THE RELATION BETWEEN THE DIELECTRIC CONSTANTS OF SOME COMPRESSED GASES AND THE DENSITY[1]

FREDERICK G. KEYES AND JOHN L. ONCLEY

Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

Received October 19, 1936

INTRODUCTION

The relation of the dielectric constant to density and temperature may be conveniently considered from the point of view of the variation of the Clausius–Mosotti[2] expression, $\frac{\epsilon - 1}{\epsilon + 2} v$, where ϵ is the dielectric constant, and v the volume of a unit of the substance of interest. The remarkable fact is that gaseous substances may be classified into those for which the C–M expression is practically independent of density and temperature and those for which the function is independent of density but *not* independent of the temperature.

Nearly a quarter of a century has now elapsed since Debye first suggested the basis that accounts for the temperature dependence of the C–M function through the assumption of the existence of permanent electric moments in the molecules of the second classification (polar molecules). During the past eighteen years, moreover, Debye has contributed steadily in expanding the range of application of his original ideas. At the same time an ever increasing number of his fellow scientists have taken part in promoting important advances which have gone far to perfect our knowledge of molecular structure, certain aspects of solution properties, anomalous dispersion and absorption at radio frequencies, and dielectric phenomena generally.

The low pressure gaseous phase is the state most suitable for testing Debye's theory, and the numerous measurements for both gases and dilute solutions of polar substances in non-polar solvents provide ample support for its validity.

In the book *Polar Molecules* (2) care is taken however to emphasize the

---

[1] Contribution No. 382 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

restrictions surrounding the deduction of the C–M relation in the Debye form which follows:

$$\frac{\epsilon - 1}{\epsilon + 2} v = P = \frac{4\pi N}{3}\left[\frac{a_{11} + a_{22} + a_{33}}{3} + \frac{\mu^2}{3kT}\right] \tag{1}$$

In this equation v is the volume of a mole at the pressure and temperature at which ϵ is measured; P is the molar polarization; N is Avogadro's number; a_{11}, a_{22}, a_{33} are quantities defining the ellipsoid made use of to visualize the dielectric distortion of the molecule; μ is the natural electric moment; and k the Boltzmann constant. Debye states that "In every other case (i.e., other than low pressure gases), for instance in the application of 1 to liquids, the calculation involves certain often questionable assumptions about the interaction with the surrounding molecules. The problem of the calculation of these interactions has, unfortunately scarcely been treated in an adequate manner." The value of high density dielectric constant measurements indeed seems clear as a preparation and foundation for additional theoretical work on the dielectric properties of matter at higher densities. The data most immediately useful are those for the gaseous phase at high temperatures, where the density may be caused to vary with relative ease over a wide range and where quantized collisions are sufficiently infrequent to be of small consequence.

The selection of the material for measurement is also important. Thus considerations relating to molecular coupling are simpler for the gases helium, hydrogen, nitrogen, and methane. These non-polar gases also have relatively low critical temperatures, and measurements made at temperatures from, for example, 50° to 200°C., correspond to temperatures which would be far higher for more complex substances in a comparable state of molecular interaction.[3]

Moreover, with the exception of methane the gases referred to do not absorb in the infra-red region, a fact which relates to our interest in the L–L refractive index expression. For this very reason however, the case of carbon dioxide is important, since fairly complete data exist for the dispersion of this substance. Finally, data for a polar substance would be welcome, although the problem of theoretical interpretation of a density dependence of the C–M function appears at present somewhat formidable. Ammonia was selected for the measurements, partly because the body of

---

[2] Throughout the remainder of the paper Clausius-Mosotti will be abbreviated to C–M and Lorentz–Lorenz to L–L.

[3] The Boyle-point temperature for low pressures may be used as a measure of that state of gas where the effect of the positive and negative molecular potentials balance. On this basis water vapor at 1200°C. would be comparable with nitrogen at about 50°C.

density data is extensive and exact, and partly also because a good deal is known about the structure and physical constants of the molecule. Data will be exhibited showing the variation of the C–M function with density at different temperatures for helium, hydrogen, nitrogen, methane, propane, carbon dioxide, and ammonia. In the case of carbon dioxide sufficient data exist to give an impression of the variation of the C–M expression for the liquid phases over a fairly wide range of density.

THE EXPERIMENTAL DATA

Measurements of the dielectric constants of the compressed gases, air, nitrogen, and hydrogen at 20°C. were made over thirty years ago by Tangl (18) and Occhialini (14, 15) for the purpose of testing the C–M function. Magri about the same time measured the refractive index for air for a range of densities corresponding to a maximum of 200 atm. at 15°C. He inferred from the data that the L–L expression, $\frac{n^2 - 1}{n^2 + 2}\, v$, was constant. Both Tangl and Occhialini first concluded that the C–M function decreased slightly with increasing density (pressures employed up to 334 atm.). This conclusion was later modified and, excluding fluctuations in the measurements amounting to 1 per cent, the C–M expression appeared to be constant.

Other or additional measurements were not reported until after the World War, when data for both compressed gases and liquids appeared. In the meantime the technique of dielectric constant measurement has steadily improved and in addition much of the necessary accurate density data have accumulated for computing the C–M function. Fortunately also for the control and correlation of the higher density dielectric constant data, increasingly exact low pressure measurements have appeared steadily. In brief it seems likely that for several of the gases the C–M function is known over a considerable range to two parts per thousand. It will appear later that the C–M relation should be known to at least this degree of precision if the data are to be of value in guiding theoretical developments.

