1080. *The Dielectric Polarization of Some Imperfect Polar Gases.*

By A. D. Buckingham and R. E. Raab.

An apparatus designed to measure the density dependence of the total dielectric polarization of polar vapours is described. Densities and dielectric constants were determined at the same temperature and pressure; pressures up to the saturated vapour pressure at room temperature were also measured. The pressure range of the apparatus is 0—2 atm., at temperatures up to 200°. The expansion of the total polarization ${}_TP$ as a power series in the density, ${}_TP = \mathscr{A} + \mathscr{B}/V_m + \ldots$, where V_m is the molar volume, is discussed. Measurements of $\mathscr{A}$ for sulphur hexafluoride, acetonitrile, arsenic trifluoride, fluoroform, and chloroform have been made at several temperatures, leading to dipole moments and polarizabilities. $\mathscr{B}$ has also been found for these polar vapours at a number of temperatures; for acetonitrile at 80°, $\mathscr{B} = -10{\cdot}1 \pm 1{\cdot}1 \times 10^5$ cm.^{6} mole^{-2}, so that at $\frac{1}{3}$ atm. $\mathscr{B}/V_m$ is over 4% of ${}_TP$. The temperature dependence of $\mathscr{B}$ and of the second virial coefficient B indicates that acetonitrile tends to dimerize, with a heat of dimerization $\Delta H_0 = -3{\cdot}8$ kcal. mole^{-1} and a dimeric dipole moment of 3·4 D; at 100° $-\Delta H_0$ decreases, and the dimer dipole moment increases, as the temperature rises. The dipole moment found for arsenic trifluoride, $2{\cdot}57 \pm 0{\cdot}02$ D, differs interestingly from the microwave Stark-effect value of $2{\cdot}815 \pm 0{\cdot}025$ D. B, $\mathscr{A}$, and $\mathscr{B}$ have been measured for arsenic trifluoride, and fluoroform at 80°.

The static dielectric constant ε of a gas is a potential source of information about the dipole moment μ and polarizability α of an isolated molecule, and, if measured over a pressure range, about intermolecular forces. The total polarization, or Clausius–Mossotti function, ${}_TP$ can be expanded as a power series in the gas density [1,2]

$$ {}_TP = \frac{\varepsilon - 1}{\varepsilon + 2} V_m = \mathscr{A} + \mathscr{B}/V_m + \mathscr{C}/V_m^2 + \ldots, \qquad (1) $$

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[1] Harris and Alder, *J. Chem. Phys.*, 1953, **21**, 1351.

[2] Buckingham and Pople, *Trans. Faraday Soc.*, 1955, **51**, 1179.

where V_m is the molar volume of the gas, that is, $1/V_m = n$, the number of moles in unit volume; $\mathscr{A}, \mathscr{B}, \mathscr{C}, \ldots$, are the first, second, third, . . ., dielectric virial coefficients, and are functions of the temperature (T) [but not of the density, for eqn. (1) is an expansion in powers of this variable]. $\mathscr{A}$ is the dielectric polarization in the limit of zero pressure and is related to the properties of the isolated molecules; it is given by the well-known Debye equation

$$\mathscr{A} = \frac{4\pi \boldsymbol{N}}{3}\left(\alpha + \frac{\mu^2}{3\boldsymbol{k}T}\right) \tag{2}$$

where $\boldsymbol{N}$ is Avogadro's number and $\boldsymbol{k}$ is Boltzmann's constant. Measurements of ${}_TP$ at low pressures and at several temperatures yield values for μ and α by way of eqn. (2). Most of the accurately known dipole moments have been found in this way.

$\mathscr{B}$, which is a measure of the initial deviation from ideal-gas behaviour, is related to the properties of an interacting pair of molecules, and it can be shown that for one mole of gas [2]

$$\mathscr{B} = \frac{2\pi \boldsymbol{N}^2}{3\Omega}\int\left\{\alpha_{12} - 2\alpha + \frac{1}{3\boldsymbol{k}T}(\mu_{12}{}^2 - 2\mu^2)\right\} \exp\left(-u_{12}/\boldsymbol{k}T\right)\mathrm{d}\tau_2, \tag{3}$$

where μ_{12} and α_{12} are the dipole moment and polarizability of the pair of molecules whose interaction potential energy is u_{12}; $\int \mathrm{d}\tau_2 = V_m\Omega$ is an integration over all positions and orientations of molecule 2 ($\int \mathrm{d}\tau_2 = \int\int\int \mathrm{d}x\mathrm{d}y\mathrm{d}z\int \mathrm{d}\omega = V_m\Omega$, so Ω, a pure number, is the integral over the orientational co-ordinates ω). If u_{12} is such that for the most favourable configuration $-u_{12} \gg \boldsymbol{k}T$, it is helpful to think of a " dimer," that is, a semistable pair of molecules. We then have an equilibrium between monomers X and dimers X_2, 2 $\rightleftharpoons$ X_2, and at reasonably low pressures the equilibrium constant $K_c = [X_2]/[X]^2 = -B + O(V_m{}^{-1})$, where B is the second virial coefficient in the equation of state of the gas: [3,4]

$$pV_m/\boldsymbol{R}T = 1 + B/V_m + C/V_m{}^2 + \ldots; \tag{4}$$

$\boldsymbol{R} = \boldsymbol{N}\boldsymbol{k}$ is the gas constant. In such a case, the dimer is well characterized, $\mathscr{B}$ depending on its polarizability $\langle\alpha_{12}\rangle$ and mean-square dipole moment $\langle\mu_{12}{}^2\rangle$; these dimeric properties may be temperature dependent, because of the accessibility of low-lying excited vibrational or torsional states.

Thus

$$\mathscr{B} = \frac{4\pi \boldsymbol{N}K_c}{3}\left\langle\alpha_{12} - 2\alpha + \frac{1}{3\boldsymbol{k}T}(\mu_{12}{}^2 - 2\mu^2)\right\rangle. \tag{5}$$

For strongly polar monomers, $\alpha_{12} - 2\alpha$ can be neglected, so that

$$\mathscr{B}/\mathscr{A} = K_c\left\{\frac{\langle\mu_{12}{}^2\rangle}{\mu^2} - 2\right\}. \tag{6}$$

If the dimer is fairly stable, $\langle\mu_{12}{}^2\rangle$ will be approximately independent of T, and

$$\frac{\mathrm{d}\ln|\mathscr{B}|}{\mathrm{d}T} = \frac{\Delta H_0}{\boldsymbol{R}T^2}, \tag{7}$$

where $\Delta H_0 = \boldsymbol{R}T^2\dfrac{\mathrm{d}}{\mathrm{d}T}\ln K_p$ is the standard heat of dimerization, $K_p = p_{X_2}/p_X{}^2$ being the equilibrium constant involving the pressures (in atm.) of the monomer and dimer; K_p is proportional to K_c/T at low pressures. $\mathrm{d}\ln|\mathscr{B}| = \dfrac{1}{\mathscr{B}}\mathrm{d}\mathscr{B}$, so that $|\mathscr{B}|$ is a positive number. If ΔH_0 is approximately independent of T, a plot of $\ln|\mathscr{B}|$ against $1/T$ will be linear with slope $-\Delta H_0/\boldsymbol{R}$.

