11}H_{22}O_2$	P. & K.	179·6	177·5	−1·2
136.	*d*-β-Hexyl *n*-valerate ...	„	„	179·0	„	−0·9
137.	*d*-β-Heptyl *n*-butyrate ...	„	„	179·7	„	−1·2
138.	*d*-β-Octyl propionate ...	„	„	177·6	„	−0·1
139.	Ethyl phthalate	$C_{12}H_{14}O_4$	P.	168·0	167·6	−0·3
140.	Ethyl terephthalate	„	„	168·2	„	−0·4
141.	*d*-β-Butyl *n*-octoate	$C_{12}H_{24}O_2$	P. & K.	195·5	192·0	−1·8
142.	*d*-β-Hexyl *n*-hexoate	„	„	194·0	„	−1·0
143.	*d*-β-Heptyl *n*-valerate ...	„	„	194·1	„	−1·1
144.	*d*-β-Octyl *n*-butyrate ...	„	„	194·2	„	−1·1
145.	Phenyl carbonate	$C_{13}H_{10}O_3$	S. R. & W.	157·2	153·5	−2·4
146.	Ethyl α-naphthoate	$C_{13}H_{12}O_2$	P.	151·9	153·9	+1·3
147.	Ethyl β-naphthoate	„	„	152·7	„	+0·8
148.	Phenyl *n*-heptoate	$C_{13}H_{18}O_2$	„	175·5	177·5	+1·2
149.	*d*-β-Butyl *n*-nonoate	$C_{13}H_{26}O_2$	P. & K.	207·3	206·5	−0·4
150.	*d*-β-Hexyl *n*-heptoate ...	„	„	207·6	„	−0·5

TABLE VIII (*contd.*)