For helium[4] and hydrogen[5] (19) the C–M function shows no definite

---

[4] Data obtained at the Massachusetts Institute of Technology and not yet published.

[5] In the course of preparing the material for the present paper all measurements of dielectric constants which had been made at the Massachusetts Institute of Technology were recomputed. Three different pressure condensers have been used, and corrections peculiar to each were applied for pressure distortion effects. In the case of the measurements reported by Uhlig, Kirkwood, and Keyes, a small error was found to have been made in correcting for distortion. Further perfection in facilities

trend with density or temperature to a density of 6.1 moles per liter (164 cc. per mole) in the case of hydrogen. Recently measurements on hydrogen by Michels, Sanders, and Schipper (13) have been extended to 1425 atm. at 25° and 100°C. without the C–M function showing any definite trend. The case of nitrogen is particularly interesting, because recently Michels, Jaspers, and Sanders (8) have reported values of the C–M expression to a density of 20.6 moles per liter (48 cc. per mole), (1000 atm. at 28° to 150°C.), twice the density reached in our own measurements.[6] Earlier, Michels and Michels (9) had reported low pressure values. The higher density data appear to show a faint positive trend with density, but the authors (see figure 2 of reference 8) state that "there exists no evidence of a deviation from the C–M relation exceeding the experimental accuracy." Our own values give the impression of a slight density dependence, which perhaps should be stated to be an expectation of a positive rather than a negative trend. Possibly no more definite statement than this can be made in the case of nitrogen, following a careful consideration of all available values of the C–M function.[7]

By way of résumé, the C–M relation for helium and hydrogen, figure 1, shows no systematic variation with either density or temperature. A like statement applies to nitrogen, except that the faint apparent trend of the C–M relation suggests the expectation of a positive rather than a negative density dependence. The average precision of the C–M values is probably not greater than about one five hundredth for these gases. The low pressure L–L function value for the gases[8] is in very good agreement with the C–M function values at zero pressure.

---

also made it possible to measure the lead correction of the condenser more accurately. The net effect of the revision of the reduction of the observations is a somewhat smaller Clausius-Mosotti function. A forthcoming publication will give the details of new measurements with the improved, No. 3 condenser.

[6] The molal volumes for nitrogen were taken in part from recent data by Otto, Michels, and Wouters (Physik. Z. **35,** 17 (1934)), and in part from unpublished results by Michels and Gerver.

[7] Data for air might be considered along with the nitrogen data. Recent measurements have been made by Waibel (Ann. Physik **72,** 161 (1923); 40 atm. at 14°C.), J. W. Broxton (Phys. Rev. **37,** 1338 (1931); also nitrogen), and A. R. Jordan, J. W. Broxton, and F. C. Walz (Phys. Rev. **46,** 66 (1934)). In the third paper the dielectric constant for air is shown to be independent of frequency to 70 kilocycles, and the C–M function shows no large variation. Formerly a minimum in the C–M function was reported at 80 atm. and 18°C. R. McNabney, Wills Moulton, and W. L. Beuschlein (Phys. Rev. **47,** 695 (1935)) also report measurements for air and hydrogen to 335 atm. The C–M function for air shows a maximum deviation of 5 per cent; in the case of hydrogen about 16 per cent.

[8] Recent precise data for nitrogen have been obtained by Clarence E. Bennett (Phys. Rev. **37,** 263 (1931); **45,** 200 (1934)). L. Ebert and W. H. Keesom found the C–M function for liquid nitrogen the same as for the gas, and Gerald (Ann. Physik **65,** 93 (1921)) found that the L–L function for liquid nitrogen has a value equal to the C–M function.

The case of carbon dioxide is of special interest in view of the type of molecule and the extent and range of data available. It is also very fortunate that new and extensive density data for carbon dioxide are now available (11, 12). Since the data of Keyes and Kirkwood (6), additional

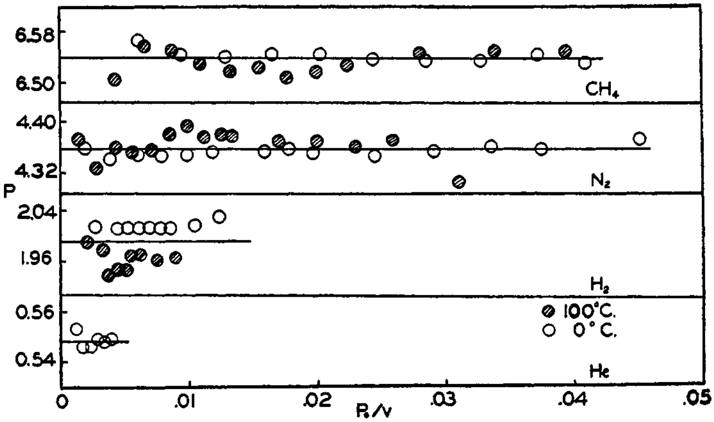

FIG. 1. C-M function for older data obtained at the Massachusetts Institute of Technology

