[CONTRIBUTION NO. 50 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

The Structure of the Organoboron Oxides

BY CORLISS R. KINNEY AND DONALD F. PONTZ

In the preceding paper it was stated that the dehydration of the organoboric acids increased their molecular weights, indicating that the products of the reaction, the organoboron oxides, do not have the simple boronyl structure RBO arbitrarily assigned to them. Consequently an elucidation of their molecular structure is necessary in order to understand their behavior. The molecular weights of several organoboron oxides are recorded in the table. The oxides were prepared by heating the corresponding boric acid derivative for thirty-three hours in a drying oven held at 110°. The products were then analyzed for boron and their molecular weights determined cryoscopically in nitrobenzene.

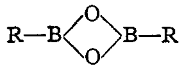
TABLE I

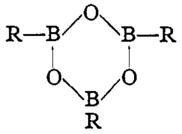
Derivative of boron oxide	% Boron Calcd.	% Boron Found		Mol. wt. Calcd.	Mol. wt. Found	
Phenyl	10.42	10.25	10.29	103.9	307	272
p-Tolyl[a]	9.18	9.15	9.11	117.9	312	249
m-Chlorophenyl[a]	7.82	7.65	7.59	138.3	581	573
p-Chlorophenyl[a]	7.82	7.73	7.69	138.3	406	462
p-Bromophenyl	5.92	5.79	5.68	182.8	331	342
α-Naphthyl[a]	7.03	7.38	7.24	153.9	391	435

[a] The acids from which these oxides were prepared were obtained from the Chemical Laboratory of the University of California through the courtesy of Dr. D. L. Yabroff.

Conclusions

A consideration of the data shows that the organoboron oxides cannot have the simple formula RBO. The variations in the values for duplicate molecular weight determinations probably indicate that mixtures of double, triple and perhaps higher molecular weights are produced. Without doubt the structure of the oxides may be compared to that of boron oxide (boric anhydride) in which at least one oxygen bridge is present (OBOBO). Since boron oxide as ordinarily prepared is a glass it is likely that it has a molecular weight higher than boric oxide, and that a number of boron atoms are linked together through oxygen. Such a comparison leads to the suggestion of the formulas below rather than to merely associated molecules.





The trimolecular formula is similar to those accepted for the trimers of the aldehydes, thioaldehydes and thioketones.

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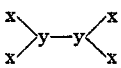
[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Polarity of the Nitrogen Tetroxide and Nitrogen Dioxide Molecules

BY J. W. WILLIAMS, C. H. SCHWINGEL AND C. H. WINNING

The structure of the molecules nitrogen tetroxide and nitrogen dioxide is incompletely understood at the present time, in spite of renewed activity in the investigation of the infra-red absorption spectra involved.[1] Thus, in the case of nitrogen tetroxide the data of Sutherland were interpreted to be exactly in accord with the expectation for a molecule of the type  in which all six atoms are co-planar, but Harris and King found some features of the spectrum which seemed to be in favor of the existence of molecules where the NO_2 groups do not lie in the same plane. The nitrogen dioxide molecule is usually assumed to be triangular rather than linear in shape, but the value of the O–N–O angle is still a matter of some dispute.[2]

There exists a somewhat similar situation in the interpretation of the vapor dielectric constant and density data to give the polarity of these two molecules. Zahn[3] has understood his observations to require a higher electric moment for nitrogen tetroxide as compared to that for the nitro-

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[1] (a) Sutherland, *Proc. Roy. Soc.* (London), **A141**, 342, 535 (1933); (b) Schaffert, *J. Chem. Phys.*, **1**, 507 (1933); (c) Strong and Woo, *Phys. Rev.*, **42**, 267 (1932); (d) Harris and King, *J. Chem. Phys.*, **2**, 51 (1934); (e) Cassie and Bailey, *Nature*, **131**, 239 (1933).

[2] Sutherland, *Proc. Roy. Soc.* (London), **A145**, 278 (1934).

[3] Zahn, *Physik. Z.*, **34**, 461 (1933).

gen dioxide molecule (NO_2, μ = 0.39 × 10^{-18} e. s. u.; N_2O_4, μ = 0.55 × 10^{-18} e. s. u.) but similar data we wish to present here, as well as those of Zahn appear to us to demand a moment for nitrogen tetroxide which does not differ greatly, if at all, from zero, and one for the dioxide which decreases as the temperature is increased. We wish to emphasize that this situation has arisen from a difference in the interpretation of the data and not because the two sets of observations are inconsistent with another. We have made every attempt to obtain results of high precision, in addition we believe our results to be much more complete, therefore their presentation seems justified.[4] At the same time it will be of value to point out why Zahn has been led to his conclusion, and why we believe his interpretation to be in error.