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
151. *d*-*β*-Heptyl *n*-hexoate	$C_{13}H_{26}O_2$	P. & K.	210·2	206·5	−1·8
152. *d*-*β*-Octyl *n*-valerate	,,	,,	209·5	,,	−1·5
153. *d*-*β*-Undecyl acetate	,,	,,	207·6	,,	−0·5
154. *d*-*β*-Heptyl *n*-heptoate	$C_{14}H_{28}O_2$	,,	223·2	221·0	−1·0
155. *d*-*β*-Octyl *n*-hexoate	,,	,,	223·3	,,	−1·1
156. *d*-*β*-Undecyl propionate	,,	,,	222·6	,,	−0·7
157. *n*-Octyl benzoate	$C_{15}H_{22}O_2$	P.	(203·4)	206·5	+1·6
158. Ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate	$C_{15}H_{22}O_8$	S. & W.	242·0	240·7	−0·5
159. *d*-*β*-Butyl *n*-undecoate	$C_{15}H_{30}O_2$	P. & K.	237·2	235·5	−0·7
160. *d*-*β*-Hexyl *n*-nonoate	,,	,,	236·3	,,	−0·4
161. *d*-*β*-Heptyl *n*-octoate	,,	,,	238·1	,,	−1·1
162. *d*-*β*-Octyl *n*-heptoate	,,	,,	237·0	,,	−0·7
163. *d*-*β*-Undecyl *n*-butyrate	,,	,,	236·5	,,	−0·4
164. *d*-*β*-Butyl *n*-dodecoate	$C_{16}H_{32}O_2$	,,	252·1	250·0	−0·8
165. *d*-*β*-Heptyl *n*-nonoate	,,	,,	252·2	,,	−0·9
166. *d*-*β*-Octyl *n*-octoate	,,	,,	251·5	,,	−0·6
167. *d*-*β*-Undecyl *n*-valerate	,,	,,	250·8	,,	−0·3
168. *d*-*β*-Hexyl *n*-undecoate	$C_{17}H_{34}O_2$	,,	264·5	264·5	±0·0
169. *d*-*β*-Octyl *n*-nonoate	,,	,,	266·8	,,	−0·9
170. *d*-*β*-Undecyl *n*-hexoate	,,	,,	265·2	,,	−0·3
171. *d*-*β*-Butyl myristate	$C_{18}H_{36}O_2$	,,	280·2	279·0	−0·4
172. *d*-*β*-Hexyl *n*-dodecoate	,,	,,	278·7	,,	+0·1
173. *d*-*β*-Heptyl *n*-undecoate	,,	,,	280·0	,,	−0·4
174. *d*-*β*-Undecyl *n*-heptoate	,,	,,	279·7	,,	−0·3
175. *d*-*β*-Heptyl *n*-dodecoate	$C_{19}H_{38}O_2$	,,	296·6	293·5	−1·0
176. *d*-*β*-Octyl *n*-undecoate	,,	,,	294·2	,,	−0·2
177. *d*-*β*-Butyl palmitate	$C_{20}H_{40}O_2$	,,	307·1	308·0	+0·3
178. *d*-*β*-Hexyl myristate	,,	,,	307·3	,,	+0·2
179. *d*-*β*-Octyl *n*-dodecoate	,,	,,	308·3	,,	−0·1
180. *d*-*β*-Undecyl *n*-nonoate	,,	,,	307·7	,,	+0·1
181. *d*-*β*-Heptyl myristate	$C_{21}H_{42}O_2$	,,	323·1	322·5	−0·2
182. *d*-*β*-Butyl stearate	$C_{22}H_{44}O_2$	,,	334·7	337·0	+0·7
183. *d*-*β*-Hexyl palmitate	,,	,,	337·0	,,	±0·0
184. *d*-*β*-Octyl myristate	,,	,,	337·6	,,	−0·2
185. *d*-*β*-Undecyl *n*-undecoate	,,	,,	335·1	,,	+0·6
186. *d*-*β*-Heptyl palmitate	$C_{23}H_{46}O_2$	,,	352·3	351·5	−0·2
187. *d*-*β*-Undecyl *n*-dodecoate	,,	,,	349·9	,,	+0·5
188. *d*-*β*-Hexyl stearate	$C_{24}H_{48}O_2$	,,	360·6	366·0	+1·5
189. *d*-*β*-Octyl palmitate	,,	,,	376·1	,,	−2·8
190. *d*-*β*-Heptyl stearate	$C_{25}H_{50}O_2$	,,	377·2	380·5	+0·9
191. *d*-*β*-Undecyl myristate	,,	,,	377·2	,,	+0·9
192. *d*-*β*-Octyl stearate	$C_{26}H_{52}O_2$	,,	403·9	395·0	−2·2

Table IX contains the data for a number of nitro-compounds for which the structure  $-\mathrm{N}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$, containing one non-polar and one semipolar bond, has been assumed. If both the double bonds were non-polar, the value of V_0 (calc.) would have to be increased by 8·0 c.c. and would be much larger than the experimental figures.

The nitriles in Table X are assumed to have the structure —C≡N, which is confirmed by the good agreement between the observed and the calculated values. The same conclusion has been reached from a study of the parachor of a number of nitriles (Sugden and Wilkins, *loc. cit.*), so that Langmuir's assumption of a special structure containing two kernels within one octet is unnecessary.

TABLE IX.

Nitro-compounds.