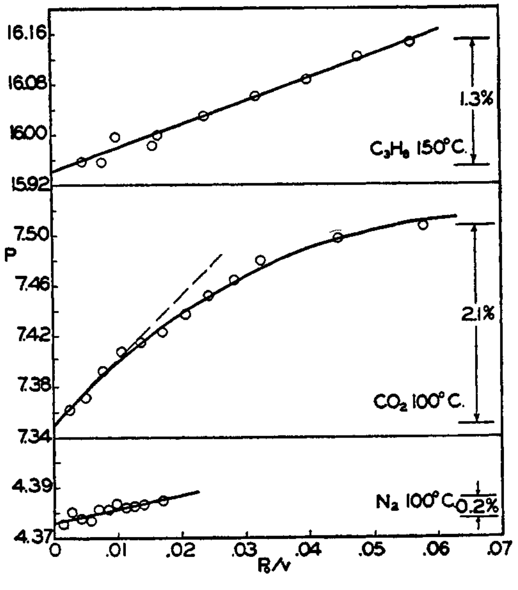

FIG. 2. C-M function; recent data obtained at the Massachusetts Institute of Technology, using the new cell

data have been obtained by Uhlig, Kirkwood, and Keyes (19), by Oncley[9] (shown in figure 2), and by A. Michels and C. Michels (10) for twelve temperatures from 25° to 150°C. and to a density of 25.5 moles per liter (39 cc. per mole, 25°C.; 966.6 atm.). The density data of the 1933 paper were taken from Amagat's work. Later however new data of A. Michels and C. Michels (11, 12) have been used to compute values of the C–M function for the dielectric constant data at 30,° 100,° and 150°C. The 1933 paper of A. Michels and C. Michels, using Amagat's density data, leads to C–M values which the authors state show no effect of temperature but "with increasing pressure the C–M constant shows a tendency to decrease." This statement is apparently opposed to our present conclusion. The data of Michels and Michels at 100° and 150°C. incorporated in figure 3 have, however, been adjusted on the following basis.

It is fairly certain that the molar polarization or the C–M function for carbon dioxide at approaching zero density (P^0) is very close to 7.35 cc. (Zahn, 7.25; Watson, Stewart, McAlpine and Smyth, and Massachusetts Institute of Technology, 7.35 cc.). On examination of the original data of Michels and Michels in the C–M form for the various series of measurements, they exhibit characteristics similar to our own unadjusted data, namely, they do not extrapolate closely to the value 7.35 but instead show a widening spread as lower densities are approached. In fact the Michels and Michels data at 100° and 150°C. may be represented analytically by the following expression

$$P = \frac{a_{-1}}{\rho} + 7.35 + a_1\rho + a_2\rho^2$$

in which the a's are temperature functions and ρ the density. Now by plotting the expression $\frac{\epsilon - 1}{\epsilon + 2}$ for our original data versus density, it was in general found that the data did not quite lie on a line passing through the zero value of the coördinates. The data of Michels and Michels show a similar effect and when a correction in the amount of the "origin failure"[10] is applied to all the values of $\frac{\epsilon - 1}{\epsilon + 2}$ the systematic trend in the low pressure

---

[9] Recent data on nitrogen, carbon dioxide, and propane shown in figure 2 will be published shortly.

[10] The "origin failure" in our cells is due undoubtedly to a variable displacement given the internal parts of the condenser when subjected to stresses induced by the presence of the high pressure gas. Our most recent condenser design (unpublished) was carried out with a view to reducing the amount of the effect, and in practice it has proved almost negligible.

C–M function referred to above is eliminated. The data in figure 3 have been treated in the way described and the inferences relative to trend in

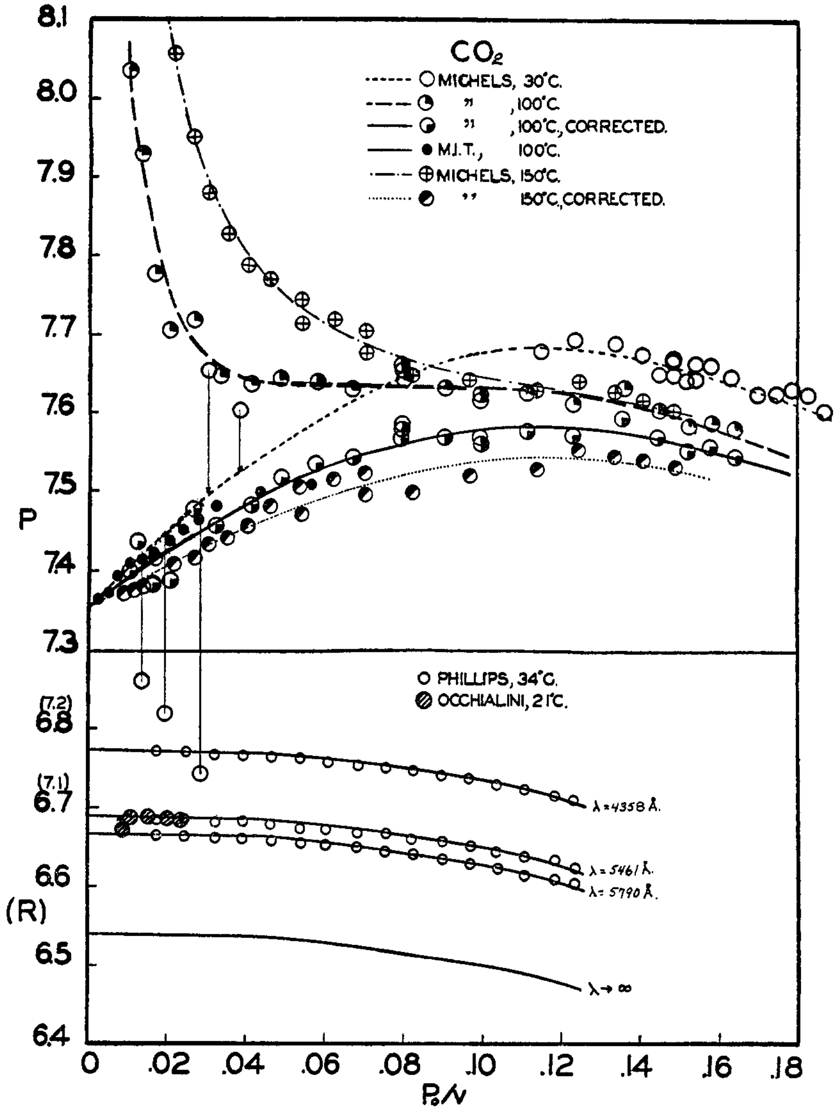

FIG. 3. C–M and L–L functions for carbon dioxide

the C–M function favor a positive trend for the gas or low density phase and a negative trend in the high density phase with a maximum at about 16.3 moles per liter (61.4 cc. per mole; 14 cc. per gram). The inference of

