[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Moments and Internal Potential Energies of Two Molecules Containing Movable Dipoles

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The trimethylene chloride molecule, which contains two movable dipoles in the carbon–chlorine bonds, and the 1,1,2,2-tetrachloroethane molecule, which contains two movable pairs of similar dipoles, offer an opportunity for the investigation of intramolecular energy through the effective resultant moments of the dipoles. The moments have, therefore, been determined in the vapor state and examined in the light of the potential energies calculated approximately between the movable parts of the molecules containing dipoles.

Purification of Materials

Trimethylene Chloride.—Material from the Eastman Kodak Company was dried over calcium chloride and distilled; b. p. 120.2° (750 mm.); n^{20}_D 1.44867.

1,1,2,2-Tetrachloroethane.—Material from the Eastman Kodak Company was shaken thoroughly with two small portions of 5% potassium permanganate solution rendered alkaline. It was then washed thoroughly with water, dried over calcium chloride and phosphorus pentoxide and distilled; b. p. 145.2° (748 mm.); n^{20}_D 1.49419.

Experimental Results

The dielectric constants ϵ were determined with the apparatus previously described,[1] trimethylene chloride being measured in a gold–palladium cell, the other in a copper cell. The polarization P was calculated by means of the equation $P = [(\epsilon - 1)/(\epsilon + 2)]\ V$, in which V is the molar volume. From five to eight determinations at each temperature were made over a range of pressures between 760 and 150 mm., and the polarizations were extrapolated to zero pressure to obtain a value P_0 which should be free from error due to deviations from the gas laws. For 1,1,2,2-tetrachloroethane the temperature range of the measurements was so limited by the thermal decomposition of the substance at higher temperatures that the dipole moment was calculated at each temperature by means of the equation $\mu = 0.01273[(P - MR_D)T]^{1/2}$, in which MR_D is the molar refraction for the D sodium line. The same method was used for trimethylene chloride to show the constancy of its moment, but the more accurate equation $P = a + b/T$ was also applied to obtain a more exact value $\mu = 0.01273 \times 10^{-18} b^{1/2}$ given below the other values. The atomic polarization was obtained as $P_A = a - P_E$, the difference between a, the total induced polarization, and P_E, the molar refraction extrapolated to infinite wave length.

TABLE I

POLARIZATIONS AND DIPOLE MOMENTS

T, °K.	P_0	$\mu \times 10^{18}$
Trimethylene chloride		
374.1	98.2	2.09
394.5	94.25	2.09
413.0	91.7	2.10
434.3	88.5	2.10
454.7	85.5	2.09
484.6	82.0	2.10
$a = 27.4$, $P_A = 2.2$, $\mu = 2.07 \times 10^{-18}$		
1,1,2,2-Tetrachloroethane		
401.2	58.8	1.36
417.4	57.4	1.35
436.2	56.6	1.36

Discussion of Results

The data for trimethylene chloride in Table I show a constant moment over a temperature range of 110°. The values calculated at each temperature by subtracting the molar refraction are, of course, slightly higher than the correct value 2.07 obtained by plotting the polarizations against the reciprocals of the temperature, since this latter method shows the existence of a small atomic polarization 2.2. The value 2.07 is lower than that found at 25° in benzene solution, 2.24,[2] and slightly higher than those found for trimethylene bromide, 1.98 at 50° in benzene solution[3] and 2.03 at 50° in heptane solution.[4] Since the same moment values are assigned to the C–Cl and the C–Br dipoles, the values for the chloride and the bromide should be near one another and be more or less similar in any possible variation with temperature.

If a moment of 1.7 is assigned to the C–Cl

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[1] McAlpine and Smyth, THIS JOURNAL, **55**, 453 (1933).

[2] Gross, *Physik. Z.*, **32**, 587 (1931).

[3] Smyth and Walls, THIS JOURNAL, **54**, 2261 (1932).

