

On the Theory of Dielectric Polarization

John G. Kirkwood

Citation: *J. Chem. Phys.* **4**, 592 (1936); doi: 10.1063/1.1749911

View online: <http://dx.doi.org/10.1063/1.1749911>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v4/i9>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

Instruments for advanced science

Gas Analysis



- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

Surface Science



- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

Plasma Diagnostics



- plasma source characterization
- etch and deposition process
- reaction kinetic studies
- analysis of neutral and radical species

Vacuum Analysis



- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details

HIDEN
ANALYTICAL

info@hideninc.com
www.HidenAnalytical.com

CLICK to view our product catalogue



On the Theory of Dielectric Polarization

JOHN G. KIRKWOOD, *Department of Chemistry, Cornell University*

(Received May 18, 1936)

The polarization of a nonpolar dielectric in a homogeneous field is investigated from a molecular point of view. A statistical calculation of the average local field in a molecule shows that fluctuations in the induced molecular moment give rise to a deviation from the Lorentz field. As a result, small but significant deviations from the Clausius-Mosotti formula are to be expected. A series expansion for $(\epsilon-1)v/3$ of the following form is obtained

$$(\epsilon-1)v/3 = P_0[1 + (1+\gamma+\sigma)P_0/v + \dots],$$

where ϵ is the dielectric constant, v the molal volume and P_0 the molecular polarization. The coefficients in the corresponding expansion of the Clausius-Mosotti formula are all equal to unity. The correction γ , arising from translational fluctuations, is about 0.1 for most substances. The correction σ depends upon the optical anisotropy of the molecule and its shape.

INTRODUCTION

THE relation of the dielectric constant of a substance to the structural properties of its constituent molecules depends upon the average local field acting in the interior of a molecule. This average field is not in general equal to the field, \mathbf{E} , entering into the macroscopic field equations, since \mathbf{E} is obtained by averaging the local field in a different way, for example, over a physically small volume element, still large enough to contain many molecules. The classical method of Lorentz¹ provides an approximate estimate of the average local field in a molecule, which leads to the well-known Lorentz-Lorenz formula for the refractive index and to the Clausius-Mosotti formula for the dielectric constant. Lorentz actually calculated only the contribution to the internal field arising from external sources, and from the polarization of the molecules outside a spherical surface, of sufficient size to contain many molecules, and concentric with the molecule, in which the field is desired. Thus his result, $\mathbf{E} + 4\pi\mathbf{P}/3$, is valid only if the contribution from the polarization of the other molecules in the spherical cavity vanishes. Lorentz did not attempt to give a general answer to this question. He demonstrated that the contribution from molecules inside the cavity vanishes in a cubic crystal, and remarked that it also vanishes in fluid for a random distribution of other molecules around the central one. These conclusions involve the implicit assumption that

the electric moment of a molecule retains its average value through all phases of thermal motion. While this is doubtless an excellent approximation in crystals, it cannot be accepted without reservation for fluids. Keyes and Kirkwood² have pointed out that fluctuations in the induced moment of a molecule require a correction to the Lorentz field, $\mathbf{E} + 4\pi\mathbf{P}/3$, and to the formulas based upon it. In the present article, we shall be concerned with an extended and more exact investigation of this question in nonpolar dielectrics. Since the approach is statistical and the dielectric is treated from the outset as a system of molecules, rather than a continuum, we do not need to employ the artifice of the Lorentz cavity at all.

We shall neglect the influence of molecular multipole moments of higher order than the dipole, as well as effects arising from inhomogeneity of the local field in the region occupied by a molecule. From the properties of spherical harmonics, it may be shown that these influences make no primary contribution to the average field, but at most can produce small corrections in the fluctuation terms to be calculated here. We also suppose the moment of a molecule to be equal to the product of its polarizability in vacuum and the average field acting in its interior. We thus assume no dependence of the molecular polarizability on the density of the dielectric. There is evidence from the Raman and absorption spectra of liquids, that this is not always a justifiable

¹ H. A. Lorentz, *Theory of Electrons*, p. 303.

² Keyes and Kirkwood, *Phys. Rev.* **37**, 202 (1931).

assumption, particularly for molecules having optically active infrared frequencies, which can make an appreciable contribution to the polarizability, for example carbon dioxide. Negative frequency shifts between gas and liquid in excess of the Lorentz-Lorenz shift³ have been observed, which would tend to increase the contribution of infrared terms to the dispersion. A satisfactory treatment of this question demands a special investigation, which will be the subject of a later article.

TRANSLATIONAL FLUCTUATIONS

In the present section, we shall confine our attention to a uniformly polarized dielectric, consisting of isotropic nonpolar molecules. We may suppose the dielectric to be bounded by two parallel planes, perpendicular to an applied homogeneous electrostatic field. These conditions are realized in the interior of an ordinary plane condenser.

The polarization, \mathbf{P} , is equal to average density of electric moment. If the dielectric consists of N molecules of a single species, occupying the volume v , we have

$$\mathbf{P} = N\bar{\mathbf{p}}/v, \quad (1)$$

where $\bar{\mathbf{p}}$ is the average electric moment of a molecule. Although all molecules have the same average moment, the electric moment \mathbf{p}_i of any molecule i would be found to vary if followed through the phases of thermal motion of the system. With the neglect of electrical saturation effects and the influence of inhomogeneity in the local field, it is a sufficient approximation to write

$$\mathbf{p}_i = \alpha \mathbf{F}_i, \quad (2)$$

where α , the polarizability, is a molecular constant, and \mathbf{F}_i is the field acting at the center of gravity of molecule i . The field \mathbf{F}_i is produced in part by external charge distributions and in part by the electric moments of the remaining $N-1$ molecules. The contribution from external charge distributions, for example the surface charge on the plates of a plane condenser, is evidently equal to the dielectric displacement \mathbf{D} , defined* in the

macroscopic theory as the field in an excised cavity of such a shape as to make the contribution from the polarization of the dielectric vanish. The dipole moment of each molecule k makes the following contribution to \mathbf{F}_i

$$\mathbf{p}_k \cdot \nabla_i \nabla_k (1/r_{ik}),$$

where r_{ik} is the distance between i and k , and ∇_i and $\nabla_k (= -\nabla_i)$ are the gradient operators associated with the coordinates of the centers of gravity of the respective molecules. The total field acting on i is therefore,

$$\mathbf{F}_i = \mathbf{D} - \sum_{\substack{k=1 \\ \neq i}}^N \mathbf{T}_{ik} \cdot \mathbf{p}_k, \quad (3)$$

$$\mathbf{T}_{ik} = \nabla_i \nabla_k \left(\frac{1}{r_{ik}} \right) = \frac{1}{r_{ik}^3} \left[1 - 3 \frac{\mathbf{r}_{ik} \mathbf{r}_{ik}}{r_{ik}^2} \right],$$