Michels and Michels regarding a negative trend referred to earlier evidently related to the higher densities.

We believe the total available C–M function data for carbon dioxide lead to the following conclusions[11]:

(1) The C–M function at higher densities, or at least to a density of 15 moles per liter, exceeds systematically the value 7.35.
(2) The C–M function exhibits a maximum for P^0/v about 0.12, or 16.3 moles per liter.
(3) The increase in the C–M function with density at low densities is larger at the lower and smaller at the higher temperatures.
(4) The C–M values available from all sources are in good agreement.

The refractive index of carbon dioxide has been measured (16; see also 1) over a wide range of wave length values at low pressures and in the visible region over a considerable range of density.[12] Fuchs (3) has formulated all the low-pressure measurements into a single dispersion expression containing four Sellmeier-like terms covering the range $\lambda = 720.4$ A.U. to $\lambda = 14.91\mu$. We may use the formula to compute the L–L expression for $\lambda \rightarrow \infty$ and zero density. The result is 7.28, in very good agreement with the value 7.35, the mean of all the low-pressure values. It is therefore evident that the infra-red absorption characteristics of carbon dioxide account for the low values of the polarization deduced by extrapolation (to infinite wave length) of the data on the index of refraction for visible light.

In the case of propane gas, figure 2, there is also a positive drift of the

---

[11] These conclusions are quite different from those arrived at by P. O. John (Phil. Mag. **22**, 274 (1936)), who discusses the data of Michels and Michels and of Phillips on the basis of the Raman-Krishman theory (Proc. Roy. Soc. **117 A**, 589 (1928)). He uses the value 7.82 for P^0,—a value obtained from a considerable extrapolation of Michels' data to low pressures. All recent determinations show that 7.35 is not far from the correct value.

[12] Phillips found the reciprocal of the L–L function for wave length 5461 A. U. was given by the expression $6.581 + 0.113\,\rho^2$, where ρ is the density. Brown reports that the L–L function does not remain constant, and that the $(\text{L–L})^{-1}$ function shows a marked increase at higher densities. The data included densities in excess of 0.8 g. per cubic centimeter. That the $(\text{L–L})^{-1}$ function should be linear in ρ^2 for carbon dioxide seems astonishing, in view of current ideas on the Maxwell relation $n^2 = \epsilon\mu$, where μ is the permeability, leading to the expectation that the sign of the density dependence for the C–M and L–L functions might be similar. It is to be regretted that we lack L–L function data at high densities for structurally simpler substances, for example, the rare gases. As a matter of fact, we do have Magri's findings (Physik. Z. **6**, 629 (1905)) for air densities corresponding to 200 atm. at 15°C., and the L–L function shows no drift. Phillips' values indicate roughly a decline of only 1 in 500 for the L–L function for a 170-fold increase in density,—a rather small density effect.

C–M function with density. At the moment we have no data for the liquid phase.[13]

The only polar gas (figure 4) for which dielectric constant data exist at high densities is ammonia (6). The density data available are very reliable, and the positive trend of the C–M function with density is unmistakable at all temperatures. The permanent moment deduced from the zero density value of the polarization is 1.466 Debye units, to be compared with 1.44 obtained by Zahn and 1.48 by Watson. In fact, there appears to be no change in μ to the highest density[14] (4.48 moles per liter or 223 cc. per mole).

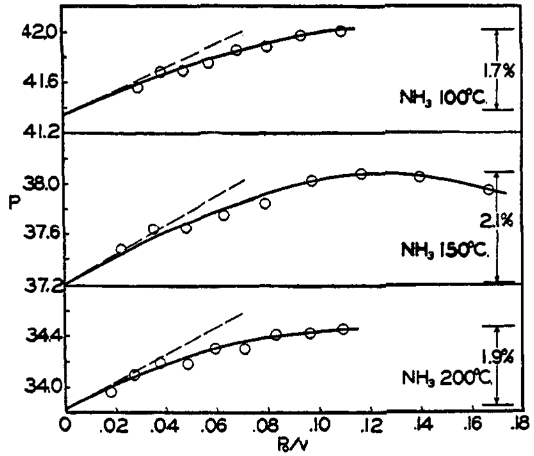

FIG. 4. C–M function for ammonia

---

[13] W. E. Danforth (Phys. Rev. **38**, 1224 (1931)) found that the reciprocal of the C–M function for liquid pentane and carbon disulfide exhibited an inflection in relation to density (corresponding to a maximum pressure of 12,000 atm.). For the latter substance a temperature effect apparently exists (30° and 75°C.) The $(C\text{–}M)^{-1}$ function for the polar liquids measured is linear (except for ether) and a temperature function. Charlotte Franks (Ann. Physik **77**, 159 (1925)) also reported dielectric constant values for liquid benzene, heptane, hexane, and carbon tetrachloride to 800 atm. Grenacher in the same volume, p. 138, gives values for a number of polar liquids. There is a negative drift of the C–M relation in every instance with a larger effect for the polar substances. A considerable number of investigators have reported dielectric constant data for liquids under pressure, beginning with Röntgen (Ann. Physik **52**, 591 (1894)). Density data are lacking for computing the C–M function in many cases of interest.

