

Dielectric Constants of NonPolar Fluids. II. Analysis of Experimental Data

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specialized assumptions; their formulas can also be derived from the general formulas of I by methods described there.

The molecules were assumed to be spherically symmetric in their mechanical and electrical properties and to interact electrostatically as point dipoles. For molecules with any resemblance to spherical symmetry these approximations are probably admissible, if the radial distribution function and polarizability are interpreted as averages over all orientations; the neglect of quadruple and higher moments introduces appreciable error only for molecules very close together. But for highly asymmetric molecules, the averaging of the properties of two molecules individually before they are allowed to interact, rather than of the properties of the interacting pair (or of clusters of higher order), no doubt introduces a serious error. Furthermore there are cases in which the electrostatic interactions are so far from being of a dipole-dipole nature that it is not even permissible to regard the molecule as equivalent to a dipole plus a quadruple and so on; this is obviously true of long chain molecules.

For these reasons, Yvon was reluctant to apply his formulas to any substances except monatomic ones and a few others; the number of measurements remaining for analysis was small indeed, and no very conclusive test of the formulas was possible. Kirkwood and Böttcher applied their formulas to cases in which data were plentiful, and by suitable choice of the constants in the formulas succeeded in fitting the data better than by use of the Clausius-Mosotti formula; but this is also no very conclusive test, for Kurtz and Ward⁵ accomplished as much by use of purely empirical formulas.

The application to actual liquids and gases of specific formulas based on the spherical molecule is not a step that I wish to defend; but the formulas based on this model do suggest the form (1-1) as a possibly suitable form in which to represent the observed data analytically. If it turns out that the data generally lend themselves to this mode of representation, and if the constants have the orders of magnitudes predicted by the simple theory, then the goal of a more ambitious theory becomes more specific: to calculate the magnitudes of these constants for actual substances. The values of the constants also indicate, more definitely than the original data, to what degree any actual substance departs from the idealized behavior assumed in the simple theory.

I will present here the results of a numerical analysis of representative data, based primarily on the formula (1-1). A direct fit to some of the more specialized formulas has also been made, for comparison. The conclusions are that the more specialized formulas, such as Böttcher's, have no advantage over the general formula (1-1); and that in order to detect and study deviations of the substances studied from the behavior predicted

by the spherical molecule theory, it would be necessary to have available both detailed knowledge of the (average) radial distribution and more precise data on the dielectric constant.

The left member of (1-1) is the reciprocal of the quantity which, according to the Clausius-Mosotti formula, should be proportional to the density. In the right member, therefore, the terms after the first represent the deviation from the Clausius-Mosotti formula. The left member as it stands is the ratio of the Lorentz local field intensity $E+4\pi P/3$ to $4\pi P$ (E =macroscopic electric field intensity, P =polarization). By subtraction of 1 and division by 3 it becomes $1/(\epsilon-1)$, the ratio of the macroscopic field intensity to $4\pi P$; by addition of 2 and division by 3 it becomes $\epsilon/(\epsilon-1)$, the ratio of the electric displacement $D=E+4\pi P$ to $4\pi P$. Either of these ratios or any linear combination of them might be used instead of the one chosen here, and essentially only the value of c_0' would be affected.

The calculations reported here were exploratory, and their primary object was to establish satisfactory procedures for analysis of data rather than to carry out an extensive analysis. Only a few sets of data have been analyzed, but they have been analyzed systematically and quite completely. Numerical, not graphical, methods have been used in order that the relative success of different formulas might be judged as accurately as possible; and the estimates of the success achieved take account of the number of disposable constants in each formula.