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[3] Beattie and Stockmayer, in Taylor and Glasstone, " Treatise on Physical Chemistry," Macmillan, London, 1951, Vol. II, chap. 2.

[4] Buckingham and Raab, *Trans. Faraday Soc.*, 1959, **55**, 377.

If both monomer and dimer are non-polar, as would be the case for the equilibria

$$2\mathrm{I} \rightleftharpoons \mathrm{I}_2 \text{ and } 2\mathrm{Al(CH_3)_3} \rightleftharpoons \mathrm{Al_2(CH_3)_6}$$

(assuming the monomeric trimethylaluminium to be planar), the polarizability term in (5) is dominant, and

$$\mathscr{B}/\mathscr{A} = K_c\left\{\frac{\langle\alpha_{12}\rangle}{\alpha} - 2\right\}, \quad \frac{\mathrm{d}\ln|\mathscr{B}|}{\mathrm{d}T} = \frac{\Delta H_0}{\boldsymbol{R}T^2} + \frac{1}{T}; \qquad (8)$$

$\Delta H_0/\boldsymbol{R}T$ may be of the order -10 at room temperature, so that eqn. (7) indicates that $|\mathscr{B}|$ may decrease by a few units % for each degree rise in temperature.

Measurements of ${}_TP$, leading to values for $\mathscr{A}$ and $\mathscr{B}$, have been reported for a number of polar and non-polar gases; results are summarized in Table 1. It is clear that $\mathscr{B}$ can be of either sign, and varies considerably from one substance to another. For the inert gases, μ and μ_{12} are zero (but $\mu_{123} \neq 0$), and $\mathscr{B}$ arises purely from the effects of the interaction on the polarizability; for the non-dipolar gases methane, nitrogen, carbon dioxide, and ethane, although $\mu = 0$, $\mu_{12} \neq 0$, and a substantial contribution to $\mathscr{B}$ arises from the dipole moment induced in a molecule by the quadrupole or octopole moment of its neighbour.[5,10] Much larger values of $\mathscr{B}$ are found for highly polar gases, and the non-polar contributions may be neglected. The sign of $\mathscr{B}$ has been interpreted[2] in terms of a " shape " effect, rod-like polar molecules (methyl fluoride being a not very good example of this class) having a tendency towards an antiparallel alignment, leading to a small μ_{12} and hence to a negative $\mathscr{B}$, while disc-shaped molecules such as ammonia tend to form pairs with parallel dipoles, producing a positive $\mathscr{B}$.

All the substances in Table 1 are permanent gases, and the measurements of ε and p were made up to quite high pressures (~100 atm.). At lower reduced temperatures, $|\mathscr{B}|$ will presumably be larger, but the maximum attainable pressures will be smaller. This paper reports new measurements of ${}_TP$ for some highly polar vapours in the pressure range 0—2 atm.

TABLE 1.

Previous values of dielectric virial coefficients.

Substance	Temp.	$\mathscr{A}$(cm.^{3} mole^{-1})	$\mathscr{B}$(cm.^{6} mole^{-2})	Ref.
He	23°	0·522	−0·5	5
Ar	−31	4·14	0·6	5
Ar	33	4·14	1·0	5
N_2	−31	4·39	4·2	5
N_2	71	4·39	0·0	5
CH_4	−31	6·52	9·0	5
CO_2	22	7·35	64 ± 10	6
C_2H_4	50	10·69	25 ± 7	7
NH_3	100	41·35	440	8
CH_3F	50	70	−600	9

EXPERIMENTAL

To measure ${}_TP$, both ε and V_m must be determined. ε has frequently been obtained, as in this investigation, by determining the change in capacity of a condenser when a gas is admitted to it, a precision variable condenser being used to keep the total capacity constant.

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[5] Johnston, Oudemans, and Cole, *J. Chem. Phys.*, 1960, **33**, 1310.

[6] Michels and Kleerekoper, *Physica*, 1939, **6**, 586; de Wijn and Heineken, *Physica*, 1959, **25**, 615.

[7] David, Hamann, and Pearse, *J. Chem. Phys.*, 1951, **19**, 1491.

[8] Keyes and Kirkwood, *Phys. Rev.*, 1930, **36**, 1570.

[9] David, Hamann, and Pearse, *J. Chem. Phys.*, 1952, **20**, 969.

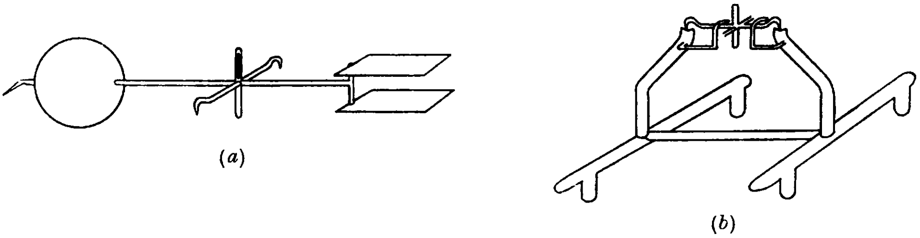
[10] Buckingham and Pople, *Trans. Faraday Soc.*, 1955, **51**, 1029.

In earlier work, V_{m} was found through p (and T), and the ideal-gas equation $pV_{\mathrm{m}} = \boldsymbol{R}T$, or, when imperfections were being studied, eqn. (4). From eqns. (1) and (4) we have

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{\boldsymbol{R}T}{p} = \mathcal{A} + \frac{p}{\boldsymbol{R}T}(\mathcal{B} - \mathcal{A}B) + O(p^2), \qquad (9)$$

and the initial slope of the experimental quantity $\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{\boldsymbol{R}T}{p}$ as a function of $p/\boldsymbol{R}T$ is $\mathcal{B} - \mathcal{A}B$, while the desired quantity is $\mathcal{B}$. For methyl fluoride at 50°, $\mathcal{B}/\mathcal{A} = -8$ cm.^{3} mole^{-1}, while $B = -171$ cm.^{3} mole^{-1}.[11] To determine $\mathcal{B}$ by that means to an accuracy of 10%, B must be known to better than 0·5%; an uncertainty of 0·1° in the temperature at which ε is measured would lead to an error of 10% in $\mathcal{B}$. These difficulties are avoided in the present experiments by using a precision gas-density balance alongside the gas condenser, so ε and V_{m} are determined directly at the same temperature.

FIG. 1. The gas density balance and its support.