where \mathbf{r}_{ik} is the vector distance between i and k and \mathbf{T}_{ik} is a symmetric tensor operating on \mathbf{p}_k . It is convenient to express \mathbf{T}_{ik} in dyadic form. Multiplication to the right or left with a vector signifies scalar multiplication with the right or left member of the vector pair in each term of the dyadic. The unit dyadic, 1, may be expressed as $\mathbf{s}_1 \mathbf{s}_1 + \mathbf{s}_2 \mathbf{s}_2 + \mathbf{s}_3 \mathbf{s}_3$, where \mathbf{s}_1 , \mathbf{s}_2 , and \mathbf{s}_3 are any convenient set of mutually orthogonal unit vectors. In subsequent calculation, we shall find it convenient to choose \mathbf{s}_1 , parallel to \mathbf{D} , and \mathbf{s}_2 and \mathbf{s}_3 in a plane parallel to the boundaries of the dielectric. From Eqs. (2) and (3) we obtain the following set of linear equations, which determine the electric moments $\mathbf{p}_1, \dots, \mathbf{p}_N$ as functions of the configuration of the centers of gravity of the N molecules

$$\mathbf{p}_i + \alpha \sum_{\substack{k=1 \\ \neq i}}^N \mathbf{T}_{ik} \cdot \mathbf{p}_k = \alpha \mathbf{D} \quad i=1, \dots, N. \quad (4)$$

always correct, but it is true in the interior of a homogeneous dielectric between charged plates, in which D is known to be equal to $4\pi\sigma$, where $\pm\sigma$ is the density of the surface charge on the plates. Moreover, there is no loss in generality in considering this case alone, for the relationship between the dielectric constant and molecular polarizability must be independent of the special type of field considered; so that it is sufficient to determine it for any particular field, to know it for all others. In electromagnetic theory, \mathbf{D} is of course defined as $\mathbf{E} + 4\pi\mathbf{P}$, or when \mathbf{P} is linear in \mathbf{E} and the dielectric is isotropic as $\epsilon\mathbf{E}$. If the dielectric is inhomogeneous, and if there are surfaces of discontinuity in its interior, D need not be simply the local field produced by the external distribution.

³ Breit and Salant, Phys. Rev. **36**, 871 (1930); Salant and Sandow, Phys. Rev. **31**, 503 (1930); West and Arthur, J. Chem. Phys. **2**, 215 (1934).

* The statement that the contribution to the local field from the external charge distribution is equal to D is not

Solution of these equations together with a mean value operation would yield $\bar{\mathbf{p}}$, the mean moment of a molecule. We shall presently obtain a solution in powers of the polarizability α , the most convenient form for taking mean values. First, however, it is worth while to point out the relationship of the present method to the Lorentz theory.

We take mean values of both sides of Eqs. (4), remembering that $\alpha\mathbf{D}$ is a constant vector, with the result

$$\bar{\mathbf{p}}_i + \alpha \sum_{\substack{k=1 \\ \neq i}}^N \overline{\mathbf{T}_{ik} \cdot \mathbf{p}_k} = \alpha\mathbf{D}. \quad (5)$$

We now add and subtract a quantity $\alpha\mathbf{n}_i$ from the left side of Eq. (5), where \mathbf{n}_i is a fluctuation, defined as follows.

$$\mathbf{n}_i = \sum_{\substack{k=1 \\ \neq i}}^N [\overline{\mathbf{T}_{ik} \cdot \mathbf{p}_k} - \overline{\mathbf{T}_{ik}} \cdot \bar{\mathbf{p}}]. \quad (6)$$

Eq. (5) then becomes

$$\bar{\mathbf{p}}_i + \alpha \sum_{\substack{k=1 \\ \neq i}}^N \overline{\mathbf{T}_{ik}} \cdot \bar{\mathbf{p}} + \alpha\mathbf{n}_i = \alpha\mathbf{D}. \quad (7)$$

Since the mean moments of all molecules of the homogeneous dielectric must have the same value $\bar{\mathbf{p}}$, we may write

$$\bar{\mathbf{p}} + \alpha \left(\sum_{\substack{k=1 \\ \neq i}}^N \overline{\mathbf{T}_{ik}} \right) \cdot \bar{\mathbf{p}} + \alpha\mathbf{n} = \alpha\mathbf{D}. \quad (8)$$

The fluctuation \mathbf{n}_i is of course the same for all molecules. It may be written in a slightly different form.

$$\mathbf{n} = \sum_{\substack{k=1 \\ \neq i}}^N \overline{\mathbf{T}_{ik}} \cdot (\mathbf{p}_k - \bar{\mathbf{p}}). \quad (9)$$

It will vanish only if the moment \mathbf{p}_k maintains its average value $\bar{\mathbf{p}}$ through all phases of thermal motion. This condition is not in general fulfilled in fluid dielectrics, although it probably is very nearly true in crystalline solids. We shall assume for the moment that the fluctuation \mathbf{n} can be neglected. In this approximation, we have

$$\bar{\mathbf{p}} + \alpha \left(\sum_{\substack{k=1 \\ \neq i}}^N \overline{\mathbf{T}_{ik}} \right) \cdot \bar{\mathbf{p}} = \alpha\mathbf{D}. \quad (10)$$

In fluid dielectrics, $\overline{\mathbf{T}_{ik}}$ has the same value for every molecular pair. A simple calculation yields (see appendix)

$$\overline{\mathbf{T}_{ik}} = \frac{4\pi}{v} \left(\mathbf{s}_i \mathbf{s}_1 - \frac{1}{3} \right), \quad (11)$$

where \mathbf{s}_1 is a unit vector parallel to \mathbf{D} . From (10) and (11) we obtain

$$\left(1 - \frac{4\pi N\alpha}{3v} \right) \bar{\mathbf{p}} + 4\pi \frac{N\alpha}{v} (\bar{\mathbf{p}} \cdot \mathbf{s}_1) \mathbf{s}_1 = \alpha\mathbf{D}. \quad (12)$$

This vector equation yields the following scalar equations

$$(\bar{\mathbf{p}} \cdot \mathbf{s}_1) \left(1 + \frac{8\pi N\alpha}{3v} \right) = \alpha D, \quad (13)$$

$$(\bar{\mathbf{p}} \cdot \mathbf{s}_2) = (\bar{\mathbf{p}} \cdot \mathbf{s}_3) = 0,$$

where $\bar{\mathbf{p}} \cdot \mathbf{s}_2$ and $\bar{\mathbf{p}} \cdot \mathbf{s}_3$ are the components of the average moment parallel to any pair of mutually orthogonal unit vectors in the plane perpendicular to \mathbf{D} . We then obtain the following expressions for $\bar{\mathbf{p}}$, the average molecular moment, and \mathbf{P} , the average polarization of the dielectric.