The special formulas tested, in addition to the general one (1-1), are:

(a) The empirical Eykman formula, (5-19) of I:

$$\frac{\epsilon-1}{\epsilon^{\frac{1}{3}}+0.4} = \frac{3}{1.4} \frac{d}{d_0} \quad (1-2)$$

(b) Böttcher's formula, (7-4) of I:

$$\frac{d}{d_0} = \frac{\epsilon-1}{9\epsilon} \left\{ (2\epsilon+1) - 2(\epsilon-1) \frac{\alpha}{a^3} \right\} \quad (1-3)$$

(c) Formula (5-3) of I for the simple distribution function $\rho_0(r)$ (Kirkwood's non-attracting spheres):

$$\frac{\epsilon+2}{\epsilon-1} = \frac{d_0}{d} - \frac{2\alpha}{a^3} + \frac{15}{16} \frac{d}{d_0} = \frac{d_0}{d} - c_0 + \frac{15}{16} \frac{d}{d_0} \quad (1-4)$$

(d) The higher order approximation (6-8) of I for the same distribution function:

$$\frac{\epsilon+2}{\epsilon-1} = \frac{d_0}{d} - c_0 + c_1 \frac{d}{d_0} - c_2 \left(\frac{d}{d_0} \right)^2, \quad (1-5)$$

with

$$\begin{aligned} c_0 &= (2/3) \ln[(1+x)/(1-2x)], \\ c_1 &= 0.9375 + 1.55257x, \\ c_2 &= 0.744708, \\ x &= \alpha/a^3. \end{aligned} \quad (1-6)$$

⁵ S. S. Kurtz, Jr. and A. L. Ward, J. Franklin Inst. **222**, 563-592 (1936); **224**, 583-601 and 697-728 (1937).

The Clausius-Mosotti formula itself is (1-1) with only one term retained. Reference will also be made to the basic theoretical formula from which (1-1) is derived, Eq. (3-10) of I:

$$\frac{\epsilon+2}{\epsilon-1} \frac{d_0}{d} = -2C, \quad (1-7)$$

where C (not a constant) is given by an integral involving the radial distribution function $\rho(r)$ and other functions, Eq. (3-9) of I.

Formula (1-4) received more attention in these calculations than it deserves in any subsequent ones. When the calculations were made, the importance of the correction term in Eqs. (5-6) of I was underestimated.

The data will be discussed in the chronological order of the measurements.

2. CARBON DISULFIDE

As representative data on a liquid I have taken the data on carbon disulfide under high pressure at 30°C. Two sets of data have been published, by Chang⁶ and by Danforth.⁷ Both sets were taken in Bridgman's laboratory; Bridgman⁸ states that Chang's, though published later, were taken earlier.

Chang gives 11 values of dielectric constant ϵ at known density d ; for definiteness I have used the values at frequency 2000 c.p.s.⁹ The range of pressure is 1 to 12,000 kg/cm², of density 1.247 to 1.687 g/cm³, and of dielectric constant 2.624 to 3.580. An accuracy of 1/10 percent is claimed in the dielectric constant, but it is not stated what precision measure this is (whether standard deviation or "probable error") or how it was estimated. The densities at given pressures are derived from older data of Bridgman.¹⁰

The first step is to obtain a reliable estimate of the random error in the value of ϵ at given d ; this can be obtained by least squares analysis of the data themselves. If the function $\epsilon(d)$ is expressed analytically by means of an approximating function containing s adjustable constants, such as a polynomial of degree $s-1$, and if the constants are evaluated by a least squares fit to n points (where n considerably exceeds the minimum number s necessary to determine all the constants), an estimate of the variance σ^2 of the data (mean square error for many experiments) may be obtained by dividing the sum of the squares of the deviations by $n-s$.¹¹ If this process is carried out suc-

cursively for $s=1, 2, \dots$, then on the average for many repetitions of the experiment the corresponding variance estimates should at first decrease with increasing s and then become constant at a value equal to the actual variance of the data; after this constant value has been reached, further increase in the degree of the approximating polynomial serves only to fit the errors more faithfully and not to give a better representation of the physical relations. In any single experiment, of course, the variance estimates do not decrease in a regular manner with s but exhibit irregular fluctuations superposed on the general decrease to a constant value.

For simplicity it has been assumed throughout that all values of ϵ in any one set of data have the same variance σ^2 ; the analysis would be only slightly modified if weighting factors were introduced to correspond, for instance, to equal mean square percentage errors in ϵ (or in $\epsilon-1$).