(*a*)
(*b*)

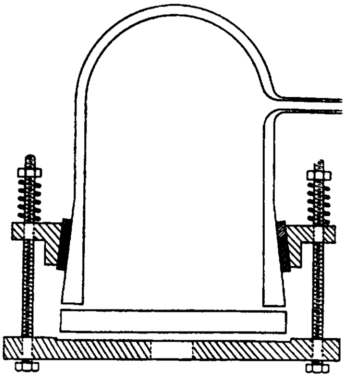


FIG. 2. The density-balance container.

Unhatched = glass,
Wide hatching = steel,
Close hatching = asbestos.

The Density Balance.—As a null instrument, the gas-density balance has been successfully used for measurements of high precision; sensitivity to a change smaller than that detectable with a mercury manometer has been claimed for the most refined balances.[12, 13] The balance described below measured densities from 0 to 0·01 g. cm.$^{-3}$ with an accuracy of better than 0·1% at the highest densities. It is shown, with its glass support, in Fig. 1. The movable parts were made from silica, and inaccuracies arising from adsorption were minimized by making the moment of the surface area of the plates equal to that of the bulb. The restoring torque was supplied by the extra weight of the solid central rod below the pivots relative to that of the hollow one above. The pivots were two silica points, supported by hemispherical cups; two small arms prevented the balance points being thrown out of the cups. The overall length of the beam was 13·5 cm., and the bulb diameter 3·1 cm. The period of a swing was 3·0 sec., and the plates were horizontal to assist damping. In a vacuum, the beam was at 27° below the horizontal and it could rise to 45° above it, yielding a full-scale vertical pointer movement of 10 cm. The pointer's position was measured with a cathetometer reading to 0·001 cm. A reading was made by determining the pressure of a standard gas (carbon dioxide or sulphur

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[11] Hamann and Pearse, *Trans. Faraday Soc.*, 1952, **48**, 101.
[12] Whytlaw-Gray, *Quart. Rev.*, 1950, **4**, 153.
[13] Lambert and Phillips, *Phil. Trans.*, 1950, *A*, **242**, 415.

hexafluoride) required to produce the same deflection; this was always done immediately after an observation on an unknown value, thereby eliminating errors arising from temperature fluctuations or from a movement of the balance points in their supporting cups.

The Density-balance Container.—The housing for the density balance was made from " Pyrex Pipeline " of 4 in. internal diameter and a Pyrex optical window ¼ in. thick. A ⅛ in. gasket-ring of polytetrafluoroethylene separated the two, and was squeezed by six spring-loaded bolts passing through a steel backing-plate. The container withstood the pressure of 3 atm. of air inside it at temperatures up to 250° without significant leakage. The backing-plate had a rectangular slit through which the balance pointer was observed.

The Gas Cell.—This has already been described.[14] It consisted of three coaxial platinum cylinders, the inner- and the outer-most one being earthed, all mounted inside a glass tube through which tungsten leads passed. The capacity of the evacuated cell at room temperature was 142 $\mu\mu$F.

The Precision Condenser.—This was of the stepped-rod type used by Le Fèvre *at al.*[15] in studies of gas dipole moments. The rod and cylinder were of stainless steel and were accurately machined so that their surfaces had no humps higher than 0·0001 in. and their diameters were constant to 0·0005 in. The rod was pushed (not turned) by a micrometer screw, contact being made through a steel ball to reduce friction. The rod was kept in contact with the micrometer by the tension in a Nylon wire supporting a weight over a pulley. The two bearings were of brass and were V-shaped. The live cylinder through which the rod moves was contained within an earthed cylindrical shield fixed to the steel base plate of the condenser. The live cylinder was supported at both ends by three glass rods mounted in brass screws threaded in the earthed outer cylinder. The glass rods fitted into small countersunk holes symmetrically cut in the outer surface of the live cylinder, whose position could easily be adjusted with the screws; the linear dependence of the capacity change on the micrometer setting was established by using the heterodyne beat oscillator (see below). End-effects were reduced by guard rings at both ends of the earthed shield. The lead from the live cylinder passed through a glass bush mounted on the earthed tube, and the rod and cylinders were enclosed in a Perspex dust cover.

The micrometer had a 5 cm. movement produced by 100 turns of the drum which had 250 divisions; each drum division could be subdivided by eye to ¼ division. The stepped-rod had a diameter of 0·6854 in. for 5·3 in., and 0·4354 in. for 6·2 in., and the live cylinder had an internal diameter of 1·0039 in. and was 7 in. long. The base-plate was 17 × 4 × 0·7 in., so the whole condenser was large and heavy. The dimensions were calculated to give a full-scale capacity change of 4 $\mu\mu$F, easily readable on the micrometer to 10^{-4} $\mu\mu$F.

The Oscillators and Detectors.—The capacity change ΔC arising from the admission of a vapour to the gas cell was measured by incorporating the precision variable condenser in parallel with the gas cell into an LC oscillator. This transitron oscillator was similar to that described by Hill,[14] but incorporated a number of modifications aimed at improving the frequency stability. The circuits of the oscillator and its buffer (whose purpose is to overcome any tendency the variable oscillator may have to be " pulled " by the fixed-frequency reference oscillator when their frequency difference is small) are shown in Fig. 3. The valve filaments were supplied from a large 6-v accumulator, and the high tension from a Solartron type AS 517 unit giving a very stable 250 v source, which was used (with a thermally insulated resistor) to provide both the required high voltages.

As described by Hill,[14] the oscillator was compared with an identical unit supplied from the same voltage sources, and the frequency difference determined by beating it against a fixed audio-oscillator, the Lissajou figures being observed on an oscilloscope. By returning to the same figure, it was possible to tune the variable oscillator to the same frequency. However, the accuracy of this method depended on the stability of the reference radio- and audio-frequencies. It was used for the calibration and alignment of the precision variable condenser, for by observing the movement of the micrometer required to reproduce a given Lissajou figure, the change in setting Δl for a fixed capacity change ΔC could be determined over different parts of the micrometer scale. For the determination of ε, a more accurate approach was used, involving direct comparison of the frequency of the variable oscillator with that of a harmonic oscillator (Fig. 4), whose frequency was locked by a 100 kc. sec.$^{-1}$ signal (stable to 1 part in 10^8) from a thermostat-controlled crystal; the harmonic at 500 kc. sec.$^{-1}$ was selected and used as

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[14] Coop and Sutton, *J.*, 1938, 1269; R. A. W. Hill, D.Phil. Thesis, Oxford, 1949.

[15] Le Fèvre, Ross, and Smythe, *J.*, 1950, 276.

the reference. This beat directly against the variable oscillator, and a microammeter served as a detector. At zero beat, the ammeter needle was stationary, and for a beat of 1 cycle sec.$^{-1}$ it made one oscillation per sec. This was highly sensitive, and frequency differences of 0·02 cycle sec.$^{-1}$ could be detected; no tendency to " pull " the variable oscillator was noticed, even at frequency differences as small as 0·02 cycle sec.$^{-1}$, so the buffer in Fig. 4, with a transformer ratio of 100 : 1, was satisfactory. The beat-detector circuit is shown in Fig. 5. The oscillators and the precision condenser were housed in a large, thermally insulated and electrically screened box; the micrometer was turned by a shaft connected to a geared wheel outside the box, and read through a double window in the top of the box. The frequency drift of the variable oscillator was rarely worse than $\frac{1}{4}$ cycle sec.$^{-1}$ in 5 min.

