CCXXXIII.—*Molecular Volumes at Absolute Zero. Part I. Density as a Function of Temperature.*

By Samuel Sugden.

During the last few years it has been shown by the author and others that there are several empirical relations between surface tension, density, and temperature which hold with considerable accuracy over a large range of the variables concerned. Of these, the most important for the present discussion are van der Waals's equation (*Z. physikal. Chem.*, 1894, **13**, 716) for the variation of surface tension with temperature,

$$\gamma = \gamma_0(1 - T_r)^{6/5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and Macleod's relation (*Trans. Faraday Soc.*, 1923, **19**, 38) between surface tension and density,

$$\gamma = C(D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In these equations, γ is the surface tension, T_r the reduced temperature, D and d are the densities of the liquid and saturated vapour, respectively, and γ_0 and C are constants.

The first equation has been shown to give the experimental values of the surface tension of non-associated liquids from the ordinary temperature to within a few degrees of the critical point (Sugden, J., 1924, **125**, 32). Equation (2) was shown by the present author to hold for a large number of liquids over a wide range of temperatures. Further, from this equation is derived the formula for calculating the parachor $[P]$ where

$$[P] = MC^{1/4} = M\gamma^{1/4}/(D - d) \quad . \quad . \quad . \quad . \quad (3)$$

(M = molecular weight). This constant is found to be an accurately additive function of certain atomic and structural constants (Sugden, J., 1924, **125**, 1177; Sugden, Reed, and Wilkins, J., 1925, **127**, 1525; Sugden and Whittaker, *ibid.*, p. 1868; Sugden and Wilkins, *ibid.*, p. 2517; this vol., p. 139), and in particular provides a clear experimental distinction between non-polar and semipolar double bonds.

These two equations, although empirical and at present not related to any theory of the liquid state, are supported by a considerable amount of experimental evidence. From them, it is obviously possible to deduce a number of other relationships between the variables concerned, including a modified form of the Ramsay-Shields equation (compare Ferguson, *Trans. Faraday Soc.*, 1923, **19**, 41, 407). The simplest of these is a relation between density and temperature

$$D - d = D_0(1 - T_r)^{3/10} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is obtained by eliminating γ between equations (1) and (2). Abundant material for testing this equation is to be found in the data of Young (*Proc. Roy. Soc. Dublin,* 1910, **12**, 374), which include measurements of the liquid and vapour densities of 30 substances. For all of them equation (4) is found to hold with remarkable accuracy; to save space, however, the calculations will only be given for the liquids to which equation (1) has been applied in a previous communication.

Equation (4) contains two constants, D_0 and the critical temperature, since $T_r = T/T_c$. These were determined by calculating the value of $(D - d)^{10/3}$ at intervals of 40°, since this quantity is a linear function of temperature, and applying the method of " zero sum " (Campbell, *Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816). The constants obtained in this manner were then used to calculate the density difference $(D - d)$ at each temperature; the results are shown in Table I, from which it will be seen that equation (4) reproduces the experimental data with a high degree of accuracy—in general the difference between the observed and the calculated values of $D - d$ is 1 part in 500 parts. A few greater deviations are found in the neighbourhood of the critical point, but in this region it is difficult to measure the density of the saturated vapour with precision.

The six liquids named in Table I belong to the class of unassociated liquids. Table II gives similar data for two associated liquids, *viz.*, acetic acid and ethyl alcohol, and shows that equation (4) holds for a part of the range; above a definite temperature, however, the density decreases more rapidly than is indicated by the formula, and the critical point is reached at a lower temperature than would be expected from the slope of the density–temperature curve at low temperatures. This effect is scarcely appreciable for acetic acid, but more pronounced for ethyl alcohol. It would seem, therefore, that association has little or no influence on the density, provided

TABLE I.

Variation of Density with Temperature.