When Chang's 11 points are fitted successively by polynomials $\epsilon(d)$ of degrees 0, 1, 2, 3, the resulting estimates of the standard deviation σ (square root of the variance) of the data are 0.32, 0.019, 0.0058, 0.0063 respectively. We may conclude that a second-degree approximating polynomial is all that is warranted by the data and that the root-mean-square random error in ϵ at a specified d is about 0.006. To fit the data within experimental error by use of a polynomial requires only three constants: therefore an equally good fit by means of any other three-constant function justifies no conclusion in regard to the theoretical significance of the function; but if a one- or two-constant formula can be made to fit the data equally well, that result may have significance.

The straightforward method of testing a formula of the form (1-1) is to carry out for the function $y d$, where

$$y = (\epsilon+2)/(\epsilon-1), \quad (2-1)$$

the same procedure just described for the function ϵ , but with weights

$$W = \left(\frac{1}{d} \frac{d\epsilon}{dy} \right)^2 \quad (2-2)$$

assigned to the points in order that the quantity minimized may still be the sum of the squares of the deviations in ϵ . If this gives an approximating polynomial

$$y d = A_0 + A_1 d + A_2 d^2 + \dots, \quad (2-3)$$

then the constants of (1-1) are

$$d_0 = A_0, \quad c_0' = -A_1, \quad c_1' = A_0 A_2, \quad c_2' = -A_0^2 A_3. \quad (2-4)$$

This procedure applied to Chang's data gives, for polynomials of degrees 0, 1, 2, 3, the estimates $\sigma=0.027$, 0.0063, 0.0064, 0.0068 respectively; the individual deviations for the first three of these are shown in Table I. It must be concluded that only two constants are significant: the data support the form (1-1) or (1-7) as an efficient representation of the relations, and

⁶ Z. T. Chang, Chinese J. Phys. 1, 1-55 (1934).

⁷ W. E. Danforth, Jr., Phys. Rev. 38, 1224-1235 (1931).

⁸ P. W. Bridgman, Rev. Mod. Phys. 18, 1-93 (1946), p. 71.

⁹ With correction of an obvious misprint in the value at 5000 kg/cm².

¹⁰ P. W. Bridgman, Proc. Am. Acad. 49, 1-114 (1913), Table XI, p. 62.

¹¹ E. T. Whittaker and G. Robinson, *The Calculus of Observations*, 4th edition (Blackie and Sons, Ltd., London, 1944), p. 245; A. C. Aitken, *Statistical Mathematics*, 4th edition (Oliver and Boyd, Edinburgh and London; Interscience Publishers, Inc., New York, 1945), p. 116.

TABLE I. Carbon disulfide at 30°C: data of Chang.

d Density g/cm ³	ϵ Dielectric constant	Deviation of ϵ from calculated value ^a						
		P_0	P_1	P_2	E	B	(1-4)	(1-5)
1.247	2.624	+0.0439	+0.0063	+0.0035	-0.0427	+0.0185	+0.0132	+0.0088
1.297	2.717	+0.0381	+0.0047	+0.0033	-0.0399	+0.0105	+0.0081	+0.0057
1.336	2.784	+0.0250	-0.0045	-0.0049	-0.0448	-0.0031	-0.0035	-0.0044
1.398	2.914	+0.0219	-0.0001	+0.0007	-0.0310	-0.0041	-0.0023	-0.0011
1.447	3.005	+0.0023	-0.0125	-0.0110	-0.0337	-0.0191	-0.0163	-0.0140
1.487	3.107	+0.0103	+0.0023	+0.0041	-0.0100	-0.0053	-0.0021	+0.0006
1.522	3.177	-0.0050	-0.0062	-0.0045	-0.0096	-0.0136	-0.0107	-0.0078
1.565	3.287	-0.0038	+0.0042	+0.0056	+0.0142	-0.0012	+0.0009	+0.0032
1.603	3.378	-0.0126	+0.0046	+0.0051	+0.0273	+0.0025	+0.0031	+0.0042
1.647	3.487	-0.0243	+0.0050	+0.0042	+0.0449	+0.0089	+0.0070	+0.0060
1.687	3.580	-0.0456	-0.0040	-0.0067	+0.0535	+0.0075	+0.0027	-0.0013
σ^b		0.0273	0.0063	0.0064	0.0368	0.0115	0.0089	0.0070
Constants used:								
A_0 or d_0		3.61458	3.31569	3.09979	3.25939	4.48135	3.85114	3.68790
A_1		—	0.19558	0.48789	—	—	—	—
A_2		—	—	-0.09814	—	—	—	—
α/a^3		—	—	—	—	0.66859	0.26476	0.18860

^a P_n , fit of $(\epsilon+2)d/(\epsilon-1)$ to polynomial of degree n in d (P_0 is the Clausius-Mosotti formula); E , Eykman formula (1-2); B , Bottcher formula (1-3); (1-4) and (1-5), see these equations in the text.