Substance.	Formula.	Observer.	V_0		Diff.,
			(obs.).	(calc.).	%.
193. Nitromethane	CH_3O_2N	W.	42·6	42·8	+0·5
,,	,,	J.	42·9	,,	−0·2
194. Ethyl nitrate	$C_2H_5O_3N$	W.	64·6	62·3	+3·5
195. Nitrobenzene	$C_6H_5O_2N$	Y.	88·0	86·3	−1·9
,,	,,	W.	86·0	,,	+0·4
196. *m*-Fluoronitrobenzene	$C_6H_4O_2NF$	J.	89·7	89·9	+0·2
197. *p*-Fluoronitrobenzene	,,	,,	89·0	,,	+1·0
198. *o*-Chloronitrobenzene	$C_6H_4O_2NCl$	S. & W.	97·8	98·9	+1·1
199. *m*- ,,	,,	,,	97·9	,,	+1·0
200. *p*- ,,	,,	J.	102·1	,,	−3·2
201. *o*-Bromonitrobenzene	$C_6H_4O_2NBr$	S. & W.	100·9	101·7	+0·8
202. *m*- ,,	,,	,,	102·0	,,	−0·3
203. *p*- ,,	,,	,,	103·3	,,	−1·6
204. *o*-Nitrotoluene	$C_7H_7O_2N$	,,	99·3	100·8	+1·5
205. *m*- ,,	,,	,,	100·0	,,	+0·8
206. *p*- ,,	,,	,,	102·2	,,	−1·4

TABLE X.

Nitriles.

Substance.	Formula.	Observer.	V_0		Diff.,
			(obs.).	(calc.).	%.
207. Acetonitrile	C_2H_3N	W.	40·6	41·4	+1·9
208. Malononitrile	$C_3H_2N_2$	W. & S.	52·3	54·9	+5·0
209. Propionitrile	C_3H_5N	W.	55·3	55·9	+1·2
210. Methyl cyanoacetate	$C_4H_5O_2N$	J.	74·4	75·0	+0·8
211. Ethyl cyanoacetate	$C_5H_7O_2N$	,,	88·2	89·5	+1·5
,, ,,	,,	W. & S.	87·8	,,	+1·9
212. Benzonitrile	C_7H_5N	W.	85·6	84·9	−0·8
213. Phenylacetonitrile	C_8H_7N	,,	97·1	99·4	+2·3
214. *o*-Toluonitrile	,,	S. & W.	100·6	,,	−1·2
215. *m*- ,,	,,	,,	100·3	,,	−0·9
216. *p*- ,,	,,	,,	101·1	,,	−1·7

TABLE XI.

Phosphorus Compounds.

Substance.	Formula.	Observer.	V_0		Diff.,
			(obs.).	(calc.).	%.
217. Phosphorus trichloride	PCl_3	Th.	69·6	70·6	+1·4
218. Phosphorus tribromide	PBr_3	S. R. & W.	78·6	79·0	+0·5
219. Phosphorus oxychloride	$POCl_3$	,,	73·4	75·6	+3·0
220. Triethyl phosphate	$C_6H_{15}O_4P$	,,	140·5	139·8	−0·5
221. Triphenylphosphine	$C_{18}H_{15}P$	W. & S.	206·4	206·8	+0·2
222. Triphenyl phosphate	$C_{18}H_{15}O_4P$	S.R.&W.	(230·2)	226·8	−1·5

Tables XI and XII record data for a number of compounds of phosphorus and sulphur. A good agreement between V_0 (obs.) and V_0 (calc.) is found in most cases, both in compounds containing only non-polar linkages and in those containing semipolar double bonds.

TABLE XII.

Sulphur Compounds.

				V_0		Diff.,
	Substance.	Formula.	Observer.	(obs.).	(calc.).	%.
223.	Thionyl chloride	$SOCl_2$	S. R. & W.	58·0	57·9	−0·2
224.	Sulphuryl chloride	SO_2Cl_2	,,	62·6	62·9	+0·5
225.	Sulphur monochloride	S_2Cl_2	J.	67·1	67·2	+0·1
226.	Carbon disulphide	CS_2	,,	48·2	45·7	+5·1
227.	Methyl thiocyanate	C_2H_3NS	W.	54·9	55·7	+1·5
228.	Methyl sulphate	$C_2H_6O_4S$	S. R. & W.	78·5	76·7	−2·3
229.	Thiophen	C_4H_4S	J.	63·5	63·3	−0·3
230.	Ethyl sulphite	$C_4H_{10}O_3S$	W. & S.	101·1	100·7	−0·4
231.	Ethyl ethanesulphonate	,,	,,	96·7	,,	+4·0
232.	Ethyl sulphate	$C_4H_{10}O_4S$	S. R. & W.	107·3	105·7	−1·5
233.	Thiophenol	C_6H_6S	W. & S.	85·6	85·7	+0·1
234.	Diphenyl sulphide	$C_{12}H_{10}S$	P.	143·0	143·7	+0·5
235.	Dibenzyl sulphide	$C_{14}H_{14}S$	,,	170·8	172·7	+1·1