[4] Smyth and Walls, *J. Chem. Phys.*, **1**, 200 (1932).

dipoles in trimethylene chloride, as seems reasonable[4,5] when the dipoles are separated by the distances between most of their possible positions in this molecule, and if all positions of rotation around the C–C axes are equally probable, the effective moment may be calculated by the equation of Smyth and Walls as $\mu = 1.7\ (2 + 2\cos^3 110°)^{1/2} = 2.36$. However, as was pointed out in the case of trimethylene bromide,[4] the positions of highest resultant moment in which the two chlorine atoms are close to a *cis* position on the inside of the C–C–C angle are made impossible by the repulsive potential between the chlorine atoms unless each carbon valence angle is distorted by a little more than 10°. The energy of rotatory oscillation about the C–C axes is insufficient in most of the molecules to cause so large a distortion.[6] It was pointed out in the case of the trimethylene bromide molecule that the repulsive potential between the halogens fell off with increasing distance until, at a certain distance, it was equal to the van der Waals attractive potential and it was thought that, at slightly greater distances, the van der Waals attraction would compensate the dipole repulsion, giving a position of minimum potential energy about which the dipoles would tend to oscillate. The curve calculated by Lennard-Jones[7] for the potential energy between two argon atoms and applied by him to the calculation of the energy between two bound chlorine atoms[8] indicates that the steric repulsive force and the van der Waals attractive force are equal at a distance of about 3.85 Å. and the maximum resultant attractive energy is about 1.7×10^{-14} erg. As the polarizability of a chlorine atom bound to carbon is 56% larger than that of an argon atom,[9] the attractive force between bound chlorine atoms is presumably larger and the use of the argon potential energy curve merely gives the order of magnitude of the energy involved. A very rough calculation of the distance at which the steric repulsive, the van der Waals attractive and the thermal energies give an approximate equilibrium may be made from the density of liquid chlorine by the method used by Smyth and Walls in the case of bromine.[4] Dipole repulsion would tend to force the chlorines farther apart than the distance 3.3 Å. thus obtained and thermal oscillation would bring the chlorines little nearer than this because of the very rapid rise in the steric repulsive energy with decrease in the distance below this figure as well as the much less rapid rise of the dipole repulsion. This distance of 3.3 Å. between the chlorine atoms corresponds to the position obtained by rotating the chlorines in opposite directions through an angle $\varphi_1 = 50°$ from the impossible position in which the two lie on the inside of the C–C–C angle in the plane of the three carbon atoms. If, as before, the mutual inductive effects between the two dipoles, which vary with φ_1, are disregarded, the moment corresponding to this position in which each of the two dipoles is rotated through an angle $\varphi_1 = 50°$ is calculated to be 2.35, a value practically identical with that previously calculated on the assumption that all values of φ_1 are equally probable. For $\varphi_1 = 0$, the moment calculated is 2.90. However, the repulsive energy makes impossible those positions near $\varphi_1 = 0°$ in which the moment is much, if any, larger than 2.35. As φ_1 for each of the two atoms increases from 50°, the resultant moment falls to zero near $\varphi_1 = 90°$ and rises again, being 1.95 at $\varphi_1 = 180°$.

It is evident that, because of the van der Waals attraction, the potential energy curve should contain two troughs about 2×10^{-14} erg in depth near $\varphi_1 = 50°$ and $\varphi_1 = 310°$. The change in dipole repulsive energy in these regions is not far from kT, which lies between 5.1 and 6.6×10^{-14} erg in the temperature range under investigation. The thermal oscillation may, therefore, overcome the dipole repulsion sufficiently in a large fraction of the molecules to carry the chlorines from a position of minimum potential energy at $\varphi_1 = 180°$ into the troughs at $\varphi_1 = 50°$ and $\varphi_1 = 310°$. Oscillation within these troughs would then give an effective moment somewhat less than 2.35 and varying little with temperature because of the steepness of the curve on the high moment side of the trough, while molecules with energy insufficient to carry their chlorines over the small humps into the troughs may have moments varying from 0 to about 2.0. The moment observed for trimethylene chloride should thus vary little over a 110° range of temperature if a large proportion of the molecules are oscillating in the troughs at $\varphi_1 = 50$ and 310°. Obviously, when the molecule is in solution, the fields of the

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(5) Smyth and Kamerling, THIS JOURNAL, **53**, 2995 (1931).

(6) *Cf.* Stuart, *Phys. Rev.*, **38**, 1327 (1931).

(7) Lennard-Jones, *Proc. Phys. Soc.*, **43**, 475 (1931).

(8) Lennard-Jones and Pike, *Trans. Faraday Soc.*, **30**, 830 (1934).