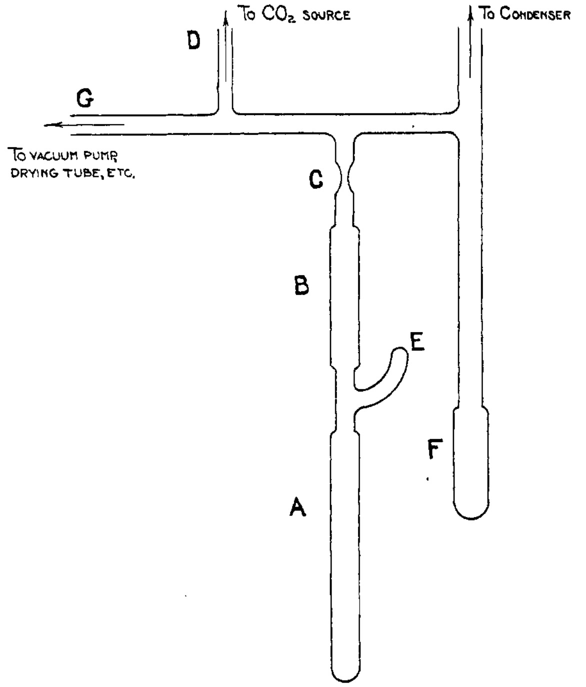

Fig. 1.

Experimental

The apparatus used for the determination of the dielectric constants of the gaseous equilibrium mixtures at the several temperatures has been described in the literature[5] so that it is only necessary to mention the changes made for the present work. The concentric condenser plates of Monel metal were supported rigidly in place by a system of clear quartz rods which replaced the mica spacers originally used.

As before, carbon dioxide gas was employed in the calibration of the apparatus. For its dielectric constant at 273°A. and one atmosphere pressure we have retained the Stuart value,[6] $(\epsilon - 1)\ 10^6 = 987$. Using converted values of the dielectric constant, determinations at the five temperatures used in this investigation gave the calibration constant a = 867.2, with mean deviation 0.32% for twenty-eight observations.

The arrangement for introducing gases and vapors into the condenser, and for maintaining the equilibrium mixture, $N_2O_4 \rightleftarrows 2NO_2$, at a definite vapor pressure, is shown in Fig. 1. For determinations with carbon dioxide the bulbs A and B were removed by sealing the tube at C, and experiments with the mixture $N_2O_4 \rightleftarrows 2NO_2$ were made with the carbon dioxide source sealed off at D. The pressure of the carbon dioxide was measured by means of a mercury manometer in the D line. This manometer is not shown in the diagram.

The procedure in the case of the $N_2O_4 \rightleftarrows 2NO_2$ mixture was as follows. The condenser chamber was baked out at a temperature of 150–200° for at least twenty-four hours while it was connected to the vacuum line containing a phosphorus pentoxide drying tube and a liquid air trap. The only stopcocks in the line were located between the pump and the trap, and between the trap and the phosphorus pentoxide drying tube. During the baking out process, the external glass parts were flamed from time to time. After the initial heating the furnace was allowed to come to the required temperature and the system was filled with dry nitrogen gas. The glass tip at E was then broken and the bulb A was immersed in liquid air. An ampoule of previously dried liquid tetroxide was cooled in a salt–ice mixture and the liquid from it introduced at E. Tip E was then resealed and the system was evacuated through the liquid air trap (0.01 mm. pressure). The solid nitrogen tetroxide contained in bulb A had practically no vapor pressure at the liquid air temperature. When the required vacuum had been attained the condenser was shut off from the pump by the stopcock located between the liquid air trap and the phosphorus pentoxide drying tube. The liquid air was removed from the tube A, allowing the nitrogen tetroxide to melt, and the liquid to come to equilibrium with its vapor. The freezing, evacuating and melting processes were repeated a second time to remove most of the dissolved foreign gases. Liquid air was next placed around tube F and the $N_2O_4 \rightleftarrows 2NO_2$ mixture was allowed to distil slowly through the phosphorus pentoxide drying tube B into bulb F. The drying tube B was filled to a depth of approximately 21 cm. with tightly packed phosphorus pentoxide. When all of the liquid had passed into bulb F, the tubes A and B were removed from the apparatus by sealing off at C. The liquid air was then removed from about the tube F and the nitrogen tetroxide was allowed to melt and come to room temperature. The stopcock was opened and approximately one-third of the liquid in the tube F was allowed to distil into the liquid air trap. The liquid remaining in tube F was frozen with liquid air and the system evacuated. The vacuum line was then removed from the condenser and reservoir by sealing off the tube at G. For each temperature the apparatus was reconstructed and an identical procedure followed.