^b Standard deviation of ϵ estimated from the deviations on the assumption that the formula is adequate.

they give clear evidence that a non-vanishing correction term $-2C$ is necessary, but they are capable of yielding only an average value of this correction term for the whole range and are not precise enough to give, by themselves, any reliable information about its variation over the range.

The two-constant fit gives

$$d_0 = A_0 = (3.316 \pm 0.022) \text{ g/cm}^3, \\ -c'_0 = A_1 = 0.196 \pm 0.015.$$

The uncertainty estimates are standard deviations computed by the usual method¹² from the standard deviation 0.0063 of ϵ . The errors in A_0 and A_1 are correlated; the coefficient of correlation (defined as the ratio of the mean product of the two errors to the product of the two standard deviations) is

$$\rho_{01} = -0.9964.$$

The net correction $-2C$ in (1-7) is clearly positive, but its separation into density-independent and density-dependent terms by this method is impossible or at least very uncertain. The three-constant fit gives

$$A_0 = (3.10 \pm 0.26) \text{ g/cm}^3, \\ A_1 = 0.49 \pm 0.34, \\ A_2 = -0.10 \pm 0.12 \text{ cm}^3/\text{g},$$

with correlation coefficients

$$\rho_{01} = -0.9989, \\ \rho_{12} = -0.9991, \\ \rho_{20} = +0.9961.$$

The signs of A_1 and A_2 are both opposite to what one

¹² See E. T. Whittaker and G. Robinson, reference 11, pp. 241, 246. A similar formula, expressing the mean product of the errors in two unknowns in terms of non-diagonal elements A_{ij} , is easily derived: see D. Brunt, *The Combination of Observations* (Cambridge University Press, London, 1917), pp. 116-117.

would expect from Section 1; but from the indicated standard deviations, there is no overwhelming assurance that the signs are right, even if the measurements are subject only to random error. Systematic error, if present, is not detected by this analysis.

For the same substance, Danforth gives eight points over about the same range; his ϵ -values are given only to two decimal places, whereas Chang's are given to three. We may forego the polynomial fit to ϵ and proceed to the polynomial fit to yd : degrees 0, 1, 2, 3 give¹³ $\sigma = 0.067, 0.018, 0.015, 0.018$ respectively (see Table II). Again the data are incapable of yielding much information except the average value of the correction to the Clausius-Mosotti formula. The two-constant fit gives

$$d_0 = A_0 = (2.971 \pm 0.068) \text{ g/cm}^3, \\ -c'_0 = A_1 = 0.429 \pm 0.045;$$

the correlation coefficient of the errors is

$$\rho_{01} = -0.9954.$$

The deviations between these values and those based on Chang's data are well outside the random error: if the samples were identical chemically then at least one set of measurements was subject to systematic error. The three-constant fit gives

$$d_0 = A_0 = (4.15 \pm 0.66) \text{ g/cm}^3, \\ c'_0 = -A_1 = +1.17 \pm 0.91, \\ A_2 = (0.54 \pm 0.30) \text{ cm}^3/\text{g},$$

with correlation coefficients

$$\rho_{01} = -0.9990, \\ \rho_{12} = -0.9991, \\ \rho_{20} = +0.9964.$$

¹³ σ^2 is the sum of a term σ_e^2 due to experimental error and a term $\sigma_r^2 = (1/12) \times 10^{-4}$ due to rounding to the second decimal place; the latter is negligible.