(9) Smyth, *Phil. Mag.*, **50**, 361 (1925).

surrounding solvent molecules may alter the energies and hence the moments. Solvent apparently diminishes the effect of the two ends of the molecule upon one another as in the case of the ethylene halides[10] and thus raises the moment, as shown by the previously mentioned value 2.24 in benzene solution.[2]

The temperature range over which 1,1,2,2-tetrachloroethane could be measured was so short that the apparent constancy of the three values in Table I cannot be taken as proof of the absence of all variation of moment with temperature. However, the moment variation, if existent at all in this region, is much smaller than that of ethylene chloride, for which interpolation from Zahn's vapor measurements[11] gives 1.37 at 401°K. and 1.43 at 436°K. In calculating the mutual potential energies of the dipoles in ethylene chloride, a moment 1.5 was assigned to the C–Cl dipole.[8,12,13] This is uncertain, but is probably not far from correct and is sufficient for the approximate calculations which can be made. Calculation has shown that two C–Cl dipoles of moment 1.85 attached to the same carbon atom should lower one another's moments by induction about 0.36,[14] which indicates 1.2 as a reasonable value for the C–Cl moment in 1,1,2,2-tetrachloroethane. On the other hand, the moment of methylene chloride is 1.57 and that of ethylidene chloride is 2.05. This increase of 0.5 would probably be canceled in the two halves of the tetrachloroethane molecule, leaving a moment of 1.6 in each half, which corresponds to a C–Cl moment of 1.4. Using this intermediate value for the C–Cl moment and neglecting the variation of inductive effect with rotation around the C–C axis and the increase in the angle caused by repulsion between the chlorines,[15] the resultant moment in each half of the molecule is taken as $m_1 = 1.6$, which makes an angle $\Theta = 127°$ with the C–C line. When substituted in the formula, $\mu = m_1(2 - 2(-\cos\Theta)^2)^{1/2}$,[3] these values give 1.81 as the moment which the $CHCl_2CHCl_2$ molecule would have if all positions of rotation around the C–C line were equally probable.

The dependence of the potential energy between the dipoles in the two halves of the molecule upon the angle φ_1 through which each half has rotated away from the *cis* position where the moment is a maximum may be calculated as in earlier work on ethylene chloride.[13] The potential energy curve thus obtained shows a difference in energy between the *cis* and *trans* positions of 8.6×10^{-14} erg per molecule, very flat maxima appearing approximately at $\varphi_1 = 55°$ and $\varphi_1 = 125°$. The dipole repulsive energy is, however, less important than the steric repulsive energy, which may be estimated approximately by the method of Lennard-Jones.[7] Lennard-Jones has calculated that, for an undistorted ethylene chloride molecule, the difference in potential energy between the *cis* and *trans* positions may be taken to be between 50 and 100×10^{-14} erg, while allowance for distortion lowers the difference to the order of 10 to 20×10^{-14} erg. An equilibrium between the forces other than those of the dipoles should, according to our previous considerations, occur when the two chlorines are about 3.3 Å. apart, which corresponds to a rotation of each through an angle $\varphi_1 = 31°$ out of the *cis* position, the angle between the projections of the C–Cl lines on a plane perpendicular to the C–C axis thus being 62°. In the molecule of 1,1,2,2-tetrachloroethane, the difference in potential energy between the *cis* position ($\varphi_1 = 0°$) and the *trans* ($\varphi_1 = 90°$) should be approximately double that in ethylene dichloride, 20 to 40×10^{-14} erg. As rotation occurs out of the *cis* position, steric repulsion falls rapidly until the equilibrium angle $\varphi_1 = 31°$ is approached. When $\varphi_1 = 30°$ the projection of one C–Cl line upon the plane perpendicular to the C–C axis is midway between those of the two C–Cl lines in the other half of the molecule. At this point, the energy dependent upon φ_1 has dropped practically to that of the dipole repulsion, which is slightly less than 4×10^{-14} erg above that in the *trans* position. With further rotation, the potential energy increases until, when one C–Cl projection coincides with one from the other half of the molecule at $\varphi_1 = 60°$, it is between 10 and 20×10^{-14} erg higher than in the *trans* position ($\varphi_1 = 90°$), to which it drops from this maximum. Of course, the other half of the curve obtained by rotating the *trans* position to obtain the *cis* ($\varphi_1 = 180°$) once more completes its symmetry.

This curve is represented very approximately in Fig. 1, the energy differences $10\text{–}20 \times 10^{-14}$ erg and $20\text{–}40 \times 10^{-14}$ being taken as 15 and 30×10^{-14}, respectively, and added to the dipole

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[10] Stearn and Smyth, THIS JOURNAL, **56**, 1667 (1934).
[11] Zahn, *Phys. Rev.*, **38**, 521 (1931).
[12] Meyer, *Z. physik. Chem.*, **B8**, 27 (1930).
[13] Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).
[14] Smyth and McAlpine, *J. Chem. Phys.*, **1**, 190 (1933).
[15] *Cf.* Bewilogua, *Physik. Z.*, **32**, 265 (1932).

repulsive energies to obtain the maxima. The fact that there is one hydrogen less on each side of the molecule than in ethylene chloride would alter these values by much less than their uncertainty and would not affect the shape of the curve to an important extent. The minima at φ_1 = 30 and 150° are higher than that at φ_1 = 90° by the difference in dipole repulsive energy. The total potential energy between the two halves of the molecule may well be higher than that shown by the curve, which should, nevertheless, be a fairly good approximation to the correct shape.