(4) *Associated Liquids.*

It has been shown (preceding paper) that acetic acid and ethyl alcohol deviate from the requirements of equation (1) at high temperatures, but that at lower temperatures they give a satisfactory agreement. For acetic acid, in fact, the deviation only becomes appreciable in the neighbourhood of the critical temperature; it is therefore to be expected that the value of V_0 calculated from density observations at lower temperatures will be reproduced by adding together suitable constants from Table II. The data in Table XIII show that this is substantially true for a number of acids.

TABLE XIII.

Acids.

				V_0		Diff.,
	Substance.	Formula.	Observer.	(obs.).	(calc.).	%.
236.	Formic acid	CH_2O_2	W.	30·7	32·5	+5·8
237.	Acetic acid	$C_2H_4O_2$	Y.	46·7	47·0	+0·7
238.	Monochloroacetic acid	$C_2H_3O_2Cl$	J.	56·4	59·6	+5·7
239.	Dichloroacetic acid	$C_2H_2O_2Cl_2$	,,	69·1	72·2	+4·4
240.	Trichloroacetic acid	$C_2HO_2Cl_3$	,,	83·3	84·8	+1·8
241.	Propionic acid	$C_3H_6O_2$	P.	60·8	61·5	+1·2
242.	*n*-Heptoic acid	$C_7H_{14}O_2$	,,	118·3	119·5	+1·1
243.	Nitric acid	HNO_3	V. & M.	32·7	33·3	+1·9
244.	Sulphuric acid	H_2SO_4	W.	47·1	47·7	+1·3
245.	Perchloric acid	$HClO_4$	Wi.	45·7	46·0	+0·7

For the alcohols, association appears to produce a small contraction in volume, and with the exception of methyl and ethyl alcohols the observed values are satisfactorily reproduced (Table XIV) by giving oxygen the value 3·0 in alcohols instead of the usual value O = 5·0. A somewhat larger contraction is found for amines (Table XV), for which N = 0 is used instead of 3·6 as in other nitrogen compounds. This contraction in zero volume is probably not a real change in volume but may be accounted for as follows. It seems probable from the behaviour of acetic acid and ethyl alcohol that equation (1) holds so long as the degree of association remains unchanged with increasing temperature, but that if the degree of association alters then the density decreases with temperature more rapidly than is predicted by this equation. For observations below the boiling point, the effect is small, and produces a small increase in the rate of change of density with temperature, which on extrapolation gives rather too high a value for the zero density, and consequently too small a value for the zero volume. This explanation is supported by the fact that methyl and ethyl alcohols, for which equation (1) holds up to temperatures well above the boiling points, do not exhibit this contraction, but give values for oxygen of about 5·0.

TABLE XIV.