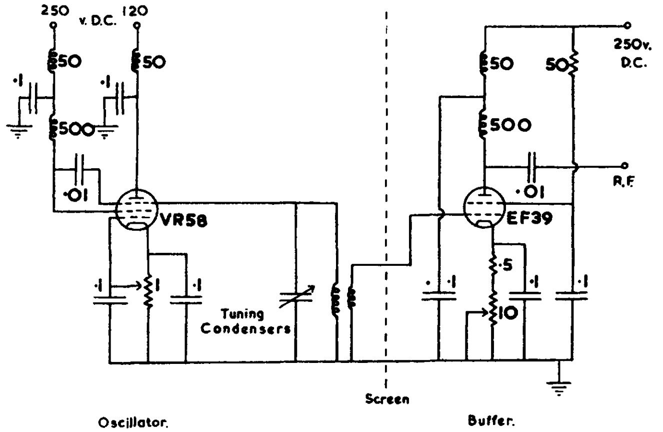

FIG. 3. Radio-frequency oscillator and buffer.
Units: R in KΩ; C in μF; L in mH.

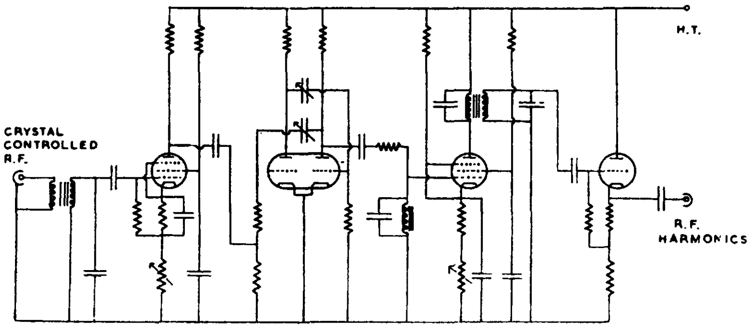

FIG. 4. The crystal-controlled harmonic oscillator.

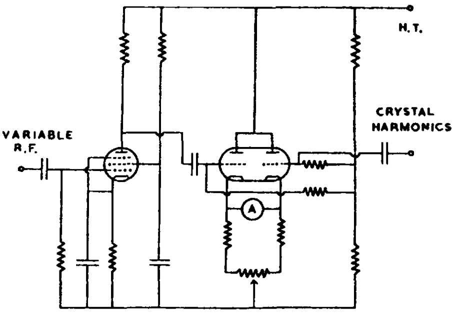

FIG 5. The zero-beat detector.

The Constant-temperature Vapour Bath.—The problem of producing constant temperatures up to 250° was solved by using a vapour bath, containing a double window of optical glass through which the density-balance pointer could be seen. The gas cell and the density balance were placed at approximately symmetrical positions inside the bath. The boiler, which was detachable from the bath, was electrically heated, and the vapour condensed at the top and returned to the bottom of the bath. The lid, window, and boiler were attached to the brass bath by steel bolts with asbestos–graphite gaskets, and as the temperature rose there was a tightening, so that vapour leaks were not troublesome. The glass leads were taken through the lid with polytetrafluoroethylene washers, and the whole bath (except the window) was well lagged on its outer surface. The liquids used were benzene (80°), methylcyclohexane (100°), chlorobenzene (131°), and cyclohexanol (160°).

The Gas Line.—Pumping was by a mercury diffusion pump backed by a rotary pump. Substances were introduced into traps by condensation with liquid air. Polar liquids were then distilled, through P_2O_5, first and last fractions being rejected. The standard gases (carbon dioxide and sulphur hexafluoride) were purified by subliming them several times over P_2O_5. The gas line to the vapour bath could be heated by nichrome wire fed by a variable voltage. Taps subjected to pressures above 1 atm. were spring-loaded, and the high temperature taps lubricated with " Kel-F " grease.

The manometer tube had a bore of 13 mm., and one limb was either evacuated or opened to the atmosphere for pressure measurements from 1 to $2\frac{1}{4}$ atm. The mercury level was observed through a microscope attached to a 1 m. cathetometer reading to 0·001 cm.

Procedure.—After the temperature inside the vapour bath had become steady, the vacuum reading of the precision condenser was recorded. Vapour was then admitted to the apparatus and as soon as equilibrium had been reached (that is, after a few minutes) the precision condenser was adjusted to give a zero beat frequency on the microammeter detector, and the density balance position was noted. The apparatus was then slowly evacuated and the precision condenser reading again found. Next, standard gas was sublimed slowly into the apparatus to give a density slightly greater than that of the vapour. The balance pointer was allowed to come to rest and the density then adjusted, by means of a capillary, until the pointer returned to its original position. The pressure of the standard gas was noted. The precision condenser was read before and immediately after evacuation of the standard to give a calibration point.

Errors.—Pressures are quoted in cm. Hg at 0°, and are accurate to 0·002 cm. Small corrections were applied because of the meniscus [16] and the thermal expansion of mercury and the brass cathetometer scale.

The temperature of the vapour bath was observed for each measurement of ε and V_m. Four mercury-in-glass thermometers were used to cover the range 80—160°; they were immersed to a definite depth in the bath, and had been compared with thermometers calibrated by the National Physical Laboratory. The maximum error is probably 0·05°. Adjustments to the final $_TP$ values were made when the temperature changed slightly during a run.

The density of the unknown vapour is equal to that of the standard gas for the same deflection of the density balance, so the molar volume V_X of a substance of molecular weight M_X is related to that of the standard (subscript s) by [see eqn. (4)]

$$V_X = \frac{M_X}{M_s} \cdot V_s = \frac{M_X}{M_s}\left\{\frac{\mathbf{R}T}{p_s} + B_s + O(p_s)\right\}. \qquad (10)$$

The required values of B_s for carbon dioxide and sulphur hexafluoride were obtained from the data of MacCormack and Schneider.[17] The reproducibility of the setting of the density balance was found to be unsatisfactory below about 3×10^{-4} g. cm.$^{-3}$ (0·2 atm. of carbon dioxide), but at higher densities the setting was accurate within 0·1%, provided the balance was not subjected to shock. (The need for care in avoiding mechanical shock and sudden draughts might be overcome by replacing the point-and-cup supports by a horizontal quartz fibre suspension; this would also render the restoring rods unnecessary.)