TABLE II. Carbon disulfide at 30°C. data of Danforth.

d Density g/cm ³	ϵ Dielectric constant	Deviation of ϵ from calculated values ^a					
		P_0	P_1	P_2	E	B	(1-4)
1.241	2.61	+0.042	-0.036	-0.022	-0.037	-0.026	-0.029
1.291	2.74	+0.074	+0.006	+0.012	+0.003	+0.011	+0.009
1.332	2.82	+0.070	+0.012	+0.012	+0.008	+0.013	+0.012
1.394	2.94	+0.057	+0.017	+0.010	+0.013	+0.013	+0.014
1.487	3.11	+0.014	+0.007	-0.004	+0.004	-0.001	+0.002
1.550	3.23	-0.022	+0.001	-0.009	-0.001	-0.005	-0.004
1.601	3.33	-0.055	-0.006	-0.010	-0.004	-0.010	-0.007
1.689	3.52	-0.111	-0.006	+0.010	+0.003	-0.001	+0.002
σ^b		0.067	0.018	0.015	0.015	0.015	0.015
Constants used:							
A_0 or d_0		3.61508	2.97082	4.14562	3.27199	3.99702	3.54361
A_1		—	0.42890	-1.17462	—	—	—
A_2		—	—	0.54183	—	—	—
α/a^3		—	—	—	—	0.54132	0.17670

^a P_n , fit of $(\epsilon+2)d/(\epsilon-1)$ to polynomial of degree n in d (P_0 is the Clausius-Mosotti formula), E , Eykman formula (1-2), B , Böttcher formula (1-3), (1-4), see this equation in the text.

^b Standard deviation of ϵ estimated from the deviations on the assumption that the formula is adequate.

Hence¹⁴

$$c_1' = A_0 A_2 = 2.2 \pm 1.6.$$

The constants c_0' and c_1' now have the right signs to be identified with c_0 and c_1 in Section 5 of I; the value $c_1 = 2.2 \pm 1.6$ is consistent with the approximate values 15/16 and 2 derived in I, but the value $c_0 = 1.17 \pm 0.91$ is larger than the estimate $2\alpha/a^3 = 1/4$ or $4\alpha/a^3 = 1/2$ for conducting spheres. These facts are perhaps worth mentioning, but their significance is doubtful. The only conclusions that can be drawn with any certainty are (1) that the deviations from the Clausius-Mosotti formula are significant, (2) that Eq. (1-1) or (1-7) is a satisfactory form for exhibiting the deviations, and (3) that the data are capable only of evaluating α and a mean value of $2C$ and not capable of revealing, with any certainty, the variation of C with density.

If, however, some knowledge of the general nature of this variation is provided by theory, the data may be capable of discriminating between various specific possibilities. Thus if a one- or two-constant formula is fitted to the data, and if the variance of the data is estimated as before, agreement of this estimate with the one obtained by use of polynomials of various degrees indicates that the formula is capable of fitting the data within experimental error. If the formula has a theoretical basis, the theory must be regarded as at least pragmatically successful; if it has no theoretical basis, it may still be useful as an empirical representation of the data. If it significantly fails to meet this test, it must be rejected.

The data already discussed have been fitted in this

¹⁴ The standard deviation σ_c of c_1' is calculated from those of A_0 and A_2 , σ_0 and σ_2 , and from their coefficient of correlation ρ_{20} , by means of the formula $\sigma_c^2 = A_0^2 \sigma_2^2 + 2\rho_{20} A_0 A_2 \sigma_0 \sigma_2 + A_2^2 \sigma_0^2$. This formula is obtained from the first-order formula for the error in a single experiment, $\Delta c_1' = A_0 \Delta A_2 + A_2 \Delta A_0$, by squaring and averaging over many experiments. The correlation between the errors in A_0 and A_2 has therefore been taken into account; but since the error in A_2 is almost as large as A_2 itself, the first-order formula is not very reliable.

manner to several formulas; in each case such weighting factors were used that the quantity minimized was the sum of the squares of the deviations in ϵ . In the case of a formula such as (1-4), where the constants do not enter linearly, it is necessary to use a successive approximation method: provisional values of the constants are used to compute the deviations; the linear equations connecting the first-order changes in these with the changes in the constants are used in a least-squares adjustment of the constants;¹⁵ the new values of the constants are used to compute (directly, without approximation) new values of the deviations; and so on, until successive approximations coincide. In each case σ^2 is estimated by dividing the sum of the squares of the deviations in ϵ by $n-s$, where n is the number of points and s the number of constants; values of σ are therefore directly comparable for one- and two-constant formulas, whereas the deviations themselves would not be.