[14] Recently Jeffries Wyman, Jr. (J. Am. Chem. Soc. **58**, 1482 (1936)) has given a summary of the dielectric constant characteristics for a large number of polar liquids. He takes as a basis of correlation the polarization constants of the substances appropriate to the low-pressure gas phase and finds the expression $\frac{\epsilon + 1}{8.5\rho}$ is linear with

CONCLUSIONS

By way of summary of the facts available at this time it appears that in the case of the gases helium, hydrogen, and nitrogen the C–M function is independent of the density and of the temperature. In the case of nitrogen there is possibly a faint indication of a positive trend of the function with density. These gases do not absorb in the infra-red and possess L–L values equal to the C–M values at low densities. In the case of nitrogen there is reason to infer that the L–L function is independent of density, in view of Magri's data on air.

In the case of carbon dioxide, methane, and propane we deal with substances which absorb in the infra-red. The C–M function for the gaseous phase is independent of density and temperature in the case of methane to densities of 6.01 moles per liter (166.3 cc. per mole), and the L–L function is equal to the C–M value. For carbon dioxide below 15 moles per liter, however, the C–M function is not quite independent of temperature and there appears to be a positive dependence on density. The C–M function for the liquid phase of carbon dioxide or for densities exceeding 16 moles per liter appears to show a negative dependence and, considering the gaseous and liquid phase data together, a maximum exists for a density of about 15 moles per liter or a volume of 1.51 cc. per gram. The magnitude of the initial variation of the function is roughly 2 per cent for

---

reciprocal T. The relation is said to be "fairly satisfactory when applied to the variation of the dielectric constant with temperature and with pressure in the case of a number of polar liquids."

In the succeeding article Lars Onsager (ibid. p. 1486) gives a theory for electric moments for molecules in liquids. He shows that the original Mosotti expression for the internal field is not applicable to permanent dipoles. The computational scheme makes use of the excised cavity device in the dielectric (assumed for this portion of the considerations to be a continuum), and a molecular model is employed consisting of a rigid sphere assumed to contain a natural dipole of value μ_0 *in vacuo*. The liquid is envisaged as a close-packed system of the spheres in contact, whose radii are determined from the L–L expression.

One form of the resulting dielectric constant expression is as follows:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\alpha}{a^3} + f(\epsilon, n^2)\,\frac{4\pi N\mu^2}{9kT}$$

where α is the polarization per spherical molecule of radius a, obtained from the L–L expression, N is the number of molecules in a unit volume of substance, and

$$f(\epsilon, n^2) \text{ is the function } \frac{3\epsilon(n^2 + 2)}{(2\epsilon + n^2)(\epsilon + 2)}$$

The derivative of the function with respect to ϵ is negative and therefore, for constant n, the C–M function would decrease if ϵ increases with pressure. This accords with fact, for as far as known the dielectric constant increases with density without exception, and the C–M function diminishes with increasing density for all polar substances in the liquid phase.

100 atmosphere increase in pressure in the gaseous phase. The C–M function for propane in the gaseous phase is a function of density, but there is insufficient data to indicate a temperature dependence.

The dispersion formula of Fuchs for carbon dioxide at low pressure indicates that the polarization calculated from the L–L function (7.28 cc.) has the same value as that from the C–M function (7.35 cc.). The trend of the L–L function for carbon dioxide with density is, however, opposite in sign to the trend of the C–M function. In fact the reciprocal of the (L–L) function is linear in the square of the density, while the C–M function is almost linear in the density to fairly high densities. If the facts are really as represented, a gap is indicated in our general knowledge of the relation between dielectric and refractive phenomena at higher densities.

The only polar substance for which C–M values exist for the gaseous phase at various densities and temperatures is ammonia. As in the case of the non-polar substances carbon dioxide and propane in the lower density range, the trend of the C–M function is positive and approximately the same for the various temperatures. The value of μ, the polar moment, deduced using the classical Debye theory, appears to be independent of density. The initial density dependence of the C–M function is about 5 per cent per 100 atmospheres.

For liquids the C–M expression trend with density, as far as present evidence goes, is negative and greater for polar liquids than for non-polar. Thus for pentane[15] Danforth found about a 5 per cent decrease in the C–M function for the density increase corresponding to 12,000 atm. and 4 per cent for carbon disulfide, both at 30°C. For chlorobenzene the decrease was at the rate of 19 per cent for 12,000 atm. and 24 per cent for ethyl alcohol, both at 30°C. The magnitude of the decreases does not appear to vary greatly with temperature increase (45°C. interval for chlorobenzene and 30°C. interval for ethyl alcohol). The recent Onsager theory of polar molecules is in general accord with these facts, but a quantitative comparison between theory and fact remains to be completed.