	Benzene.			Chlorobenzene.		
t.	D−d (obs.).	D−d (calc.).	Diff.	D−d (obs.).	D−d (calc.).	Diff.
0°	0·9000	0·8968	−0·0032	1·1279	1·1237	−0·0042
40	0·8568	0·8571	+0·0003	1·0844	1·0845	+0·0001
80	0·8118	0·8126	+0·0008	1·0411	1·0420	+0·0009
120	0·7615	0·7615	±0·0000	0·9934	0·9944	+0·0010
160	0·7012	0·7008	−0·0004	0·9412	0·9416	+0·0004
200	0·6250	0·6246	−0·0004	0·8804	0·8795	−0·0009
240	0·5137	0·5169	+0·0032	0·8056	0·8057	+0·0001
280	0·2854	0·2743	−0·0111	0·7342	0·7378	+0·0036 (270°)
	t_c (obs.), 288·5.			t_c (obs.), 359·2.		
	Ethyl ether.			Methyl formate.		
0°	0·7354	0·7368	+0·0014	1·0025	1·0030	+0·0005
40	0·6857	0·6866	+0·0009	0·9415	0·9416	+0·0001
80	0·6286	0·6260	−0·0026	0·8698	0·8692	−0·0006
120	0·5471	0·5475	+0·0004	0·7801	0·7793	−0·0008
160	0·4256	0·4270	+0·0014	0·6513	0·6550	+0·0037
180	0·3133	0·3129	−0·0004	0·4134	0·4134	±0·0000 (200°)
	t_c (obs.), 193·8.			t_c (obs.), 214.		
	Ethyl acetate.			Carbon tetrachloride.		
0°	0·9243	0·9235	−0·0008	1·6323	1·6301	−0·0022
40	0·8754	0·8760	+0·0006	1·5540	1·5558	+0·0018
80	0·8210	0·8217	+0·0007	1·4704	1·4722	+0·0018
120	0·7580	0·7571	−0·0009	1·3738	1·3758	+0·0020
160	0·6775	0·6767	−0·0008	1·2617	1·2605	−0·0012
200	0·5630	0·5641	+0·0011	1·1146	1·1134	−0·0012
240	0·3279	0·3296	+0·0017	0·8980	0·8973	−0·0007
	t_c (obs.), 250·1.			t_c (obs.), 283·15.		

that the degree of association does not change with temperature. This conclusion is supported by the fact that the value of D_0 found for acetic acid is almost identical with that for its isomeride methyl formate, whilst the values for the alcohols, as will be shown in the following paper, are those to be expected from their composition.

TABLE II.

Variation of Density with Temperature. (Associated liquids.)

	Acetic acid.			Ethyl alcohol.		
t.	D−d (obs.).	D−d (calc.).	Diff.	D−d (obs.).	D−d (calc.).	Diff.
0°	1·0697	1·0700	+0·0003	0·8065	0·8070	+0·0005
40	1·0282	1·0288	+0·0006	0·7719	0·7720	+0·0001
80	0·9825	0·9826	+0·0001	0·7331	0·7326	−0·0005
120	0·9329	0·9315	−0·0014	0·6859	0·6876	+0·0017
160	0·8740	0·8722	−0·0018	0·6137	0·6344	+0·0207
200	0·8060	0·8020	−0·0040	0·5060	0·5682	+0·0522
240	0·7138	0·7136	−0·0002	0·2110	0·4764	+0·2654
280	0·5746	0·5878	+0·0132	—	—	—
	t_c (obs.), 321·6.			t_c (obs.), 243·1.		

The critical temperatures predicted from the density observations are collected in Table III and are compared with the observed values and also with the values deduced from the variation of surface tension with density (Sugden, J., 1924, **125**, 32). It will be seen that, in general, the unassociated liquids give a good agreement between the observed and the calculated critical temperatures, whilst for associated liquids the observed critical temperature is markedly lower than that predicted from the lower part of the density curve.

TABLE III.

	Critical temperature		
Substance.	from density.	from surface tension.	obs.
Benzene	285·5°	287°	288·5°
Chlorobenzene	358	358	359·2
Ethyl ether	191	193	193·8
Methyl formate	211	212	214
Ethyl acetate	248	249	250·1
Carbon tetrachloride	278	280	283·1
Methyl alcohol	279	—	240
Ethyl alcohol	290	—	243·1
Acetic acid	324	—	321·6

Since equation (4) represents the variation of density with temperature with great precision as the temperature increases, it is reasonable to suppose that it will also hold as the temperature decreases. The constant D_0 is therefore of considerable interest, since it represents the density of the supercooled liquid at absolute zero. The values of this constant are collected in Table IV, and if these numbers are divided into the molecular weight of the liquid, the molecular volume (V_0) at absolute zero is obtained : this will be referred to as the " zero volume." The column headed $[P]$ gives the calculated value of the parachor for each liquid, and the fifth column shows that the ratio $[P]/V_0$ is nearly constant for the nine

TABLE IV.

Zero Volumes and the Parachor.