Chang's data on carbon disulfide at 30°C, when treated thus, yield the following estimates of σ (cf. Table I): Clausius-Mosotti formula (fit of γd with polynomial of degree 0, see above), 0.027; Eykman formula (1-2), 0.037, actually worse than Clausius-Mosotti; Böttcher's formula (1-3), 0.012; formula (1-4), 0.0089; formula (1-5), 0.0070. In view of the discrepancies between Chang's and Danforth's data, it is quite possible that the improvement on going from (1-4) to (1-5) is fortuitous.

Danforth's data on the same substance at the same temperature give for σ (see Table II): Clausius-Mosotti, 0.067; Eykman, 0.015, better in this case; Böttcher and formula (1-4), both 0.015. His data on the same substance at 75°C give: Clausius-Mosotti, 0.044; Eykman, 0.017; Böttcher and formula (1-4), both 0.007. The data at the two temperatures were treated independently.

¹⁵ See E. T. Whittaker and G. Robinson, reference 11, p. 214.

TABLE III. Carbon dioxide at 50°C: data of Michels and Kleerekoper.

d Density Amagat ^b	ϵ Dielectric constant	Deviation of ϵ from calculated values ^a						
		P_0	P_1	P_2	P_3	E	B	(1-4)
24.28	1.02486	-0.00029	-0.00065	-0.00002	+0.00016	-0.00054	+0.00010	-0.00027
34.86	1.03578	-0.00046	-0.00097	-0.00011	+0.00012	-0.00083	+0.00005	-0.00045
44.37	1.04566	-0.00062	-0.00125	-0.00022	+0.00005	-0.00110	-0.00003	-0.00063
61.20	1.06343	-0.00078	-0.00163	-0.00033	-0.00003	-0.00147	-0.00009	-0.00084
72.09	1.07513	-0.00080	-0.00177	-0.00035	-0.00004	-0.00162	-0.00009	-0.00091
81.93	1.08574	-0.00085	-0.00194	-0.00041	-0.00011	-0.00181	-0.00014	-0.00102
92.19	1.09712	-0.00067	-0.00187	-0.00026	+0.00002	-0.00175	+0.00002	-0.00090
104.99	1.11124	-0.00063	-0.00197	-0.00029	-0.00003	-0.00189	-0.00001	-0.00095
116.87	1.12444	-0.00061	-0.00207	-0.00035	-0.00014	-0.00204	-0.00008	-0.00103
143.31	1.15457	-0.00024	-0.00029	-0.00022	-0.00011	-0.00202	+0.00002	-0.00089
157.11	1.17057	+0.00001	-0.00177	-0.00013	-0.00008	-0.00195	+0.00009	-0.00078
174.50	1.19098	+0.00034	-0.00155	-0.00003	-0.00006	-0.00184	+0.00016	-0.00063
200.97	1.22261	+0.00091	-0.00111	+0.00016	+0.00001	-0.00160	+0.00028	-0.00035
231.23	1.25991	+0.00197	-0.00015	+0.00072	+0.00046	-0.00086	+0.00076	+0.00037
258.13	1.29328	+0.00242	+0.00027	+0.00074	+0.00041	-0.00063	+0.00070	+0.00055
303.98	1.35175	+0.00322	+0.00116	+0.00087	+0.00050	-0.00003	+0.00071	+0.00098
324.61	1.37793	+0.00279	+0.00083	+0.00019	-0.00014	-0.00046	+0.00001	+0.00044
350.40	1.41189	+0.00288	+0.00109	+0.00006	-0.00020	-0.00028	-0.00016	+0.00047
373.61	1.44240	+0.00233	+0.00075	-0.00059	-0.00076	-0.00064	-0.00083	-0.00006
395.02	1.47205	+0.00281	+0.00148	-0.00009	-0.00015	+0.00012	-0.00032	+0.00053
419.83	1.50571	+0.00205	+0.00106	-0.00067	-0.00059	-0.00019	-0.00088	+0.00002
444.32	1.54043	+0.00212	+0.00152	-0.00022	-0.00001	+0.00049	-0.00040	+0.00047
470.70	1.57801	+0.00160	+0.00151	-0.00008	+0.00025	+0.00081	-0.00019	+0.00055
490.64	1.60671	+0.00095	+0.00130	-0.00002	+0.00037	+0.00094	-0.00008	+0.00051
520.11	1.64971	-0.00032	+0.00078	+0.00013	+0.00051	+0.00108	+0.00016	+0.00039
549.90	1.69318	-0.00272	-0.00074	-0.00032	-0.00011	+0.00045	-0.00019	-0.00048
572.36	1.72744	-0.00381	-0.00109	+0.00045	+0.00037	+0.00095	+0.00065	-0.00015
595.89	1.76244	-0.00658	-0.00299	+0.00003	-0.00053	+0.00009	+0.00030	-0.00116
σ^c		0.00221	0.00146	0.00039	0.00033	0.00123	0.00040	0.00070
Constants used:								
A_0 or d_0		2920.52	2877.82	2959.87	2988.37	2893.57	2977.49	2927.23
A_1		—	0.0899206	-0.348629	-0.638717	—	—	—
$A_2 \times 10^4$		—	—	5.30918	13.7168	—	—	—
$A_3 \times 10^8$		—	—	—	-73.6745	—	—	—
α/a^3		—	—	—	—	—	0.23604	0.08722