The main cause of error in the dielectric constant is frequency drift in the variable oscillator. This is normally stable to better than $\frac{1}{4}$ cycle sec.$^{-1}$ in the time required for two successive condenser readings. For an operating frequency of 500 kc. sec.$^{-1}$ and when half the total capacity of the oscillator is supplied by the gas cell, this drift leads to an error of 2×10^{-6} in $(\varepsilon - 1)$. For 1·4 atm. of carbon dioxide, or 0·04 atm. of acetonitrile, at 100°, $(\varepsilon - 1) = 1000 \times 10^{-6}$, and this corresponds to approximately three turns of the micrometer drum;

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[16] Cawood and Patterson, *Trans. Faraday Soc.*, 1933, **29**, 514.

[17] MacCormack and Schneider, *J. Chem. Phys.*, 1950, **18**, 1269; 1951, **19**, 845.

thus the effect of the error in reading the micrometer is small compared with that of the frequency drift. At each temperature, a "calibration constant," f, was obtained (by using carbon dioxide or sulphur hexafluoride), where $\varepsilon - 1 = f\Delta l$, Δl being the movement (in cm.) of the precision condenser. It has been found that $f = 5{\cdot}5514 \times 10^{-3}(1 - 48{\cdot}83 \times 10^{-6}t)$ cm.$^{-1}$, where t is the temperature in °c. The uncertainty in f is about 0·1% at the highest temperatures, and considerably less at lower temperatures.

At the highest densities, the absolute error in $_TP$ is of the order of 0·2% (half of which is due to uncertainties in the density and half to the error in f), but at lower densities it is larger. However, the relative errors important for the determination of $\mathscr{B}$ are about half of these, and arise chiefly from the uncertainty in V_{m}. At very low densities, direct measurement of the pressure of the vapour becomes possible and at pressures of about 5 cm. Hg the error in $_TP$ for acetonitrile is only about 0·1%.

For calibration, it was assumed that $\mathscr{A}$ for carbon dioxide is 7·35 cm.^{3} mole^{-1},[18] and all our measured values of $_TP$ are proportional to this number. We have found that for sulphur hexafluoride $\mathscr{A} = 16{\cdot}41 \pm 0{\cdot}02$ cm.^{3} mole^{-1}.

Materials.—Substances were purified immediately before use, as indicated above, and rejected immediately afterwards.

Sulphur hexafluoride, supplied in a cylinder by Imperial Chemical Industries Limited, contained $H_2O < 1$, $SF_4 < 4$, and $S_2F_{10} < 1$ p.p.m.

Acetonitrile, supplied by B.D.H., was dried ($CaCl_2$, then KOH) and distilled; a middle fraction of b. p. 81·1°/75 cm. was collected.

Arsenic trifluoride was prepared by warming a mixture of calcium fluoride and arsenic trioxide with concentrated sulphuric acid. It was distilled in dry nitrogen and stored over sodium fluoride. A middle fraction of b. p. 57·7°/77 cm. was collected.

Fluoroform was obtained from Imperial Chemical Industries Limited as "Arcton 1."

Chloroform, supplied by B.D.H., was distilled over P_2O_5, a fraction boiling at 61·1°/75·4 cm. being collected.

RESULTS AND DISCUSSION

(a) *Sulphur Hexafluoride.*—The values of $\mathscr{A}$ in Table 2 are independent of temperature, confirming the non-polarity of sulphur hexafluoride; alternatively, the constancy of

TABLE 2.

Measurements on SF_6.

Temp.	p (cm. Hg)	$10^6(\varepsilon - 1)$	$_TP$ (cm.^{3} mole^{-1})	$\mathscr{A}$ (cm.^{3} mole^{-1})
80·69°	87·255	1962·9	16·42	16·42 ± 0·01
($B = -182$ cm.^{3} mole^{-1})	90·521	2034·2	16·39	
	75·937	1711·3	16·46	
	75·255	1691·9	16·42	
	75·834	1703·5	16·41	
	76·631	1723·1	16·42	
100·35°	71·518	1518·0	16·39	16·41 ± 0·01
($B = -162$)	79·431	1692·4	16·44	
	79·057	1681·1	16·41	
	76·186	1618·0	16·40	
	75·884	1611·1	16·39	
	73·801	1573·7	16·46	
	74·381	1580·0	16·40	
	75·515	1606·4	16·42	
131·78°	86·369	1693·0	16·42	16·41 ± 0·004
($B = -134$)	82·436	1615·1	16·41	
	82·998	1626·4	16·41	
	82·401	1614·3	16·41	
	81·203	1590·1	16·40	
	84·370	1653·1	16·41	

The errors quoted are standard deviations from the mean, calculated by the method of least squares. No attempt was made to determine $\mathscr{B}$.

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[18] Maryott and Buckley, "Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," Nat. Bureau Standards, Washington, 1953, Circular 537.

$\mathscr{A}$ can be considered as a check on the carbon dioxide calibration. Previous values of $\mathscr{A}$ for this fluoride are 16·5, 16·8, and 15·7 cm.^{3} mole^{-1},[18] in agreement with our mean value of 16·41 ± 0·02 cm.^{3} mole^{-1} (relative to $\mathscr{A}_{CO_2} = 7{\cdot}35$), where the stated error includes that arising from the calibration of the condenser. Sulphur hexafluoride, which is easy to purify and to handle, with its large polarizability, might prove to be a better standard than carbon dioxide for future gas dielectric constant measurements.

(b) *Acetonitrile.*—The saturated vapour pressure of this substance at room temperature (0·1 atm.) is sufficiently high to enable accurate values of $_TP$ to be obtained by direct measurement of p with the manometer, in the low-pressure region where the density balance is insensitive. The values of V_m^{-1} less than $0{\cdot}3 \times 10^{-5}$ cm.$^{-3}$ were obtained by measurements of p and the use of the second virial coefficients[19] listed in the first column of Table 3. Fig. 6 illustrates the dependence of $_TP$ on $1/V_m$ at four temperatures.

" Least squares " fitting of the values of $_TP$ to curves of the type of eqn. (1) (stopping at the third dielectric virial coefficient for $T = 81°$, 100°, and 132°, and at the second for the highest temperature) lead to the following results:

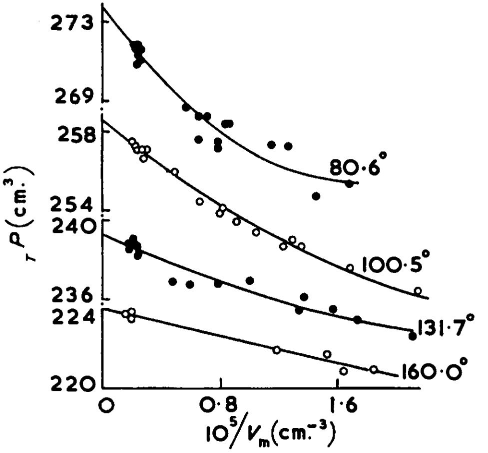

FIG. 6. The temperature and density dependence of the total polarization of $CH_3{\cdot}CN$.