$$\bar{\mathbf{p}} = \frac{\alpha\mathbf{D}}{1 + 2P_0/v},$$

$$\mathbf{P} = N\bar{\mathbf{p}}/v = \frac{3}{4\pi} \frac{P_0/v}{1 + 2P_0/v} \mathbf{D} \quad (14)$$

$$P_0 = 4\pi N\alpha/3,$$

where P_0 is the molecular polarization, N is Avogadro's number and v the molal volume. The macroscopic equations relating \mathbf{P} and \mathbf{D} , and the dielectric constant ϵ are the following:

$$\mathbf{P} = ((\epsilon - 1)/4\pi)\mathbf{E}, \quad \mathbf{D} = \epsilon\mathbf{E}. \quad (15)$$

Eqs. (14) and (15) lead to the expression

$$(\epsilon - 1)/3 = (P_0/v)' / (1 - P_0/v), \quad (16)$$

which is an alternative form of the Clausius-

Mosotti relation, usually written

$$[(\epsilon-1)/(\epsilon+2)]v=P_0. \quad (16a)$$

Thus when we ignore the fluctuation \mathbf{n} we are led to the result of the Lorentz theory, in which $\bar{\mathbf{F}}_i$ is calculated as the field at the center of an excised spherical cavity, the material in the cavity being assumed to contribute nothing.

The tensors \mathbf{T}_{ik} may be regarded as the matrix elements of a linear transformation \mathbf{T} in the $3N$ dimensional configuration space of the entire system, the electric moments \mathbf{p}_i being the projections of a $3N$ dimensional vector on the subconfiguration space of molecule i . The solutions of Eq. (4) may then be written in the form

$$\mathbf{p}_i = (\mathbf{I} + \alpha \mathbf{T})^{-1} \alpha \mathbf{D}, \quad (17)$$

where \mathbf{I} is the identity transformation. There are a number of ways of calculating $(\mathbf{I} + \alpha \mathbf{T})^{-1}$, the most common method leading to usual determinantal solution of a set of inhomogeneous linear equations. In order to facilitate the subsequent calculation of mean values, we shall find it convenient to expand $(\mathbf{I} + \alpha \mathbf{T})^{-1}$ in powers of α

$$(\mathbf{I} + \alpha \mathbf{T})^{-1} = \sum_{n=0}^{\infty} (-\alpha)^n \mathbf{T}^n. \quad (18)$$

With this expansion, the solutions of Eq. (4) take the following form

$$\mathbf{p}_i = \alpha \left\{ 1 - \alpha \sum_{\substack{k=1 \\ k \neq i}}^N \mathbf{T}_{ik} + \alpha^2 \sum_{\substack{k, l=1 \\ k \neq i, l \neq k}}^N \mathbf{T}_{ik} \cdot \mathbf{T}_{kl} + \cdots \right\} \cdot \mathbf{D}. \quad (19)$$

These solutions may be easily verified by applying the method of successive substitutions to Eqs. (4).⁴ The mean value of \mathbf{p}_i may then be written

$$\bar{\mathbf{p}}_i = \alpha \left\{ 1 - \alpha \sum_{\substack{k=1 \\ k \neq i}}^N \bar{\mathbf{T}}_{ik} + \alpha^2 \sum_{\substack{k, l=1 \\ k \neq i, l \neq k}}^N \overline{\mathbf{T}_{ik} \cdot \mathbf{T}_{kl}} + \cdots \right\} \cdot \mathbf{D}. \quad (20)$$

⁴ See Courant and Hilbert, *Methoden der Mathematischen Physik* I, Kap. I, §2. The sufficient condition for convergence given there is not a necessary one. We shall assume convergence of (17) except for rare configurations, which make no finite contribution to mean values. The series will of course diverge on the null set of configurations, which make the determinant of \mathbf{T} vanish. Other configurations for which it diverges will generally have zero probability because of molecular repulsive forces.

The fluctuation \mathbf{n} may be similarly expanded in powers of α , with the use of (19).

$$\begin{aligned} \mathbf{n} = & -\alpha^2 \sum_{\substack{k, l=1 \\ k \neq i, l \neq k}}^N [\overline{\mathbf{T}_{ik} \cdot \mathbf{T}_{kl}} - \bar{\mathbf{T}}_{ik} \cdot \bar{\mathbf{T}}_{kl}] \cdot \mathbf{D} \\ & + \alpha^3 \sum_{\substack{k, l, s=1 \\ k \neq i, l \neq k, s \neq k}}^N [\overline{\mathbf{T}_{ik} \cdot \mathbf{T}_{kl} \cdot \mathbf{T}_{ls}} - \bar{\mathbf{T}}_{ik} \cdot \bar{\mathbf{T}}_{kl} \cdot \bar{\mathbf{T}}_{ls}] \cdot \mathbf{D} + \cdots \end{aligned} \quad (21)$$

We shall undertake the calculation of mean values for a fluid represented by a classical canonical ensemble. The mean value of any function $G_{ik \dots l}$ of the relative coordinates of a group of $n+1$ molecules may be calculated from the formula

$$\bar{G}_{ik \dots l} = \frac{1}{v^n} \int \cdots \int G_{ik \dots l} e^{-\beta W_{ik \dots l}} dv_i \cdots dv_l. \quad (22)$$

The potential of the average force, $W_{ik \dots l}$, acting on the molecules of the group is given by

$$e^{-\beta W_{ik \dots l}} = \frac{v^n \int \cdots \int e^{-\beta V_N} dv_1 \cdots dv_{N-n-1}}{\int \cdots \int e^{-\beta V_N} dv_1 \cdots dv_{N-1}}, \quad (23)$$

where V_N is the potential of the intermolecular forces in the entire system and β is equal to $1/kT$. The integration in the numerator extends over the configuration space of all molecules except those of the group, while in the denominator it extends over the configuration space of all molecules except any single molecule i of the group.⁵ It is apparent that we may calculate mean values with the distribution functions valid in the absence of the external field D , since they are to be multiplied by D in the expressions for $\bar{\mathbf{p}}$ and \mathbf{n} , and we are neglecting powers of D higher than the first. The mean value, $\bar{\mathbf{T}}_{ik}$, given in Eq. (9) is independent of the magnitude and form of the average force potential W_{ik} . This is not true of the mean values of products, $\overline{\mathbf{T}_{ik} \cdots \mathbf{T}_{ls}}$. We have undertaken the calculation of the first term in the expansion of \mathbf{n} , Eq. (21) for a fluid consisting of spherical molecules, exerting no attractive forces upon one another. For such a system, a rather tedious calculation yields (see appendix)