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[4] As mentioned in a preliminary statement to the Editor of This Journal [Williams, Schwingel and Winning, This Journal, **56**, 1472 (1934)] our observations had been practically completed when the article of Zahn made its appearance.

[5] Greene and Williams, *Phys. Rev.*, **42**, 119 (1932).

[6] Stuart, *Physik. Z.*, **47**, 457 (1928).

The figure shows that the closed system contained no manometer or pressure gage for determining the pressure of $N_2O_4 \rightleftarrows 2NO_2$ in the condenser chamber. The pressures were obtained by the use of known vapor pressure data. The tube F served as a liquid reservoir which was placed in a thermostat of the proper temperature to give the desired vapor pressure in the condenser chamber. The temperatures of the thermostat were kept constant to within ±0.02°. They were measured with a thermometer which had been previously calibrated with a standard thermometer.

The values for pressure given in the tables to follow were calculated from the equation

$$\log_{10} p_{\text{mm}} = -\frac{0.05223\,A}{T} + B$$

where $A = 33430$, $B = 8.814$ and T is the temperature of the liquid.[7] Values calculated from this equation are accurate for pressures up to 760 mm. This is amply verified by the experimental results of a number of vapor pressure investigations.[8]

The procedure for determining the ΔC_s values was to take a condenser reading with the nitrogen tetroxide frozen and at liquid air temperature in the tube F. The liquid air was then removed and replaced by a constant temperature bath. Thus, the solid was allowed to melt and the liquid and vapor could come to equilibrium at the temperature of the thermostat. Readings were taken every five minutes until no further changes occurred in the condenser settings. The system was then evacuated by removing the thermostat and immersing the tube F in liquid air. The difference between the reading with the system evacuated and the reading at equilibrium gave the value of ΔC_s, which was then corrected for a slight drift. A number of readings were made at each temperature and pressure, and the results averaged. In general, the average deviation from the mean for each individual set of ΔC_s values did not vary by more than 0.3%

The nitrogen tetroxide was prepared by heating lead nitrate in the usual manner.[9] The experimental data for the tetroxide–dioxide mixture are summarized in Table I. The first column gives the temperature of the condenser. The second column gives the temperature of the thermostated bath maintained around the reservoir in order to obtain the pressure values presented in the third column. The ΔC_s values are corrected capacity differences, obtained from the readings of the calibrated precision condenser. The values for $(\epsilon - 1)10^6$ were calculated from the equation

$$\frac{1}{(\epsilon - 1)} = \frac{a^2}{\Delta C_s} + \frac{a}{\sqrt{C}} + 1$$

where $a = 867.2$ and $C = 501.5\ \mu\mu F$.[5] Curves showing the variations of dielectric constant with temperature and pressure are given in Fig. 2.