$T = 80{\cdot}64°$, $_TP = 273{\cdot}68 - 10{\cdot}13 \times 10^5 V_m^{-1} + 2{\cdot}92 \times 10^{10} V_m^{-2}$, $\mathscr{A} = 273{\cdot}68 \pm 0{\cdot}33$ cm.^{3} mole^{-1}, $\mathscr{B} = -10{\cdot}1 \pm 1{\cdot}1 \times 10^5$ cm.^{6} mole^{-2}.

$T = 100{\cdot}48°$, $_TP = 258{\cdot}50 - 6{\cdot}132 \times 10^5 V_m^{-1} + 0{\cdot}955 \times 10^{10} V_m^{-2}$, $\mathscr{A} = 258{\cdot}50 \pm 0{\cdot}17$ cm.^{3} mole^{-1}, $\mathscr{B} = -6{\cdot}13 \pm 0{\cdot}34 \times 10^5$ cm.^{6} mole^{-2}.

$T = 131{\cdot}69°$, $_TP = 239{\cdot}26 - 3{\cdot}43 \times 10^5 V_m^{-1} + 0{\cdot}54 \times 10^{10} V_m^{-2}$, $\mathscr{A} = 239{\cdot}26 \pm 0{\cdot}15$ cm.^{3} mole^{-1}, $\mathscr{B} = -3{\cdot}43 \pm 0{\cdot}58 \times 10^5$ cm.^{6} mole^{-2}.

$T = 160{\cdot}00°$, $_TP = 224{\cdot}01 - 1{\cdot}718 \times 10^5 V_m^{-1}$, $\mathscr{A} = 224{\cdot}01 \pm 0{\cdot}11$ cm.^{3} mole^{-1}, $\mathscr{B} = -1{\cdot}72 \pm 0{\cdot}11$ cm.^{6} mole^2.

Fitting the four values of $\mathscr{A}$ to eqn. (2) leads to $\mathscr{A} = 3{\cdot}304 + 95{,}550/T$, whence $\alpha = 1{\cdot}3 \pm 0{\cdot}5 \times 10^{-24}$ cm.^{3}, $\mu = 3{\cdot}96 \pm 0{\cdot}01$D. The molar refraction $[R]_D$ for the sodium D line is[18] 11·1 cm.^{3}, so there is little doubt that our α is too small. Because of the large extrapolation to infinite temperature, the error in α is large, and a small error in the carbon dioxide calibration would seriously affect α (but not μ). The dipole moment agrees well with the 3·96 D of Groves and Sugden[20,18] and the 3·92 ± 0·06 D obtained through Stark-effect measurements.[21] If the distortion polarization, $_DP$, is equal to

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[19] Lambert, Roberts, Rowlinson, and Wilkinson, *Proc. Roy. Soc.*, 1949, *A*, **196**, 113; McGlashan, " Tables of Second and Third Virial Coefficients of Gases," University of Reading, 1955.

[20] Groves and Sugden, *J.*, 1937, 158.

[21] Ghosh, Trambarulo, and Gordy, *J. Chem. Phys.*, 1953, **21**, 308; *Phys. Rev.*, 1952, **87**, 172.

TABLE 3.

Measurements on $CH_3{\cdot}CN$.

Temp.	$10^5 V_m^{-1}$ (cm.$^{-3}$)	$10^6(\varepsilon - 1)$	${}_TP$ (cm.^{3} mole^{-1})	$10^5 V_m^{-1}$ (cm.$^{-3}$)	$10^6(\varepsilon - 1)$	${}_TP$ (cm.^{3} mole^{-1})
80·64°	0·2196	1791·7	271·84	0·2696	2193·6	271·04
($B = -2420$	0·2338	1906·1	271·62	0·5670	4576·6	268·66
cm.^{3} mole^{-1})	0·2338	1907·8	271·85	0·6520	5256·0	268·24
	0·2384	1938·4	270·85	0·6575	5277·2	267·06
	0·2385	1946·5	271·82	0·7053	5685·2	268·20
	0·2397	1952·3	271·27	0·7868	6306·9	266·64
	0·2407	1960·3	271·34	0·7868	6313·6	266·91
	0·2463	2009·8	271·82	0·8381	6748·4	267·81
	0·2520	2049·7	270·94	0·8608	6933·2	267·85
	0·2537	2065·7	271·26	1·1447	9188·7	266·75
	0·2564	2086·2	271·30	1·2603	10,116·3	266·66
	0·2567	2090·2	271·21	1·4505	11,538·6	264·16
	0·2681	2185·9	271·57	1·6759	13,371·6	264·78
100·48°	0·2056	1588·6	257·44	0·8146	6221·6	254·07
($B = -1880$)	0·2225	1718·4	257·23	0·9079	6918·4	253·42
	0·2365	1824·8	257·02	1·0471	7964·7	252·87
	0·2661	2053·3	257·01	1·2289	9325·2	252·15
	0·2695	2079·5	257·06	1·2914	9813·2	252·48
	0·2805	2161·3	256·63	1·3522	10,262·4	252·13
	0·2805	2164·3	256·98	1·6824	12,724·5	251·05
	0·3030	2338·6	257·08	2·1463	16,177·4	249·90
	0·4883	3753·6	255·91	2·3228	17,529·5	250·09
	0·6648	5082·0	254·40	2·7930	20,946·5	248·26
	0·7985	6092·6	253·82			
131·69°	0·1785	1279·2	238·76	0·2464	1761·8	238·25
($B = -1410$)	0·1832	1311·2	238·50	0·2511	1796·6	238·32
	0·1870	1338·5	238·49	0·4747	3377·3	236·86
	0·1942	1391·4	238·71	0·5895	4192·4	236·70
	0·2129	1527·1	238·03	0·7822	5565·3	236·73
	0·2172	1556·4	238·69	0·9995	7119·4	236·88
	0·2190	1569·4	238·80	1·3399	9494·4	235·46
	0·2299	1648·3	238·85	1·3708	9740·9	236·09
	0·2339	1674·7	238·56	1·5624	11,078·3	235·44
	0·2343	1677·3	238·54	1·7310	12,251·0	234·95
	0·2403	1721·8	238·68	2·1053	14,865·3	234·14
	0·2438	1743·1	238·22			
160·00°	0·1550	1040·6	223·72	1·1802	7877·8	221·93
($B = -1220$)	0·1855	1246·4	223·83	1·5218	10,156·8	221·73
	0·1880	1260·8	223·51	1·6365	10,880·1	220·82
	0·1924	1290·8	223·55	1·8395	12,241·7	220·93
	0·1949	1309·2	223·85			

$[R]_D = 11{\cdot}1$ cm.^{3}, our values for A yield a mean μ of 3·90 D. Groves and Sugden[20] did not extrapolate their polarization measurements to $p = 0$, and since they worked in the pressure range from 6 to 10 cm. Hg, the $\mathscr{B}$ correction would add about 3 cm.^{3} to their $\mathscr{A}$ at 80° and about 0·5 cm.^{3} at 190°. These additions would lead to a small increase in μ.