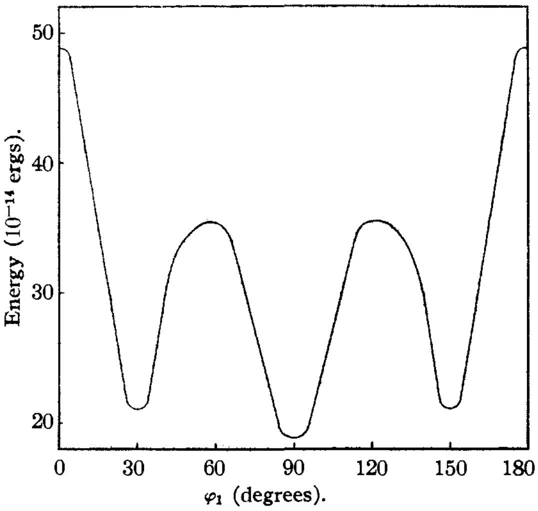

Fig. 1.—Potential energy between the two halves of the 1,1,2,2-tetrachloroethane molecule.

As even the two lower maxima are about $3kT$ above the minima, most of the molecules will be oscillating within a single trough, possessing insufficient oscillational energy to pass over the maxima. The zero energy level in each trough is calculated by representing the curve in the neighborhood of the minimum by the empirical expression, $V = 1/2k\varphi_1^2$, obtaining the value of the constant k by substituting corresponding values of φ_1 and the potential energy V above the minimum, and substituting this value of k in the expression for the frequency, $\nu = (2k/I_1)^{1/2}/2\pi$, where I_1, the moment of inertia of each half of the molecule around the C–C axis, is calculated to be 3.20×10^{-38} g. cm.^{2}. The zero level is thus found to be 0.5×10^{-14} erg above the minima at φ_1 = 30 and 150° and 0.3×10^{-14} erg above the minimum at the *trans* position (φ_1 = 90°). The zero levels in the two troughs at 30 and 150° are found from the curve to be 2.5×10^{-14} erg higher than the zero level at the *trans* position. The substitution of this energy difference E in the Boltzmann distribution equation, $n_1/n_2 = 2e^{-E/kT}$, where the factor 2 takes account of the fact that there are two of the higher energy troughs, gives the ratio of the number of molecules in the two troughs at 30 and 150° to the number in the trough at 90° as 1.27 to 1 at 401°K. and 1.32 to 1 at 436°K.

The average effective moment for the molecules oscillating in the 30 and 150° troughs must be very close to its value for φ_1 = 30 or 150°, that is, μ = 1.92. As the moment between φ_1 = 30° and φ_1 = 150° is lower, rising temperature would tend to lower this value somewhat. The calculation of cos φ_1 for the molecules in the central trough upon which the effective moment of these molecules depends, is so difficult that, in view of the uncertainties in the energy values, it seems best to assign the reasonable value 80° to φ_1. This gives the small value 0.39 for the moment. The square of the moment experimentally observed at 401°K. should then be $\mu^2 = 1.92^2 \times 1.27/2.27 + 0.39^2/2.27 = 2.13$, or $\mu = 1.46$. If the same moments are used at 436°K. the different distribution of the molecules between the troughs gives $\mu = 1.47$. Actually, the 35° rise in temperature must increase the value of $\overline{\cos \varphi_1}$ for the central trough, but a 15% increase in the effective moment of the molecules in this trough from 0.39 to 0.45, an excessive estimate, would raise the total observed moment only to 1.48. In other words, the moment of tetrachloroethane should not increase in the temperature region represented in Table I by more than 0.01 or 0.02, a change no greater than the experimental error. The difference of 0.1 between the calculated and the observed values is less than the error resulting from uncertainty in the value assigned to the C–Cl moment and from neglect of the variation of the inductive effect with φ_1, an effect which should lower the observed moment.