⁵ See R. H. Fowler, *Statistical Mechanics* (Cambridge Univ. Press), p. 181. J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

$$\overline{\mathbf{T}_{ik} \cdot \mathbf{T}_{kl}} - \overline{\mathbf{T}_{ik}} \cdot \overline{\mathbf{T}_{kl}} = -\frac{5\pi^2}{3v^2} \mathbf{1}; \quad l \neq i; \quad (24)$$

$$\overline{\mathbf{T}_{ik} \mathbf{T}_{ki}} = \overline{\mathbf{T}_{ik}^2} = \frac{16\pi^2 N}{9bv} \mathbf{1}; \quad b = 2\pi N a^3/3,$$

where a is the diameter of a molecule. In the double sum of the first term of Eq. (21), there are $(N-1)(N-2)$ terms in which l is different from i and $N-1$ terms in which l is identical with i . Approximating these numbers by N^2 and N ,

$$\mathbf{n} = -(16\pi^2/9b - 5\pi^2/3v)N^2\alpha^2\mathbf{D}/v. \quad (25)$$

The calculation of the higher order fluctuations becomes very complicated and has not been undertaken here. We may calculate $\bar{\mathbf{p}}$ either from Eqs. (8), (11) and (25) or directly from Eqs. (11), (20) and (24). If the former equations are used, the result must be expanded in powers of α , since we are not justified in retaining powers of α higher than the third in the expression for $\bar{\mathbf{p}}$, if powers of α higher than the second are discarded in \mathbf{n} . The result of either calculation is (see appendix)

$$\bar{\mathbf{p}} = \alpha \left[1 - \frac{8\pi N\alpha}{3v} + \left(\frac{16\pi^2}{9b} - \frac{49\pi^2}{9v} \right) \frac{N^2\alpha^2}{v} + \dots \right] \mathbf{D}. \quad (26)$$

Eqs. (1) and (26) together with the macroscopic Eqs. (13) allow one to express the dielectric constant as a function of α . Expansion of the result in powers of α yields

$$\frac{\epsilon - 1}{3}v = P_0 \left\{ 1 + (1 + \gamma) \frac{P_0}{v} + \frac{1}{16} \frac{P_0^2}{v^2} + \dots \right\}, \quad (27)$$

$$\gamma = P_0/b.$$

Although this is actually a power series in P_0 or α , it is convenient to arrange it in powers of $1/v$. The coefficients of $1/v$ and $1/v^2$ are therefore not complete but from dimensional considerations, it is easily seen that the neglected terms must be of the types P_0^n/vb^{n-1} and P_0^n/v^2b^{n-2} , respectively, where n is greater than two. When van der Waals forces of the attractive type, varying as the inverse sixth power of the intermolecular distance are introduced, the term γ is modified⁶ as follows

⁶ The quantity γ corresponds to λ_0/P_0 , where λ_0 is the fluctuation constant in Keyes-Kirkwood equation, as may be verified by calculating the expansion of $(\epsilon - 1)v/3$ from

(see appendix)

$$\gamma = P_0/b(1 + (A/3bRT)), \quad (28)$$

where A is the cohesive pressure constant in the van der Waals equation of state,

$$p = RT/(v - b) - A/v^2.$$

In order to compare Eq. (27) with the Mosotti formula, we expand the latter, Eq. (16), in a power series in P_0 .

$$\epsilon - 1v/3 = P_0[1 + P_0/v + P_0^2/v^2 + \dots]. \quad (29)$$

It is seen that the two series (27) and (29) agree only in their first terms. The coefficient of $1/v$ in Eq. (27) differs from that of Eq. (29) by a factor $(1 + \gamma)$, and the coefficients of $1/v^2$ differ widely. Actually, for most nonpolar substances, P_0/v is so small even at liquid densities, that the term in $(P_0/v)^2$ is practically negligible in either Eq. (27) or Eq. (29). This is true in all of the experimental tests of the Clausius-Mosotti relation on compressed gases, so that in reality only the first two terms of Eq. (29) have been tested. Moreover where the relation has been confirmed, as for the fixed gases N_2 , O_2 , H_2 , calculation shows the fluctuation correction to be within experimental error.⁷ In general the fluctuation term γ causes a positive deviation from the Mosotti formula. Such a deviation has been observed by Uhlig, Kirkwood and Keyes, and has been confirmed by measurements of Oncley on carbon dioxide and propane.⁸ The latter results will be discussed in detail in a forthcoming article by Oncley. His measurements lead to values of γ , agreeing tolerably well with those calculated from Eq. (28) with known equation of state constants. In general the experimentally determined values of γ are somewhat larger than the calculated ones. This suggests the presence of another effect, namely a variation of the polarizability with density. (See Table I.)

this equation. γ differs from λ_0/P_0 by a factor $5/2$, a discrepancy arising from a faulty calculation of \mathbf{T}_{ik}^2 in the earlier paper. There the influence of component of the electric moment in the plane perpendicular to \mathbf{D} on the fluctuation was neglected. Although this component vanishes in the mean, its contribution to the mean square of the field does not.

⁷ Tangl, Ann. d. Physik **10**, 748 (1903); **23**, 559 (1907); **26**, 59 (1908); Occhialini, Physik. Zeits. **6**, 669 (1905); Uhlig, Kirkwood and Keyes, J. Chem. Phys. **1**, 155 (1933).

⁸ Uhlig, Kirkwood and Keyes, J. Chem. Phys. **1**, 155 (1933). Oncley, unpublished work.

TABLE I*

	$P_0(\text{cc})$	$b(\text{cc})$	$A(\text{cc}^2 \text{atmos.}) \cdot 10^{-6}$	$\gamma(0^\circ\text{C})$
N_2	4.38	50.5	1.34	0.121
O_2	3.95	46.2	1.49	.127
H_2	2.10	21.0	0.20	.114

* The equation of state constants were taken from Beattie and Bridgeman, Proc. Am. Acad. 63, 229 (1928).

ANISOTROPY AND ROTATIONAL FLUCTUATIONS

Raman and Krishnan⁹ have discussed in a general manner the influence of molecular anisotropy on the polarization of a dielectric. They regard the molecule as constituting a cavity of arbitrary shape in a statistical continuum. Even though the polarization field in such a cavity were identical with the Lorentz field, when averaged over all molecular orientations, the average molecular moment induced by the polarization field need not be $(\mathbf{E} + 4\pi\mathbf{P}/3)\bar{\alpha}$ where $\bar{\alpha}$ is the mean polarizability. This arises from the fact that the average moment is the mean value of the product of the polarizability tensor and the polarization field. Unless the molecule is optically isotropic or spherical in shape, both of these quantities depend upon molecular orientation, so that the mean value of their product over all orientations is not in general equal to the product of their mean values. This is a type of fluctuation different from the one considered in the previous section. Without detailed calculation, Raman and Krishnan observe that if the shape of the molecule corresponds qualitatively to its polarization ellipsoid, a negative deviation from the Mosotti formula will result.