Substance.	D_0.	V_0.	$[P]$.	$[P]/V_0$.
Benzene	1·0965	71·2	207·1	2·91
Chlorobenzene	1·3323	84·4	244·3	2·89
Ethyl ether	0·9616	77·1	210·0	2·73
Methyl formate	1·2863	46·7	138·0	2·96
Ethyl acetate	1·1538	76·4	216·0	2·83
Carbon tetrachloride	2·0015	77·4	222·0	2·87
Methyl alcohol	0·9936	32·3	93·2*	2·89
Ethyl alcohol	0·9846	46·8	132·2*	2·82
Acetic acid	1·2853	46·7	138·0*	2·96

* Calculated from the atomic and structural constants.

substances tabulated. This constancy must, however, be regarded as fortuitous, since from equations 1, 3, and 4 it is readily shown that

$$[P] = \gamma_0^{1/4} V_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

For organic substances γ_0 has values ranging from about 60 to 80, so the fourth root of this, which gives the ratio $[P]/V_0$, does not vary much. If, however, the range is extended on the one hand to hydrogen, which has a small value of γ_0, and on the other hand to metals and their salts, which have large surface tensions, it is found that the zero volume is no longer proportional to the parachor.

A relation of greater significance is exhibited in Table V, which shows that the zero volume is very nearly a constant fraction of the critical volume. The data for hydrogen are given by Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 528), and those for the other substances by Young (*loc. cit.*). Except in the case of hydrogen the ratio V_0/V_c is very nearly constant over the whole range considered.

TABLE V.

Zero Volumes and Critical Volumes.

Substance.	V_0.	V_c.	V_0/V_c.
Hydrogen	22·0	46·9	0·373
Ethyl ether	77·1	281·9	0·273
Carbon tetrachloride	77·4	276·1	0·280
Methyl formate	46·7	172·0	0·271
Methyl acetate	61·1	227·8	0·268
Methyl propionate	75·5	282·0	0·268
Ethyl acetate	76·4	286·3	0·267
Propyl formate	76·7	284·8	0·269
Methyl butyrate	90·7	340·1	0·267
Methyl *iso*butyrate	90·6	338·9	0·267
Ethyl propionate	90·9	344·3	0·264
Propyl acetate	91·3	345·3	0·264
n-Pentane	83·9	310·3	0·270
*iso*Pentane	86·1	307·0	0·280
Di*iso*propyl	99·9	357·3	0·280
n-Heptane	114·9	427·1	0·269
n-Octane	130·8	490·7	0·267
Di*iso*butyl	116·7	417·5	0·280
Benzene	71·2	256·1	0·278
Fluorobenzene	75·1	271·2	0·277
Chlorobenzene	84·4	307·8	0·274
Bromobenzene	88·3	323·5	0·273

Formulæ of the type of equation (1) have been suggested by earlier workers. Thus van der Waals (*Z. physikal. Chem.*, 1894, **13**, 695) gave the equation

$$V - v = mV_c(1 - T_r)^{\frac{1}{4}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

based on the theory of corresponding states. Here V and v are the specific volumes of vapour and liquid, respectively. Verschaffelt

(Commun. of Leiden, No. 28, 1896) advanced the general formula

$$D - d = mD_c(1 - T_r)^n \quad . \quad . \quad . \quad . \quad . \quad (6)$$

making $n = 0{\cdot}367$ for carbon dioxide. Goldhammer (*Z. physikal. Chem.*, 1910, **71**, 577) tested this formula on Young's density data, using $n = 1/3$ with fairly satisfactory results. It is readily shown that the exponent 3/10 gives results in better agreement with the available data than does Goldhammer's exponent 1/3, for $(D - d)^{10/3}$ is a linear function of temperature (see Table VI), as it should be according to equation (4), whereas $(D - d)^3$ exhibits a temperature coefficient which definitely increases with rise of temperature.

TABLE VI.

t.	$D-d$.	$(D-d)^{10/3}$.	Temp. coeff. × 10^5.	$(D-d)^3$.	Temp. coeff. × 10^5.
			Ether.		
0°	0·7354	0·3589	186	0·3976	185
40	0·6857	0·2844	179	0·3237	188
80	0·6286	0·2129	197	0·2484	212
120	0·5471	0·1340	190	0·1638	216
160	0·4256	0·0580	186	0·0771	231
180	0·3133	0·0209		0·0308	
			Ethyl acetate.		
0°	0·9243	0·7691	319	0·7896	297
40	0·8754	0·6416	309	0·6709	294
80	0·8210	0·5180	302	0·5532	294
120	0·7580	0·3972	310	0·4356	312
160	0·6775	0·2730	314	0·3109	331
200	0·5630	0·1473	308	0·1785	358
240	0·3279	0·0243		0·0353	

Summary.

1. The variation of density with temperature from the freezing point to the critical point is represented accurately for normal liquids by the equation $D - d = D_0(1 - T/T_c)^{3/10}$, where D and d are the densities of the liquid and saturated vapour, respectively, at T° Abs.
2. This equation also holds for associated liquids over the lower part of the temperature range, and in some cases nearly to the critical point.
3. The "zero volume," V_0, obtained by dividing the molecular weight by the constant D_0, is nearly proportional to the critical volume for a large number of substances.

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4.

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