RELATION OF THE FACTS TO THEORY FOR GASES

Various aspects of the unsatisfactory characteristics of Lorentz' (and also Mosotti's, of course) calculation of the local polarization field have been recited by many commentators. The computation is indeed based on an interesting, if not unusual, blend of continuum and discrete-particle argument. The interpretation of the dielectric properties of substances in relation to their molecular structure and other phenomena has, however,

---

[15] W. E. Danforth observed that the reciprocal of the C–M function was linear in density in the case of polar substances, exclusive of ethyl ether. Carbon disulfide and pentane do not quite follow the rule.

advanced very markedly since the epochal work of Debye, thereby emphasizing the importance of extending and perfecting the theory for the interpretation of the facts. Moreover the recent rapid period of evolution of dynamical theory has led to new concepts of molecular interaction and revitalized old interpretations of physical phenomena, in a way to increase the importance of dielectric phenomena. For this reason there is ground for believing that some of the disabilities of the older theory should be eliminated and progress made in putting the entire theory on a satisfactory statistical mechanical basis. Of course much solid ground must be won before, for example, highly compressed gases or liquids can be dealt with satisfactorily, but even in the latter case Lars Onsager has recently set out some very interesting results.

A modest attempt (7) to form the outline of a molecular statistical theory of the dielectric constant for non-polar molecules may be of interest in connection with the variation of the C–M function with density for non-polar substances. The calculation, of a wholly statistical kind, has led to the following expression

$$\frac{\epsilon - 1}{\epsilon + 2} v = P^0\left(1 + \lambda \frac{P^0}{v} + - -\right) \tag{2}$$

where λ is given by the function

$$\frac{P^0}{\beta}\left(1 + \frac{1}{3} \frac{A}{RT\beta}\right)$$

where β and A are constants appropriate to the van der Waals concept of the molecular field.[16] The values of λ derived from the experimental data are given in table 1.

For nitrogen the average magnitude of the density coefficient, $\lambda = 0.1$, would call for less than 1 per cent increase in the C–M function[17] for the highest density measured by Michels, Jaspers, and Sanders, namely, 20.625 moles per liter, corresponding to 1011.6 atm. at 25.3°C. There is reason to believe that $\lambda_{\text{calcd.}}$ for nitrogen should be less than 0.1, owing to an anisotropic fluctuation effect σ.[18] For nitrogen, $\sigma = -0.04$ is obtained

---

[16] Kirkwood (J. Chem. Physics 4, 592 (1936)) has given a more exact treatment of the problem. He takes account of a neglected item of the earlier paper causing λ to be increased by 5/2. We have used the modified λ in the present comments.

[17] For helium and hydrogen the predicted effect is far less than the experimental error for the highest densities reached in the dielectric constant measurements.

[18] Kirkwood's recent paper (J. Chem. Physics 4, 592 (1936)) on "Anisotropy and Rotational Fluctuations" leads to the following expression for σ:

from Stewart's (17) data assuming the ratio of major to minor axis for the polarization ellipsoid to be in the same ratio as α_1 to α_2. The value of $\lambda_{\text{calcd.}}$ now becomes almost one-half its early predicted value, or 0.5 per cent and therefore not a great deal larger than corresponds to the present probable experimental error of the C–M values at the highest densities.

TABLE 1

Correlation between the density trend of the C-M function and a statistical theory of gaseous dielectrics for non-polar molecules

SUBSTANCE	β IN CC. PER MOLE	$A \times 10^{-6}$ IN CC.-ATM. PER MOLE	P_0	$\lambda_{\text{obsd.}}$(4)	$\lambda_{\text{calcd.}}$(6)
He	14.0	0.0216	0.548	*	0.04
H_2	21.0	0.1975	2.01	*	0.10
N_2	50.5 (45.9)(1)	1.3445	4.376	*	0.11
CH_4	55.9 (47.0)	2.2769	6.57	*	0.17
CO_2	104.8 (47.2)	5.0065	7.35	0.63	0.11 (0.37)
C_3H_8	210.2	13.17	15.94	0.30	0.12
NH_3	(40.9)	5.3(2)	41.28(3) 37.22 33.86	0.26	2.0 (0.37)(5)

(1) From viscosity data. All other values are from p-v-T data.

(2) Mean value for 50°, 100°, 150°, and 200°C. For a polar substance A is a strong temperature function at low temperatures.

(3) Values corresponding to 100°, 150°, and 200°C.

(4) Defined from C–M = $P_0(1 + \lambda P_0/v)$. Values are for $\rho \rightarrow 0$.

(5) Value using "distortion" polarization value 6.0.

(6) $\lambda = \dfrac{P_0}{\beta}\left(1 + 1/3\dfrac{A}{RT\beta}\right)$.

* The precision of the data makes the limiting value of $\lambda_{\text{obsd.}}$ uncertain.

In the case of carbon dioxide $\lambda_{\text{obsd.}}$ is about 0.63 for zero density at the average temperatures. The most representative values for β and A for

---

$$\sigma = \frac{2(\alpha_1 - \alpha_2)}{(\alpha_1 + 2\alpha_2)}\left[\frac{1 - e^2}{e^3}\sinh^{-1}\frac{e}{(1 - e^2)^{1/2}} - \frac{1 - e^2}{e^2} - 1/3\right]$$

$$= -2/3\,\frac{\alpha_1 - \alpha_2}{\alpha_1 + 2\alpha_2} \text{ when } e \rightarrow 1$$

where α_1 and α_2 are the polarizabilities corresponding to the major and minor axes or a symmetrical ellipsoid assumed for the molecular model. The eccentricity for long molecules $e \rightarrow 1$ leads to the second expression.

computing λ is however open to some question.[19] For example, if β is derived from Amagat's data, λ is found to be about 0.11. There is reason to believe, however, that for substances whose critical state is at ordinary temperatures and higher, the value of β derived from viscosity (4) gives a more reliable number. Using then the viscosity data, $\lambda_{\text{calcd.}}$ becomes 0.37. This must be reduced by the amount of the σ whose value is roughly -0.09, leaving $\lambda_{\text{calcd.}}$ equal to 0.28, or less than one-half the value observed.