It is evident that both of these molecules here discussed have moments of a predictable magnitude, which might vary with temperature but which should vary less than the moment of ethylene chloride and might easily vary by an amount so small as to escape detection in these measurements. The dipole moment behavior thus gives evidence of the qualitative correctness of our ideas of intramolecular forces and energies in these molecules.

Summary

The dielectric constants of the vapors of trimethylene chloride and 1,1,2,2-tetrachloroethane have been measured and the results used to calculate the dipole moments of the two molecules, which show no variation with temperature over the range studied. Calculation of the internal energies of the molecules shows that the movable dipoles should oscillate in potential energy troughs in such a way as to give effective resultant moments not far from those observed and possessing a variation with temperature considerably smaller than that of ethylene chloride and, possibly, so small as to be undetectable in the temperature region studied.

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Low Temperature Specific Heats. V. The Heat Capacity of Tricalcium Phosphate between 15 and 298°K.

BY J. C. SOUTHARD AND R. T. MILNER

A knowledge of the heat capacity of tricalcium phosphate was desired in connection with some phases of a phosphate investigation. Since no published data could be found, measurements were made on two crystalline forms of this substance in the apparatus previously described.[1]

The data are given in Tables I–III and shown in the figure. All results are expressed in calories per mole degree (one calorie = 4.1833 int. joules = 4.185 absolute joules). The errors are discussed in connection with the description of the apparatus. All weights are corrected to vacuum.

The two forms of tricalcium phosphate have

TABLE I

MOLAL HEAT CAPACITY OF α CALCIUM PHOSPHATE FROM 15 TO 285°K.

T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree
15.27	0.391	107.43	25.79	199.61	43.37
18.03	.733	112.62	26.99	204.01	43.81
22.05	1.307	117.66	28.20	205.00	44.01
26.38	2.082	122.57	29.26	210.37	44.78
30.81	3.085	127.76	30.50	216.05	45.49
35.60	4.314	133.22	31.64	222.03	46.35
40.58	5.702	138.56	32.80	227.99	47.03
46.33	7.728	143.81	33.91	234.08	47.82
52.10	9.277	148.98	34.90	239.99	48.62
57.10	11.00	154.39	35.95	245.88	49.31
62.22	12.75	160.13	36.88	252.75	50.03
67.50	14.26	165.80	37.95	257.60	50.65
72.40	15.86	171.40	38.80	263.44	51.30
77.57	17.51	176.95	39.78	269.26	52.08
83.23	19.30	182.44	40.63	275.06	52.74
88.54	20.71	187.89	41.48	280.85	53.26
96.46	22.95	193.30	42.34	286.63	54.00
102.06	24.43	198.67	43.11		

TABLE II

MOLAL HEAT CAPACITY OF β CALCIUM PHOSPHATE (97.8% $Ca_3(PO_4)_2$) FROM 15 TO 300°K.

T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree
15.26	0.310	73.02	15.89	190.26	41.69
17.90	.572	77.92	17.40	195.88	42.44
21.66	1.085	82.88	18.97	201.46	43.26
22.32	1.158	88.41	20.57	207.01	44.08
25.81	1.756	91.40	21.30	212.52	44.77
27.63	2.118	94.11	22.14	213.25	44.98
30.26	2.667	97.78	23.10	218.70	45.58
33.79	3.556	102.95	24.43	224.13	46.36
35.02	3.839	119.36	28.41	229.54	46.93
37.75	4.535	124.64	29.56	234.92	47.66
39.73	5.11	129.79	30.72	240.29	48.40
42.87	5.97	135.18	31.81	245.64	48.94
44.37	6.41	140.82	33.03	250.98	49.64
48.60	7.75	146.35	34.21	256.30	50.25
48.62	7.73	151.78	35.26	262.43	51.06
53.87	9.595	157.15	36.25	268.31	51.62
55.08	10.04	162.40	37.16	274.17	52.32
60.29	11.93	167.63	38.06	280.02	52.88
61.81	12.43	173.13	38.93	285.86	53.65
66.36	13.79	178.90	39.90	291.68	54.19
67.70	14.28	184.60	40.76	297.48	55.00
71.81	15.58				

TABLE III

MOLAL HEAT CAPACITIES OF β $Ca_8(PO_4)_2$ (CORRECTED FOR IMPURITIES) AT EVEN TEMPERATURES

T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree
20	0.83	90	20.82	200	42.68
30	2.64	100	23.52	220	45.41
40	5.10	120	28.32	240	47.92
50	8.17	140	32.59	260	50.29
60	11.62	160	36.40	280	52.53
70	14.88	180	39.74	300	54.76
80	17.96				

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(1) Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).