We shall develop this idea in somewhat more detail on the basis of the method used in the previous section. For optically anisotropic molecules, Eqs. (4) become

$$\mathbf{p}_i + \sum_{\substack{k=1 \\ \neq i}}^N \alpha^{(i)} \cdot \mathbf{T}_{ik} \cdot \mathbf{p}_k = \alpha^{(i)} \cdot \mathbf{D}, \quad (30)$$

where $\alpha^{(i)}$ is the polarizability tensor, and depends upon the orientation of i . If $\mathbf{n}_1^{(i)}$, $\mathbf{n}_2^{(i)}$, and $\mathbf{n}_3^{(i)}$ are unit vectors defining the principal optical axes of molecule i , $\alpha^{(i)}$ may be written in dyadic form as follows

⁹ Raman and Krishnan, Proc. Roy. Soc. A117, 589 (1927).

$$\alpha^{(i)} = \sum_{s=1}^3 \alpha_s \mathbf{n}_s^{(i)} \mathbf{n}_s^{(i)}, \quad (31)$$

where α_1 , α_2 , and α_3 are the principal polarizabilities of a molecule. Solution of these equations and averaging over all molecular orientations as well as over all configurations of the molecular centers of gravity leads to equations similar to Eq. (20).

$$\begin{aligned} \bar{\mathbf{p}}_i = \bar{\alpha} \mathbf{D} - \sum_{\substack{k=1 \\ \neq i}}^N \overline{\alpha^{(i)} \cdot \mathbf{T}_{ik}} \cdot \mathbf{D} \\ + \sum_{\substack{k, l=1 \\ \neq i \neq k}}^N \overline{\alpha^{(i)} \cdot \mathbf{T}_{ik} \cdot \alpha^{(k)} \cdot \mathbf{T}_{kl}} \cdot \mathbf{D} + \cdots, \end{aligned} \quad (32)$$

$$\bar{\alpha} = (\alpha_1 + \alpha_2 + \alpha_3)/3.$$

The mean value $\alpha^{(i)} \mathbf{T}_{ik}$ for a molecule of arbitrary shape may be calculated. (see appendix)

$$\overline{\alpha^{(i)} \cdot \mathbf{T}_{ik}} = 4\pi \bar{\alpha} \mathbf{s}_i \mathbf{s}_1 - \frac{4\pi}{3} \sum_{l=1}^3 \alpha_l J_l \mathbf{1}, \quad (33)$$

$$J_l = -\frac{1}{4\pi} \int \nabla \left(\frac{1}{r} \right) \cdot \mathbf{n} \mathbf{n}_l \cdot d\mathbf{A},$$

where the integrals are to be extended over the surface of a molecule with outwardly directed normal. This expression becomes identical with Eq. (11) if the molecule is optically isotropic ($\alpha_1 = \alpha_2 = \alpha_3 = \bar{\alpha}$) or if it is spherical in shape. With some algebraic transformations similar to those used in the foregoing section, we obtain the following expansion for $(\epsilon - 1)/3$.

$$((\epsilon - 1)/3)v = P_0[1 + (1 + \gamma + \sigma)(P_0/v) + \cdots],$$

$$\begin{aligned} \sigma = (1/3\bar{\alpha})[(\alpha_1 - \alpha_2)(J_1 - J_2) \\ + (\alpha_1 - \alpha_3)(J_1 - J_3) + (\alpha_2 - \alpha_3)(J_2 - J_3)], \end{aligned} \quad (34)$$

$$\gamma = (3v/4\pi\bar{\alpha}) \overline{\alpha^{(i)} \cdot \mathbf{T}_{ik} \cdot \alpha^{(k)} \cdot \mathbf{T}_{ki}},$$

where γ is the part of the fluctuation arising from the diagonal terms of the double sum in Eq. (32). We do not attempt to carry the expansion to terms in $1/v^2$ as in the case of isotropic spherical molecules, but we may assume that this term will not differ in magnitude from $1/16(P_0/v)^2$.

Since γ itself is of the nature of a small correction, we are justified in neglecting optical anisotropy in calculating it. With this approximation, we may write

$$\gamma = \frac{3\bar{\alpha}}{2\pi} \int_0^\infty \frac{1}{r^6} e^{-\beta\bar{W}} dv, \quad (35)$$

where \bar{W} is the potential of the force acting between a pair of molecules, averaged over all configurations of the other molecules, and over the orientation of one member of the molecular pair. The shape of the molecule is of course reflected in the potential \bar{W} , $e^{-\beta\bar{W}}$ vanishing within a cavity of dimensions determined by molecular repulsion. The integral in Eq. (35) is not extremely sensitive to the form of the cavity of exclusion, so that the fluctuation γ will be approximately given by Eq. (28) even for nonspherical molecules. The term σ has been calculated for a molecule having the shape of an ellipsoid of rotation, its axes being assumed to coincide with the principal optical axes of the molecule. If α_1 is the polarizability along the major axis and α_2 the value of the other two principal polarizabilities, we have

$$\sigma = \frac{2}{3} \frac{\alpha_1 - \alpha_2}{\alpha} \left[\frac{1 - e^2}{e^3} \sinh^{-1} \frac{e}{(1 - e^2)^{1/2}} - \frac{1 - e^2}{e^2} - \frac{1}{3} \right], \quad (36)$$

where e is the eccentricity of the ellipse. For extremely elongated molecules, σ approaches the value

$$\sigma_0 = -2(\alpha_1 - \alpha_2)/9\bar{\alpha}, \quad (37)$$

corresponding to unit eccentricity. For a ratio of minor to major axis of $1/3$, the numerical factor of $(\alpha_1 - \alpha_2)/\bar{\alpha}$ is about $2/3$ of the σ_0 value. If the polarizabilities of the molecule correspond in magnitude to its linear dimensions, α_1 is greater than α_2 and σ is negative. The ratio α_2/α_1 may be obtained experimentally from the degree of depolarization in the scattering of light and from the Kerr effect.¹⁰ Since γ is always positive, the two terms γ and σ are in general opposite in sign. For extremely elongated molecules, with a corresponding optical anisotropy, it is likely that σ predominates, causing a resultant negative deviation

¹⁰ See Marx, *Handbuch der Radiologie*, Teil II; Debye and Sack, *Theorie der elektrischen Molekulareigenschaften*; Placzek, *Rayleigh-Streuung und Raman-Effekt*.