It will be further observed that expression 2 requires that λ vary linearly in the reciprocal of temperature. Reference to figure 3 indicates that the slope of the 150°C. low density data is less than for the 100°C. data and this in turn is less than the 30°C. data, in qualitative accord with the requirements of the equation. From equation 2, using the value of β from viscosity data, the initial difference in slopes for the 30°–100°C. data amounts to $\Delta(P_0)_{\text{calcd.}} = 0.31$,—a quantity considerably less than would be deduced from the smooth line for 100°C. and the dotted line for 30°C. It will be noted, however, that the data at lower densities are scarcely precise enough to establish the values of the slopes exactly.

The theory of the dielectric constant for a polar substance along the lines of Keyes and Kirkwood's development has not been carried through. On the other hand, the recent theory of Lars Onsager could scarcely be applied to a gas, as in fact he emphasizes. The value of $\lambda_{\text{obsd.}}$ for ammonia is 0.26, while the value of $\lambda_{\text{calcd.}}$ is 2, an altogether different order of magnitude. If, however, the distortion polarization for ammonia is used in computing λ, the number 0.37 results.[20] Of course the value of $\lambda_{\text{calcd.}}$ of the table should be reduced, owing to the Kirkwood anisotropic fluctuation effect σ for a polar molecule. The theory for this effect has likewise not yet been worked out. [We have just learned from J. H. Van Vleck that he has calculated the value of λ for polar molecules. The details will be published elsewhere shortly. In the case of ammonia the computed value of λ is 0.4, in good agreement with our data as regards order of magnitude.]

No reference has been made to "association" as a factor in accounting for departures from the C–M relation. The term does not appear to have any closely defined connotation,—a defect very likely related to the fact that estimates of its magnitude derived from quite varied phenomena seldom lead to comparable numbers. In spite, however, of the often contradictory aspects of applications of the idea, there does exist a well justi-

---

[19] The values b and a from van der Waals theory using critical data should not be used. See the following section.

[20] This fact was noted by H. H. Uhlig in his thesis submitted for the degree of Doctor of Philosophy, Massachusetts Institute of Technology, 1932.

fied impulse to incorporate into certain correlative attempts some allowance for a tendency of molecules to agglomerate or aggregate.[21]

Statistical theory includes within its scope the full possibility of dealing, in principle, with the association or aggregation effect, having its origin in the increasing degree of merging of the molecular fields with density increase. The computational difficulties involved in applications of immediate interest are of course great, and it is for this reason that the application of statistical theory leading to the λ factor was limited to a region where calculations may be made with precision.

The theory of dielectrics attempted by Keyes and Kirkwood, and recently more adequately developed by Kirkwood, is qualitatively in accord with the facts as at present known. Quantitative comparisons will probably, however, never be quite satisfactory using the van der Waals molecular field concept, and a less specialized representation of the field should be employed.

NOTE ON THE QUANTITIES β AND A

The quantities β and A of the λ in equation 2 have the same significance as the b and a of van der Waals theory, except that they are not derived from critical data. Instead they may be derived from actual p-v-T data or from viscosity data. Only in the case of a few of the elementary gases (hydrogen, nitrogen, carbon monoxide) is there a fair accord between β and b, A and a, while in the case of helium and hydrogen at ordinary temperatures and nitrogen above 150°C., the van der Waals molecular field concept is quite inadequate.

It is, however, now well known that the van der Waals equation is quantitatively quite inadequate to represent the p-v-T behavior of fluids, except approximately in certain cases at low pressure. It follows, therefore, that the a and b quantities derived from critical data will in general prove quite valueless for representing accurately the effects of the molecular field appropriate to any given molecule. Values of β and A derived from viscosity data at low pressure or from p-v-T data under favorable conditions may, however, correspond to characteristic values of the molecular field appropriate to the rough approximation of the actual molecular field characteristic of the van der Waals concept.

Some insight into the meaning of the quantities β and A as they relate to the van der Waals concept of the molecular field may be obtained by considering the phase integral for low pressures. The integral may be written as follows:

---

[21] One of the authors has on several occasions proposed the term "aggregation" to denote the effect of intramolecular field coupling.

$$B^0 = 2\pi N \int_0^\infty \left(1 - e^{-\frac{\text{Pot.}}{kT}}\right) r^2\, dr \tag{3}$$

where B^0 is a pure temperature function in the equation of state, $p = \frac{RT}{v - B^0}$, for low (strictly $p \rightarrow 0$) pressures. The quantity "Pot." represents the molecular potential which may be computed from quantum theory with fair accuracy for helium and hydrogen, for example. The dotted continuous curve in figure 5 represents the course of "Pot." as a function of the distance separating a molecular pair.

The van der Waals concept of the molecular field assumes a spherically symmetrical short range attractive field surrounding the molecules of invariable diameter σ. A pair of the molecules in contact are further assumed to develop an infinite repulsion. The trace in a "Pot." vs. R diagram would therefore be represented by the continuous line in the diagram, figure 5, and it is evident that for some molecules the approximation may be too rough for many purposes. In general, where the attractive field or the negative potential is small relative to the repulsion, the approximation will be very bad (case of helium, for example) (5).