A graph of log $|\mathscr{B}|$ against $1/T$ is shown in Fig. 7, and the slope yields, through eqn. (7), $\Delta H_0 = -6{\cdot}8$ kcal. mole^{-1}, which is substantially larger than the value of $-3{\cdot}8$ kcal. mole^{-1} at 100° obtained from a plot of log $(-B/T)$ against $1/T$. Fig. 8 shows how $-\Delta H_0$ decreases with rising temperature, which is to be expected for a loosely bound dimer, whereas eqn. (6) shows that $\langle\mu_{12}{}^2\rangle^{\frac{1}{2}}$ increases from 2·67 D at 80° to 4·62 D at 160°. The increasing polarity of the dimer offsets its decreasing stability as the temperature rises, producing an approximately linear graph in Fig. 7. These trends in ΔH_0 and $\langle\mu_{12}{}^2\rangle^{\frac{1}{2}}$ are to be expected for a weakly bound dimer.

(c) *Arsenic Trifluoride.*—The molecular weight and saturated vapour pressure of arsenic trifluoride are sufficiently large to enable accurate measurements of p and V_m to be made. Thus B, as well as ${}_TP$, has been measured. The results are in Table 4 and Figs. 9 and 10.

TABLE 4.

Measurements on AsF_3.

Temp.	p (cm. Hg)	$10^5V_m^{-1}$ (cm.$^{-3}$)	$10^6(\varepsilon-1)$	$_TP$ (cm.^{3} mole^{-1})	$10^5V_m^{-1}$ (cm.$^{-3}$)	$10^6(\varepsilon-1)$	$_TP$ (cm.^{3} mole^{-1})
80·61°	9·557	0·4345	1657·5	127·08	1·0729	4116·3	127·71
	11·294	0·5137	1964·2	127·38	1·1844	4537·3	127·50
	11·514	0·5239	2001·1	127·24	1·4470	5529·2	127·14
	13·458	0·6130	2333·1	126·78	1·4529	5533·2	126·71
	14·164	0·6451	2461·9	127·11	1·7200	6575·4	127·15
		0·5186	1980·4	127·20	2·2323	8530·6	127·02
		0·6811	2602·1	127·24	2·5777	9847·0	126·92
		0·7287	2775·7	126·86	3·1433	12,007·7	126·83
		0·8837	3374·5	127·14	3·2363	12,393·0	127·12
159·88°	11·112	0·4125	1317·0	106·37	0·7066	2257·6	106·42
	12·228	0·4521	1449·4	106·81	0·8806	2804·0	106·04
	12·673	0·4711	1502·4	106·25			
	14·354	0·5310	1702·2	106·80			

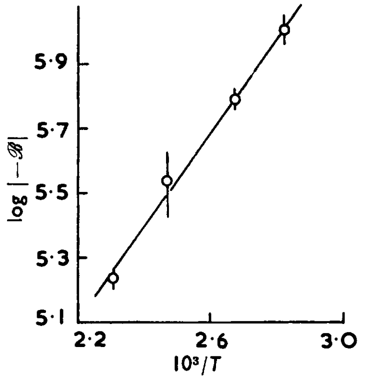

FIG. 7. The dependence of log $|\mathscr{B}|$ on $1/T$ for $CH_3{\cdot}CN$.

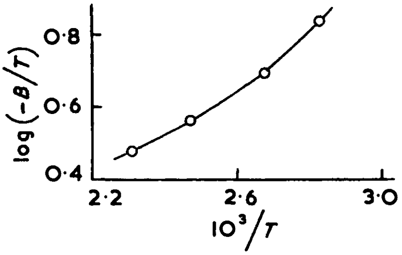

FIG. 8. The dependence of $\log(-B/T)$ on $1/T$ for $CH_3{\cdot}CN$.

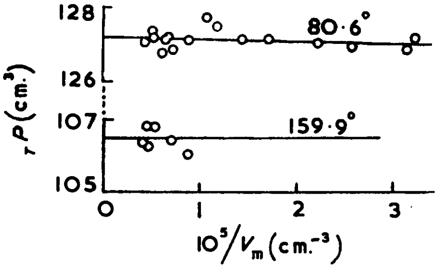

FIG. 9. The density dependence of the total polarization of AsF_3.

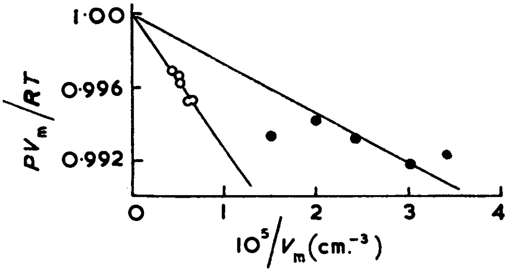

FIG. 10. The density dependence of pV_m/RT for AsF_3 and CHF_3 at 80°.

● CHF_3 at 80·5°. ○ AsF_3 at 80·6°.

$T = 80{\cdot}61°$, $_TP = 127{\cdot}22 - 7900V_m^{-1}$, $\mathscr{A} = 127{\cdot}22 \pm 0{\cdot}10$ cm.^{3} mole^{-1}, $\mathscr{B} = -7900 \pm 7000$ cm.^{6} mole^{-2}, $B = -730 \pm 30$ cm.^{3} mole^{-1}.

$T = 159{\cdot}88°$, $_TP = \mathscr{A} = 106{\cdot}45 \pm 0{\cdot}13$ cm.^{3} mole^{-1}.

Hence $\alpha = 5{\cdot}45 \times 10^{-24}$ cm.^{3}, $\mu = 2{\cdot}57 \pm 0{\cdot}02$ D. This dipole moment is substantially less than the value $2{\cdot}815 \pm 0{\cdot}025$ D obtained [22] from the Stark effect on the microwave spectrum; the Stark energy was comparable with that of the nuclear quadrupoles, so the

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[22] Shulman, Dailey, and Townes, *Phys. Rev.*, 1950, **78**, 145.

Stark splittings were not of the simple first-order type normally encountered in symmetric tops. However, we have verified the difficult quantum-mechanical analysis, so the disagreement is puzzling, and both the dielectric constant and the microwave experiments should now be repeated. If the disagreement turns out to be real, the two sets of data might be used jointly as evidence for the effect of an electric field on the electric field-gradient at the arsenic nucleus—this dependence is presumably a first-order one.

(d) *Fluoroform.*—Since fluoroform is a gas at room temperature and pressure, measurements of p, V_m, and $(\varepsilon - 1)$ were made (see Table 5), leading to $\mathscr{A}$, $\mathscr{B}$, and B. The precision of low-pressure readings enabled an accurate value of $\mathscr{A}$ to be found at 80·5° by means of eqn. (9), *viz.*, $\mathscr{A} = 55{\cdot}30 \pm 0{\cdot}03$ cm.³ mole⁻¹, and this was then used with the polarizations in Table 5 to obtain $\mathscr{B}$. No attempt was made to evaluate $\mathscr{B}$ at 160·6°, the values of $_TP$ merely being averaged to give $\mathscr{A}$. The results are plotted in Figs. 10 and 11.