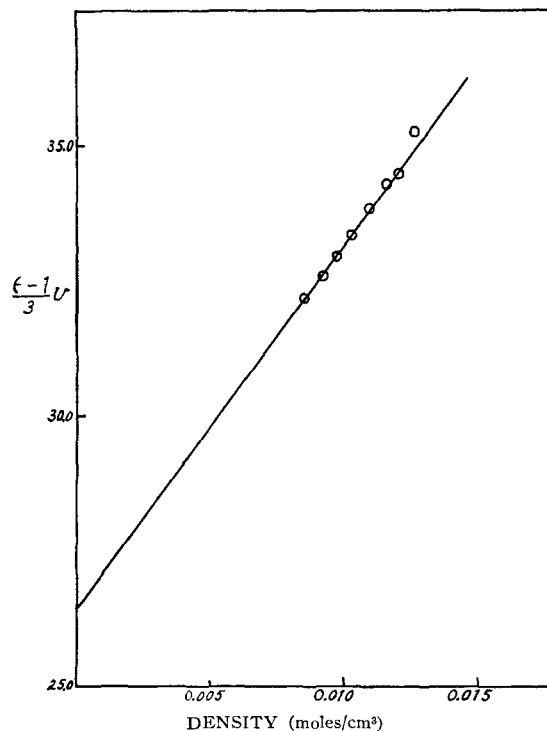


FIG. 1. Dielectric constant of liquid pentane as measured by Danforth.

tion from the expanded Mosotti formula, Eq. (29). According to measurements of Danforth,¹¹ this appears to be true in the case of pentane. When $(\epsilon - 1)v/3$, calculated from his measurements, is plotted as a function of density, all but the last point lie on a straight line (Fig. 1). Extrapolation to zero density yields a value of P_0 equal to 26.5 cc. The slope of the line deviates from P_0^2 , the Mosotti value, by a factor of 0.95 leading to a value of -0.05 for $\gamma + \sigma$. Unfortunately, adequate data on the equation of state of pentane vapor and on the optical anisotropy of the pentane molecule are not available for the calculation of γ and σ . However, since γ has about the same value for all nonpolar molecules, a reasonable estimate is 0.15. With this value σ becomes about -0.20 . From Eq. (37) the ratio α_2/α_1 is then estimated as about 0.5, a reasonable value for the optical anisotropy of the pentane molecule. It should also be remarked that the essential linearity of the experimental points in Fig. 1, confirms the adequacy of the expansions (27) and (34) even at liquid densities.

¹¹ Danforth, *Phys. Rev.* **38**, 1224 (1931).

APPENDIX

Outlines of the more important calculations, upon which the foregoing formulas are based will be presented here. Use is made of the generalized Green's theorem

$$\int^v \nabla \mathbf{F} = \int^A \mathbf{F} d\mathbf{A},$$

where the surface integral is extended over the boundaries of the volume v . The dyadic $\nabla \mathbf{F}$ may be written as follows

$$\nabla \mathbf{F} = \sum_{l,k}^3 \mathbf{s}_l \mathbf{s}_k (\partial F_l / \partial x_k)$$

and the theorem may be proved by consideration of the components

$$\int^v \frac{\partial F_l}{\partial x_k} dv = \int^A F_l \mathbf{s}_k \cdot d\mathbf{A}$$

as for the usual Green's theorem. For brevity, we shall generally suppress the symbol $\mathbf{1}$ for the unit dyadic in what follows.

Calculation of $\overline{\mathbf{T}}_{ik}$:

From Eqs. (3) and (22), we may write after dropping subscripts, which are here superfluous

$$-\overline{\mathbf{T}}_{ik} = \frac{1}{v} \int^v \nabla \nabla (1/r) e^{-\beta W(r)} dv,$$

where $W(r)$ is the potential of the average force between a pair of spherical molecules and r is their separation. The integration is of course to be extended over the volume occupied by the dielectric. We may suppose that molecular repulsion, $W \rightarrow \infty$, causes the integrand to vanish in the neighborhood of $r=0$. Thus, the region within a sphere of arbitrarily small radius constructed about the origin can make no contribution to $\overline{\mathbf{T}}_{ik}$,

$$-\overline{\mathbf{T}}_{ik} = \frac{1}{v} \int_0^v \nabla \nabla (1/r) e^{-\beta W(r)} dv,$$

where the small sphere is excluded from the region of integration. Making use of the identity $e^{-\beta W} = 1 + (e^{-\beta W} - 1)$, we may now write

$$-\overline{\mathbf{T}}_{ik} = \frac{1}{v} \int_0^v \nabla \nabla \left(\frac{1}{r} \right) dv + \frac{1}{v} \int_0^\infty \nabla \nabla \left(\frac{1}{r} \right) (e^{-\beta W(r)} - 1) dv.$$

The second integral can be extended over the whole of space, since the integrand, by virtue of the known properties of $W(r)$ will diminish asymptotically at least as rapidly as r^{-4} , and no significant contribution can arise from distant regions, outside the volume occupied by the dielectric. Transformation to polar coordinates and integration over angles shows immediately the second integral vanishes and we have

$$-\overline{\mathbf{T}}_{ik} = \frac{1}{v} \int_0^v \nabla \nabla (1/r) dv.$$

From this point on the calculation is formally identical with the classical one, the small sphere about the origin, playing the role of the Lorentz cavity. Transformation to

a surface integral by means of Green's theorem yields

$$-\overline{\mathbf{T}}_{ik} = (1/v) \left\{ \int^{A_e} \nabla (1/r) d\mathbf{A} - \int^{A_i} \nabla (1/r) d\mathbf{A} \right\},$$

where the first integral is taken over the exterior surface A_e , consisting of a pair of parallel planes, and the second integral over the interior surface A_i , consisting of the small sphere, all normals being outwardly directed. Evaluation of these integrals leads to Eq. (11).

Calculation of $\overline{\mathbf{T}}_{ik} \cdot \mathbf{T}_{kl}$:

Making use of Eq. (22), we may write

$$\overline{\mathbf{T}}_{ik} \cdot \mathbf{T}_{kl} = \frac{1}{v^2} \int^v \int^v \mathbf{T}_{ik} \cdot \mathbf{T}_{kl} e^{-\beta W_{ikl}} dv_k dv_l,$$

where W_{ikl} is the potential of the average force acting between the group of three molecules. In order to make the calculation feasible, we ignore attractive forces and assume the molecules to be rigid spheres of diameter a . For this case, we have

$$\overline{\mathbf{T}}_{ik} \cdot \mathbf{T}_{kl} = \frac{1}{v^2} \int_\omega \int^v \mathbf{T}_{ik} \cdot \mathbf{T}_{kl} dv_k dv_l,$$

where the integrations extend over the volume of the dielectric, excluding a region ω determined by two spheres of radius a , concentric with the molecules i and k . We first integrate over the configuration space of molecule l , transforming to surface integrals by means of Green's theorem.