^a P_n , fit of $(\epsilon+2)d/(\epsilon-1)$ to polynomial of degree n in d (P_0 is the Clausius-Mosotti formula); E , Eykman formula (1-2); B , Bottcher formula (1-3), (1-4), see this equation in the text.

^b The Amagat unit is so chosen, for each substance, that the density is unity at 0°C and atmospheric pressure.

^c Standard deviation of ϵ estimated from the deviations on the assumption that the formula is adequate.

Chang's 75° data, fitted with formula (1-4), give $\sigma=0.0076$, as compared with 0.0088 at 30°, the data at each temperature being treated independently. When the whole group of data is fitted to a single curve the fit is appreciably worse: $\sigma=0.0098$.

3. CARBON DIOXIDE

As representative data on a gas at high pressure, I have used the data of Michels and Kleerekoper¹⁶ on carbon dioxide at 49.71°C. Here there are 28 points, the number of points and the precision of the data are sufficient to yield more conclusive results than in the previous cases. The polynomial fit to yd gives, for degrees 0, 1, 2, and 3, $\sigma=0.0022$, 0.0015, 0.00039, and 0.00033 respectively (see Table III). The improvement by going from degree 1 to degree 2 is clearly significant, and the improvement from degree 2 to degree 3 probably so (the deviations for degree 2 show a systematic trend; see Table III). Degree 2 (3 constants) gives

$$\begin{aligned} d_0 &= A_0 = 2959.9 \pm 4.8 \text{ Amagat}, \\ c_0' &= -A_1 = 0.349 \pm 0.024, \\ A_2 &= (5.31 \pm 0.28) \times 10^{-4} \text{ Amagat}^{-1}, \end{aligned}$$

¹⁶ A. Michels and L. Kleerekoper, *Physica* 6, 586-590 (1939)

with correlation coefficients

$$\begin{aligned} \rho_{01} &= -0.9656, \\ \rho_{12} &= -0.9849, \\ \rho_{20} &= +0.9090, \end{aligned}$$

whence

$$c_1' = A_0 A_2 = 1.571 \pm 0.086.$$

Degree 3 (4 constants) gives

$$\begin{aligned} d_0 &= A_0 = 2988.4 \pm 7.8 \text{ Amagat}, \\ c_0' &= -A_1 = 0.639 \pm 0.071, \\ A_2 &= (13.7 \pm 2.0) \times 10^{-4} \text{ Amagat}^{-1}, \\ A_3 &= (-74 \pm 17) \times 10^{-8} \text{ Amagat}^{-2}, \end{aligned}$$

with correlation coefficients

$$\begin{aligned} \rho_{01} &= -0.9626, \\ \rho_{02} &= +0.9084, \\ \rho_{03} &= -0.8598, \\ \rho_{12} &= -0.9864, \\ \rho_{13} &= +0.9610, \\ \rho_{23} &= -0.9931, \end{aligned}$$

whence

$$\begin{aligned} c_1' &= A_0 A_2 = 4.10 \pm 0.18, \\ c_2' &= -A_0^2 A_3 = 6.6 \pm 1.6. \end{aligned}$$

Either fit gives constants with the signs and orders of magnitude predicted by the various approximate forms of the theory.