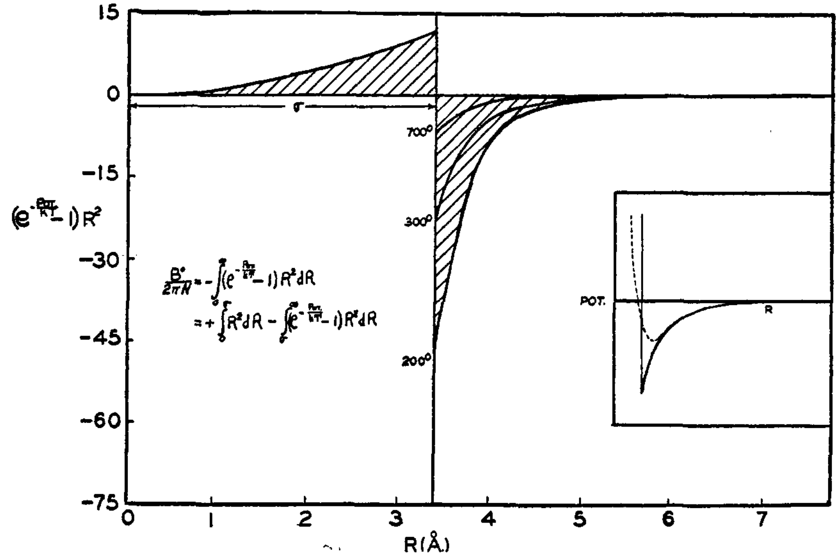

FIG. 5. Potential curve and phase integral

The use of the van der Waals concept in evaluating B^0 in equation 3 causes the quantity $e^{\frac{-\text{Pot}}{kT}}$ to vanish on contact, where "Pot." becomes infinite, and it therefore becomes convenient to consider equation 3 resolved into two integrals as follows:

$$
\begin{aligned}
B^0 &= 2\pi N \int_0^\sigma r^2\,dr - 2\pi N \int_\sigma^\infty \left(e^{-\frac{\text{Pot.}}{kT}} - 1\right) r^2\,dr \\
&= \frac{2}{3}\pi N\sigma^3 - I = \beta - \frac{A}{RT}\sum_{j=1}^{j=\infty} \frac{1}{(2j-1)j!}\left(\frac{A}{RT\beta}\right)^{j-1} \qquad (4) \\
&= \left(\beta - \frac{A}{RT}\right) \text{ for } T \text{ large}
\end{aligned}
$$

when the negative potential varies as the inverse sixth power of the distance.

In figure 5 the graphical scheme for evaluating B^0 of the equation of state is represented for the case of nitrogen, and the discontinuity introduced by the van der Waals concept of an infinite positive potential becomes evident. The approximation will, in general, be more satisfactory at lower temperatures, where the negative area is large relative to the constant positive area, or β.

In practice it is necessary to deduce B^0 (virial coefficient) values from the experimental p-v-T data and relate them to T^{-1} as required by formula 4. If sufficiently high temperature data are available, extrapolation to $T^{-1} = 0$ to obtain β will not be uncertain, as in the case of nitrogen. For carbon dioxide, however, the B^0 data all lie in the negative portion of the B^0, T^{-1} diagram, and extrapolation to $T^{-1} = 0$ for the "best" value of β becomes difficult.

From the brief statement given it will be clear that representative values of β and A are not easy to obtain for carbon dioxide and for gases of high critical temperature generally. The "constants", particularly β, obtained from viscosity data are in fact likely to be much more reliable for use in representing the effect of the molecular field.

REFERENCES

(1) BROWN, F. L.: Abstract, Phys. Rev. **43,** 373 (1933).

(2) DEBYE, P.: Polar Molecules. The Chemical Catalog Co., Inc., New York (1929).

(3) FUCHS, O.: Z. Physik **46,** 519 (1928).

(4) KEYES, F. G.: Z. physik. Chem., Cohen Festschrift, p. 709 (1927).

(5) KEYES, F. G.: Chem. Rev. **6,** 175 (1929).

(6) KEYES, F. G., AND KIRKWOOD, J. G.: Phys. Rev. **36,** 754, 1570 (1930).

(7) KEYES, F. G., AND KIRKWOOD, J. G.: Phys. Rev. **37,** 202 (1931).

(8) MICHELS, A., JASPERS, A., AND SANDERS, P.: Physica **1,** 627 (1934).

(9) MICHELS, A., AND MICHELS, C.: Phil. Mag. **13,** 1192 (1932).

(10) MICHELS, A., AND MICHELS, C.: Phil. Trans. Roy. Soc. London **231,** 409 (1933).

(11) MICHELS, A., AND MICHELS, C.: Proc. Roy. Soc. London **153,** 201 (1935).

(12) MICHELS, A., MICHELS, C., AND WOUTERS, H.: Proc. Roy. Soc. London **153,** 214 (1935).

(13) Michels, A., Sanders, P., and Schipper, A.: Physica **2**, 753 (1935).
(14) Occhialini: Physik. Z. **6**, 669 (1905).
(15) Occhialini and Bodareu: Ann. Physik **42**, 67 (1913).
(16) Phillips, P.: Proc. Roy. Soc. London **97A**, 225 (1920).
(17) Stewart, H. A.: Molekülstruktur, table 45, p. 173. J. Springer, Berlin (1934).
(18) Tangl: Ann. Physik. **10**, 748 (1903); **23**, 559 (1907); **26**, 59 (1908).
(19) Uhlig, H. H., Kirkwood, J. G., and Keyes, F. G.: J. Chem. Physics **1**, 155 (1933).