$$\int \mathbf{T}_{ik} \cdot \mathbf{T}_{kl} dv_l = v \overline{\mathbf{T}}_{ik} \cdot \mathbf{T}_{kl} - \frac{4\pi a^3}{3} \mathbf{T}_{ik}^2 + \mathbf{T}_{ik} \cdot \mathbf{t}_{ik}$$

where $\overline{\mathbf{T}}_{kl}$ is given by Eq. (11) and

$$\begin{aligned} \mathbf{T}_{ik} \cdot \mathbf{t}_{ik} &= 0 \quad r_{ik} > 2a \\ &= \frac{2\pi}{3r_{ik}^3} \left\{ \left[-\frac{3}{8} \frac{r_{ik}}{a} + \frac{1}{16} \frac{r_{ik}^3}{a^3} + \frac{2a^3}{r_{ik}^3} \right] \right. \\ &\quad \left. - \frac{3\mathbf{r}_{ik}\mathbf{r}_{ik}}{r_{ik}^2} \left[+\frac{3}{8} \frac{r_{ik}}{a} - \frac{1}{16} \frac{r_{ik}^3}{a^3} - \frac{2a^3}{r_{ik}^3} \right] \right\} \\ &\quad a \leq r_{ik} < 2a. \end{aligned}$$

The term \mathbf{t}_{ik} arises from the overlapping of the spheres of exclusion for l about i and k when r_{ik} is less than $2a$, which decreases the interior surface over which the integration extends. Integration of the above expression over all configurations of k outside the sphere of exclusion round i yields

$$\overline{\mathbf{T}}_{ik} \cdot \mathbf{T}_{kl} = \overline{\mathbf{T}}_{ik} \cdot \mathbf{T}_{kl} - 5\pi^2/3v^2,$$

the result given in Eq. (24), the symbol for the unit dyadic being suppressed.

Calculation of $\overline{\mathbf{T}}_{ik}^2$:

From Eqs. (3) and (22) we may write

$$\overline{\mathbf{T}}_{ik}^2 = \frac{1}{v} \int^v \frac{1 + 3\mathbf{r}\mathbf{r}/r^2}{r^6} e^{-\beta W(r)} dv,$$

where r is the distance between the pair of molecules i and k , the subscripts being omitted here as superfluous. Since the potential of average force $W(r)$ is independent of the

angular coordinates, we get after integrating over them

$$\overline{T_{ik}^2} = \frac{8\pi}{v} \int_0^\infty \frac{1}{r^4} e^{-\beta W(r)} dr,$$

the integration being taken over all of space instead of just the volume of the dielectric since the integrand diminishes sufficiently rapidly to make distant contributions entirely negligible. If attractive forces are neglected and the molecules are treated as hard spheres

$$W(r) = \infty \quad 0 \leq r < a \\ = 0 \quad r > a$$

we have

$$\overline{T_{ik}^2} = \frac{8\pi}{3v} \frac{1}{a^3} = \frac{16\pi^2 N}{9v} \frac{1}{b} \\ b = 2\pi N a^3/3,$$

which is the result of Eq. (24). If attractive forces are not altogether neglected, but the dependence of $W(r)$ on density is ignored, we have

$$W(r) = \infty \quad 0 \leq r < a \\ = V(r) \quad r > a$$

where $V(r)$ is the potential of the attractive van der Waals forces between an isolated pair of molecules. According to modern theory this potential has the form $-C/r^6$ where C is a constant. Expanding $e^{+C/r^6 kT}$ in series and neglecting terms of order $1/T^2$ and higher we obtain

$$\overline{T_{ik}^2} = (16\pi^2 N/9vb)(1 + \frac{1}{3} NC/a^6 RT).$$

However, from the theory of the equation of state, the van der Waals A constant is given by

$$A = -2\pi N^2 \int_a^\infty V(r) r^2 dr = \frac{2\pi N^2 C}{3a^3},$$

so that we may write

$$NC/a^6 = A/b$$

and we have

$$\overline{T_{ik}^2} = (16\pi^2 N/9vb)(1 + A/3bRT),$$

leading to Eq. (28) for γ .

Calculation of $\overline{\alpha^{(i)} \cdot T_{ik}}$ for Anisotropic Molecules:

Since $\alpha^{(i)} T_{ik}$ depends only on the coordinates of the centers of gravity of i and k and on the orientation of i alone, we may write with a slight generalization of Eq. (23)

$$\overline{\alpha^{(i)} \cdot T_{ik}} = \frac{1}{8\pi^2 v} \int d\omega_i \int_\Omega \alpha^{(i)} \cdot T_{ik} e^{-\beta \bar{W}} dv_k,$$

where \bar{W} is the potential of the force acting between i and k averaged over all configurations of the other molecules and over the orientation of k . The above integral is extended over all positions of the center of gravity of k and over all orientations of i . Molecular repulsive forces will cause $e^{-\beta \bar{W}}$ to vanish in a region Ω containing the center of i and bounded by a surface A , fixed relative to a set of axes in i , for example the principal optical axes n_1, n_2, n_3 . If we neglect attractive forces outside Ω , we may write

$$\int_\Omega \alpha^{(i)} \cdot T_{ik} e^{-\beta \bar{W}} dv_k = \int_\Omega \alpha^{(i)} \cdot T_{ik} dv_k.$$

Making use of Green's theorem and Eq. (3) we may transform the above integral as follows

$$\int_\Omega \alpha^{(i)} \cdot T_{ik} dv_k = - \int^{A_e} \alpha^{(i)} \cdot \nabla \left(\frac{1}{r} \right) dA + \int^{A_i} \alpha^{(i)} \cdot \nabla \left(\frac{1}{r} \right) dA,$$

where r is the distance between i and k , and A_e is the exterior boundary consisting of two infinite parallel planes. Since A_e is independent of the orientation of molecule i , we may evaluate the first surface integral at once

$$- \int^{A_e} \alpha^{(i)} \cdot \nabla \left(\frac{1}{r} \right) dA = 4\pi \alpha^{(i)} \cdot \mathbf{s}_1 \mathbf{s}_1.$$