TABLE 5.

Measurements on CHF_3.

Temp.	p (cm. Hg)	$10^5 V_m^{-1}$ (cm.$^{-3}$)	$10^6(\varepsilon - 1)$	$_TP$ (cm.^{3} mole^{-1})	p (cm. Hg)	$10^5 V_m^{-1}$ (cm.$^{-3}$)	$10^6(\varepsilon - 1)$	$_TP$ (cm.^{3} mole^{-1})
80·49°	33·300	1·5201	2513·1	55·06	66·094	3·0218	5001·3	55·08
	44·046	2·0090	3326·3	55·13	74·883	3·4217	5674·3	55·17
	53·412	2·4386	4039·9	55·15				
160·57°	34·971	1·2951	1821·4	46·85	60·944	2·2609	3158·3	46·52
	41·620	1·5458	2156·6	46·47	72·083	2·6739	3748·5	46·67
	49·219	1·8277	2556·3	46·58				

$T = 80{\cdot}49°$, $_TP = 55{\cdot}30 - 6500 V_m^{-1}$, $\mathscr{A} = 55{\cdot}30 \pm 0{\cdot}03$ cm.³ mole⁻¹, $\mathscr{B} = -6500 \pm 1400$ cm.⁶ mole⁻², $B = -273 \pm 30$ cm.³ mole⁻¹.

$T = 160{\cdot}57°$, $_TP = \mathscr{A} = 46{\cdot}62 \pm 0{\cdot}07$ cm.³ mole⁻¹.

Hence $\alpha = 3{\cdot}28 \times 10^{-24}$ cm.³, $\mu = 1{\cdot}65 \pm 0{\cdot}01$ D. Previous values of μ are $1{\cdot}64 \pm 0{\cdot}02$ D from microwave measurements [21] and 1·60 D from ε.[18]

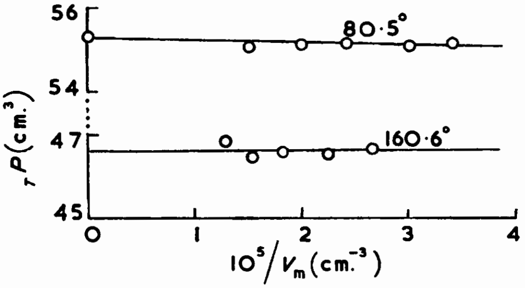


FIG. 11. The density dependence of the total polarization of CHF_3.

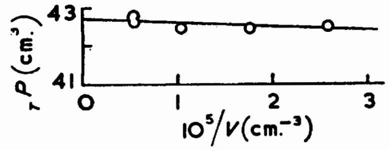


FIG. 12. The density dependence of the total polarization of $CHCl_3$ at 79·7°.

(e) *Chloroform.*—$_TP$ was determined at 80°, by using direct pressure and density measurements at the three lowest densities (see Table 6). The results are plotted in Fig. 12.

TABLE 6.

Measurements on $CHCl_3$.

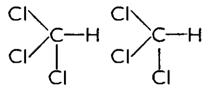
Temp.	p (cm. Hg)	$10^5 V_m^{-1}$ (cm.$^{-3}$)	$10^6(\varepsilon - 1)$	$_TP$ (cm.^{3} mole^{-1})	$10^5 V_m^{-1}$ (cm.$^{-3}$)	$10^6(\varepsilon - 1)$	$_TP$ (cm.^{3} mole^{-1})
79·70°	11·494	0·5235	672·4	42·81	1·0386	1324·7	42·50
	11·892	0·5430	695·4	42·68	1·7638	2251·3	42·51
	12·210	0·5566	715·9	42·86	2·5808	3298·1	42·55

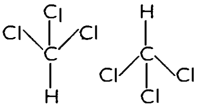
$_TP = 42{\cdot}76 - 10{,}800V_m^{-1}$, $\mathscr{A} = 42{\cdot}76 \pm 0{\cdot}08$ cm.^{3} mole^{-1}, $\mathscr{B} = -11{,}000 \pm 6000$ cm.^{6} mole^{-2}.

If $_DP = 25{\cdot}28$ cm.^{3} mole^{-1},[23] our $\mathscr{A}$ yields $\mu = 1{\cdot}00 \pm 0{\cdot}01$D, in agreement with the accepted value.[18]

The shapes of the arsenic trifluoride, fluoroform, and chloroform molecules are such that we had felt their $\mathscr{B}$s should have been positive, for we believed that arrangements of type (I) would be more stable than those of type (II); but the observed small negative $\mathscr{B}$s favour type (II). Measurements were also attempted on paraldehyde $(CH_3{\cdot}CHO)_3$, because its shape and moment (1·44 D [24]) indicate [2] that it might have a substantial positive $\mathscr{B}$. However, decomposition into acetaldehyde occurred in our apparatus, even at temperatures as low as 79°, in spite of stringent precautions to remove acidic impurities; perhaps the tap greases, or the platinum of the gas cell, catalysed the depolymerization. Our dielectric-constant measurements provided a very sensitive method of detecting depolymerization, for three acetaldehyde molecules contribute much more than one of paraldehyde to $(\varepsilon - 1)$. Decomposition at 79·1° and at 99·3° was slow enough for us to find evidence for a positive $\mathscr{B}$, and $\mathscr{A}$ values of 85 and 82 cm.^{3} mole^{-1}, which are substantially larger than the previously determined values [24] of 80·8 and 78·8 cm.^{3} mole^{-1}; however, decomposition seriously affected the accuracy of our measurements. Possibly 1,3,5-trioxan with its moment of 2 D, or H_2O with its hydrogen bonds, has large positive $\mathscr{B}$s.

(I)





(II)

Our results have shown that highly polar vapours can show substantial deviations from the Clausius–Mossotti formula $_TP = \mathscr{A}$, even at pressures of a few cm. Hg. $\mathscr{B}/\mathscr{A}$ can be comparable to B, and sometimes, as in acetonitrile at low temperatures, can dominate the pressure dependence of $\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{RT}{p}$ [see eqn. (9)]. The simple polar molecules ($CH_3{\cdot}CN$, AsF_3, CHF_3, and $CHCl_3$) all apparently possess short-range intermolecular forces favouring antiparallel dipolar alignments as in (II); measurements of $\mathscr{B}$ at several temperatures provide a method of studying these forces, which are probably dependent upon the repulsions associated with molecular shape.

The authors are grateful to Dr. L. E. Sutton, F.R.S., for many very helpful discussions, and to the Rhodes Trustees for the award of a Scholarship (to R. E. R.)

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[*Received, May* 24*th*, 1961.]

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[23] Maryott, Hobbs, and Gross, *J. Amer. Chem. Soc.*, 1941, **63**, 659.
[24] Le Fèvre, Mulley, and Smythe, *J.*, 1950, 290.