The value of c_1' by degree 2, 1.571, is closer to the Böttcher value 2 than to the Kirkwood value (Eq. (1-4)) 15/16. It is therefore not surprising that a direct fit to Böttcher's formula is more successful than a fit to formula (1-4), giving $\sigma=0.00040$ against the latter's 0.00070. Going over to the quadratic formula (1-6) does not improve the fit in this case; the constants c_1 and c_2 of this formula are rather far from the values of c_1' and c_2' obtained by analysis of the data. All these formulas are more reliable than the Clausius-Mosotti, which is the polynomial of degree zero ($\sigma=0.0022$). Eykman's formula (1-2) gives $\sigma=0.0012$.

4. CONCLUSIONS

For future analyses of experimental data, it is recommended that not the Clausius-Mosotti function but its reciprocal, $(\epsilon+2)d/(\epsilon-1)$, be used. The departure of this quantity from the Clausius-Mosotti value d_0 is what one can hope to calculate directly from molecular distribution functions when they become known with sufficient completeness. In this recommendation the use of $\epsilon-1$ as denominator is more important than the use of $\epsilon+2$ in the numerator: the function $d/(\epsilon-1)$ or $ed/(\epsilon-1)$, or any linear combination of them, would do equally well.

It is further recommended that for the time being this function be merely expressed as a polynomial in the density, to as many terms as are significant. The weights to be assigned to the various experimental values should correspond to the estimated relative precisions of the measurements at various values of ϵ ; and the numerical values of the polynomial coefficients should be accompanied by estimates of their uncertainties and of the coefficients of correlation between them (or of the mean squares and products of the errors), in order that when further quantities are calculated from them the uncertainties in these further quantities may be easily estimated. The coefficients in this polynomial can be given a fairly direct theoretical interpretation and can eventually be calculated from molecular theory.

Formulas of special form, such as Eykman's and Böttcher's, can be fitted to the data more or less successfully; but no one of these has either enough theoretical basis or (if the data analyzed here are representative) enough empirical reliability to justify its use in preference to the straightforward method recommended. Within the precision of present data, use of such special forms is equivalent to specification of auxiliary conditions to be imposed on the coefficients in the polynomial; and anything that can be accomplished by their use can also be accomplished by merely assigning fixed numerical values to one or more of the constants c_0' , c_1' , etc. Thus it may turn out upon analysis of all available data that the second-degree polynomial, i.e. Eq. (1-1) with $(d/d_0)^2$ neglected, gives sufficient precision for practical purposes if c_0' and c_1' are assigned fixed values, independent of the fluid (at least for a large class of fluids). From the limited number of data analyzed here, it appears that the best value of c_0' is probably somewhat larger than the value 1/4 based on a very crude model, and that the best value of c_1' may be intermediate between the Kirkwood value 15/16 and the Böttcher value 2.

Tables I-III show the actual deviations computed by some of the formulas, together with the experimental data and the constants used in the formulas. Formulas (1-3) (Böttcher), (1-4), and (1-5) yield somewhat different values of $d_0 (= 3m_0/4\pi\alpha)$ and $2\alpha/a^3$. Values of α and a^3 calculated from these are of the expected order of magnitude.

In a recent empirical study, Rosen¹⁷ has fitted dielectric constant and refractive index data on a number of fluids (polar as well as non-polar) with a formula equivalent to the first two terms of Eq. (2-3). His use of $(\epsilon+2)/(\epsilon-1)$ rather than of its reciprocal is supported by the present analysis of data and by the theory of I; but it appears that a third term is already significant in some modern data. It will probably become more clearly significant as experimental techniques continue to improve.

¹⁷ Joseph S. Rosen, J. Chem. Physics 17, 1192-1197 (1949). Rosen's values of A_0 and A_1 (his m and b) for carbon disulfide at 30° differ slightly from those given here because of the different weights used.