The interior surface depends upon the orientation of i , but we may write

$$dA_i = \sum_{l=1}^3 \mathbf{n}_l (\mathbf{n}_l \cdot d\mathbf{A}_i),$$

where $\mathbf{n}_l \cdot d\mathbf{A}_i$ is independent of the orientation of i . Using Eq. (31), we obtain

$$\int_\Omega \alpha^{(i)} \cdot T_{ik} dv_k = 4\pi \alpha^{(i)} \cdot \mathbf{s}_1 \mathbf{s}_1 - 4\pi \sum_{l,s=1}^3 \mathbf{n}_l \mathbf{n}_s \alpha_s J_{ls},$$

$$J_{ls} = - \frac{1}{4\pi} \int^{A_i} \mathbf{n}_s \cdot \nabla \left(\frac{1}{r} \right) \mathbf{n}_l \cdot d\mathbf{A}_i,$$

where J_{ls} is independent of the orientation of i . When the above expression is averaged over all orientations we obtain

$$\overline{\alpha^{(i)} T_{ik}} = \frac{1}{v} \left(4\pi \bar{\alpha} \mathbf{s}_1 \mathbf{s}_1 - \frac{4\pi}{3} \sum_{l=1}^3 \alpha_l J_{ll} \right),$$

which is identical with Eq. (33). This follows from the fact that

$$(1/8\pi^2) \int \mathbf{n}_l \mathbf{n}_s d\omega_l = \delta_{ls}/3.$$

The vector \mathbf{n}_l may be expressed as

$$\mathbf{n}_l = \sum_{m=1}^3 \mathbf{s}_m (\mathbf{n}_l \cdot \mathbf{s}_m),$$

where \mathbf{s}_m is one of the set of mutually orthogonal unit vectors fixed relative to the external field and boundaries. Thus an average of $\mathbf{n}_l \mathbf{n}_s$ over all orientations of the set of axes $\mathbf{n}_1, \mathbf{n}_2$, and \mathbf{n}_3 is

$$\overline{\mathbf{n}_l \mathbf{n}_s} = \sum_{m,m'=1}^3 \overline{\mathbf{s}_m \mathbf{s}_{m'}} (\mathbf{n}_l \cdot \mathbf{s}_m) (\mathbf{n}_s \cdot \mathbf{s}_{m'}).$$

Since the average of the product of any pair of direction cosines, $(\mathbf{n}_l \cdot \mathbf{s}_m) (\mathbf{n}_s \cdot \mathbf{s}_{m'})$ which transform one set of orthogonal vectors into another, vanishes unless $l=s$ and

$m'=m$, when it is $\frac{1}{3}$, and $\sum_{m=1}^3 \mathbf{s}_m \mathbf{s}_m$ is equal to the unit dyadic.

Note Added in Proof:

Instead of expanding $(\epsilon-1)v/3$ in powers of α as we have done in Eq. (27), we may expand the Mosotti expression $(\epsilon-1)v/(\epsilon+2)$.

$$\frac{\epsilon-1}{\epsilon+2} v = \frac{P_0}{v} \left[1 + \gamma \frac{P_0}{v} - \left(\frac{15}{16} + 2\gamma \right) \left(\frac{P_0}{v} \right)^2 + \dots \right].$$

We note that when P_0/v is small, the fluctuations cause a

positive deviation from the Mosotti law. As the density is increased, this deviation becomes smaller, and vanishes when v is approximately equal to b or $2\pi Na^3/3$. The corresponding density is about twice ordinary liquid densities. This is reasonable, for one might expect translational fluctuations to become relatively unimportant not only in solids but also in liquids. Not much significance is to be attached to the value $v=b$ predicted by the above formula since it is probably necessary to take terms of higher order in P_0/v into account as liquid densities are approached. It should be emphasized, however, that although the Mosotti value of $(\epsilon-1)v/(\epsilon+2)$ is approached

at some particular density, the Mosotti formula cannot give the correct variation of ϵ with density. This consideration may at first sight seem to make the application of our equations to liquid pentane seem questionable. However, we must remember that although the translational fluctuation may become small at liquid densities, this is not true of the rotational fluctuation. It might, therefore, be better to suppose that the γ contribution to the slope vanishes and that only σ is important. The value of σ in liquid pentane would then be -0.05 , with a ratio of 0.86 instead of 0.5 . It is apparent that we can attach only qualitative significance to these figures.

SEPTEMBER, 1936

JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

Thermal Transitions in Copper Sulphate Pentahydrate Molecular Rotation and the Dehydration of Hydrates

T. IVAN TAYLOR* AND HAROLD P. KLUG, *University of Idaho, Moscow, Idaho*

(Received July 15, 1936)

A study of the thermal transitions in copper sulphate pentahydrate has been made from warming curves obtained by a differential thermocouple method. Small transitions were observed at 29°C , 35°C , 53.7°C , and dehydrations at 96.5°C , 102°C , and at 113°C . The first three of these may be interpreted as transitions from oscillation to rotation of the water molecules in the crystal. The last three are associated with the stepwise dehydration to the tetra-, tri-, and monohydrates, respectively. The existence of the tetrahydrate, not previously known, has been demonstrated. A discussion of the dehydration in the light of its crystal structure is given. A mechanism of dehydration by heat, based on the concept of molecular rotation, has been suggested.

SINCE Pauling's explanation¹ of certain observed transitions in solids on the basis of a gradual transition from oscillational motion of the molecules about equilibrium positions to complete rotation, the phenomenon has proved to be of rather wide occurrence in accordance with his prediction. In many substances the excitation of rotation of the molecules or groups is accompanied by gradual and sometimes sharp changes in such properties as dielectric constant, heat capacity, specific volume, coherent scattering of x-rays, and crystal structure. Pohlman² has studied the adsorption spectra of a number of ammonium salts in the neighborhood of the transition temperatures. Shearin³ has also recently found that there is an infrared absorption at wave-lengths of about 3.7μ for solid hydrogen

chloride which indicates hindered rotation. This observation is in contrast to the results of Errera and Sack⁴ working with Hertizian waves. Evidence that molecular rotation in certain organic crystals is initiated simultaneously with atomic vibrations has been given by White and Morgan⁵ and Yager and Morgan.⁶

As is shown by x-ray studies of the transitions observed in certain crystals, for example, sodium nitrate,⁷ ammonium nitrate,⁸ and *n*-amyl ammonium chloride,⁹ rotation of the molecules or groups may or may not be initiated at a polymorphic inversion. If the transition is accompanied by a change in crystal structure, the con-

* Now at Columbia University, New York City.

¹ Pauling, *Phys. Rev.* **36**, 430 (1930).

² Pohlman, *Zeits. f. Physik* **79**, 394 (1932).

³ Shearin, *Phys. Rev.* **48**, 299 (1935).

⁴ Errera and Sack, *Trans. Faraday Soc.* **30**, 687 (1934).

⁵ White and Morgan, *J. Am. Chem. Soc.* **57**, 2078 (1935).

⁶ Yager and Morgan, *J. Am. Chem. Soc.* **57**, 2071 (1935).

⁷ Kracek, Posnjak and Hendricks, *J. Am. Chem. Soc.* **53**, 3339 (1931).

⁸ Hendricks, Posnjak and Kracek, *J. Am. Chem. Soc.* **54**, 2766 (1932).

⁹ Southard, Milner and Hendricks, *J. Chem. Phys.* **1**, 95 (1933).