Alcohols.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
246.	Methyl alcohol	CH_4O	Y.	32·3	30·9	−4·3
247.	Ethyl alcohol	C_2H_6O	,,	46·8	45·4	−2·9
248.	Ethylene glycol	$C_2H_6O_2$	W.	48·4	48·4	±0·0
249.	*n*-Propyl alcohol	C_3H_8O	P.	60·6	59·9	−1·2
250.	*d*-Methylethylcarbinol	$C_4H_{10}O$	P. & K.	74·4	74·4	±0·0
251.	*d*-Methyl-*n*-propylcarbinol	$C_5H_{12}O$	,,	88·1	88·9	+0·9
252.	Phenol	C_6H_6O	P.	74·3	74·4	+0·1
	,,	,,	B.	74·3	,,	+0·1
253.	*d*-Methyl-*n*-butylcarbinol	$C_6H_{14}O$	P. & K.	102·4	103·4	+1·0
254.	*o*-Chlorophenol	C_6H_5OCl	B.	86·2	87·0	+0·9
255.	*o*-Cresol	C_7H_8O	,,	86·9	88·9	+2·3
256.	*m*- ,,	,,	,,	88·6	,,	+0·4
257.	*p*- ,,	,,	,,	89·5	,,	−0·7
258.	Benzyl alcohol	,,	P.	88·3	,,	+0·7
	,, ,,	,,	W.	87·9	,,	+1·1
259.	*d*-Methyl-*n*-amylcarbinol	$C_7H_{16}O$	P. & K.	116·2	117·9	+1·5
260.	Methyl salicylate	$C_8H_8O_3$	P.	106·6	108·0	+1·3
261.	Cinnamyl alcohol	$C_9H_{10}O$	,,	110·2	112·5	+2·1
262.	Ethyl salicylate	$C_9H_{10}O_3$	,,	122·3	122·5	+0·2
263.	*d*-Methyl-*n*-heptylcarbinol	$C_9H_{20}O$	P. & K.	145·3	146·9	+1·1
264.	Cuminol	$C_{10}H_{14}O$	P.	135·1	132·4	−2·0
265.	Thymol	,,	,,	130·4	,,	+1·8
266.	*d*-Methyl-*n*-octylcarbinol	$C_{10}H_{22}O$	P. & K.	159·7	161·4	+1·1
267.	*d*-Methyl-*n*-nonylcarbinol	$C_{11}H_{24}O$	,,	174·3	175·9	+0·9
268.	*d*-Methyl-*n*-decylcarbinol	$C_{12}H_{26}O$	,,	186·4	190·4	+2·3

TABLE XV.

Amines.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
269. Ammonia	NH_3		19·1	20·1	+5·0
270. Methylamine	CH_5N	J.	33·7	34·6	+2·7
271. Dimethylamine	C_2H_7N	,,	50·1	49·1	−2·0
272. Ethylamine	,,	,,	48·2	,,	+1·8
273. Trimethylamine	C_3H_9N	,,	65·6	63·6	−3·0
274. *n*-Propylamine	,,	,,	62·7	,,	+1·4
275. Diethylamine	$C_4H_{11}N$	,,	78·0	78·1	+0·1
276. Piperidine	$C_5H_{11}N$	,,	79·7	79·8	+0·1
277. Aniline	C_6H_7N	Y.	77·7	78·1	+0·4
,, ...	,,	B.	76·8	,,	+1·7
278. *m*-Phenylenediamine	$C_6H_8N_2$	P.	82·5	84·8	+2·8
279. Triethylamine	$C_6H_{15}N$	J.	108·1	107·1	−0·9
280. Di-*n*-propylamine	,,	,,	108·0	,,	−0·8
281. *o*-Toluidine	C_7H_9N	P.	90·5	92·6	+2·3
282. Benzylamine	,,	,,	91·2	,,	+1·5
283. Dimethylaniline	$C_8H_{11}N$	,,	105·7	107·1	+1·3
284. Tripropylamine	$C_9H_{21}N$	J.	153·1	150·6	−1·7

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Summary.

(1) It has been shown that zero volumes can be predicted by adding together certain characteristic constants for the atoms and structures present in the molecule. Of the 284 compounds considered, 236 are within 2% and 149 within 1% of the calculated value. The agreement is not quite so good as is found with the parachor; the zero volume is, however, extrapolated from the

experimental data and is therefore subject to a greater error in its determination.

(2) Non-polar and semi-polar double bonds can be clearly distinguished by their effect upon the zero volume.

(3) The zero volumes of associated liquids, *e.g.*, alcohols and amines, can be predicted by making a small change in the values for oxygen and nitrogen.

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[*Received, June* 10*th*, 1927.]