TABLE I

DIELECTRIC CONSTANT DATA FOR EQUILIBRIUM MIXTURE $N_2O_4 \rightleftarrows 2NO_2$

Temp., °A. Condenser	Temp., °C. Liquid	V. p., mm. Liquid	ΔC_s	$(\epsilon - 1)10^6$
297.6	−10.0	150.5	284	372.1
298.1	0.0	263.4	510	660.4
298.3	+6.0	361.4	722	924.8
298.1	10.0	443.0	882	1120.6
298.0	13.0	514.1	1065	1340.7
297.8	17.0	624.1	1304	1622.3
298.1	21.0	753.5	1572	1930.1
318.1	0.0	263.4	414	538.7
318.1	7.0	380.5	605	779.6
318.1	10.0	443.0	720	922.3
318.1	13.0	514.1	846	1076.8
318.1	15.5	580.7	999	1261.8
318.1	18.0	654.5	1114	1399.0
318.1	21.0	753.5	1308	1626.9
343.1	0.0	263.4	323	422.3
343.1	7.0	380.5	465	603.5
343.1	10.0	443.0	548	708.2
343.1	13.0	514.1	658	845.6
343.1	15.5	580.7	754	964.2
343.1	18.0	654.5	861	1095.1
343.1	21.0	753.5	987	1247.4
368.1	0.0	263.4	272	356.6
368.1	7.0	380.5	364	474.9
368.1	10.0	443.0	425	552.7
368.1	13.0	514.1	524	678.0
368.1	15.5	580.7	585	754.6
368.1	18.0	654.5	702	900.1
368.1	21.0	753.5	804	1025.5
398.1	0.0	263.4	238	312.6
398.1	7.0	380.5	328	428.7
398.1	10.0	443.0	365	476.2
398.2	13.0	514.1	440	571.8
398.4	15.5	580.7	490	635.1
398.1	18.0	654.5	570	735.8
398.1	21.0	753.5	667	856.7

Calculations

According to the familiar Debye equation, the mean electric moment $\overline{m}$ of a molecule in an external field F varies with the temperature in the following way.

$$\overline{m} = (\alpha_0 + \mu^2/3kT)F$$

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[7] "Int. Crit. Tables," Vol. III, McGraw-Hill Book Co., Inc., New York City, 1928.

[8] Millasch, Kuss and Schlueter, *Z. anorg. Chem.*, **159**, 1 (1927); Scheffer and Treub, *Z. physik. Chem.*, **81**, 308 (1912).

[9] Daniels, Mathews and Williams, "Experimental Physical Chemistry," 2d Edition, McGraw-Hill Book Co., Inc., New York City, 1934.

Here α_0 is the deformation polarization and μ is the permanent electric moment of the molecule in question. The molar polarization P is, therefore

$$P = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{\rho} = \frac{4\pi N}{3}\alpha = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu^2}{3kT}\right) = A + \frac{B}{T}$$

in which ϵ is the dielectric constant, M is the molecular weight, ρ is the density, N is the Avogadro constant, $A = (4\pi N/3)\,\alpha_0$ (molar polarization due to deformation) and $B = 4\pi N\ \mu^2/9k$ (molar polarization due to presence of permanent moment in the molecule). Thus, in the ordinary case, dielectric constant and density data permit the evaluation of the constant B, and therefore the electric moment μ, of the molecule. But it should be mentioned there are some molecules for which, in a given temperature interval, P is not a linear function of $1/T$, and the evaluation of the data is much more complicated.

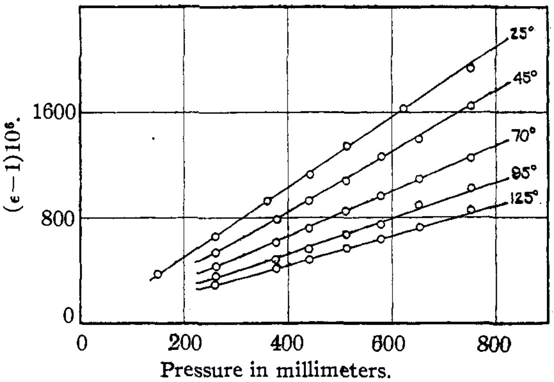

Fig. 2.

If we are dealing with a system composed of two kinds of molecules in equilibrium with one another the calculations for the electric moment of each molecule require the division of the total molar polarization into the two parts, the contributions of each molecule. It can be accomplished without difficulty in the present case since the equilibrium constants for the dissociation are known at the several temperatures and pressures involved. Thus, in Table II are presented molar polarization data for the equilibrium mixture at a number of temperatures and pressures; at the same time the composition of the mixture is expressed as mole fraction of nitrogen dioxide, n_1, and as mole fraction of nitrogen tetroxide, n_2. Dissociation data for the temperatures 25 and 45°C. were obtained from the results of Verhoek and Daniels[10] while those for 70, 95 and 125°C. were calculated from the Bodenstein equation.[11]

TABLE II

MOLAR POLARIZATION DATA FOR EQUILIBRIUM MIXTURE $N_2O_4 \rightleftarrows 2NO_2$

Pressure, mm.	$(\epsilon - 1)10^6$ (from graph)	P_{molar}	n_1	n_2
	Equilibrium at 25°			
200	504	15.61	0.506	0.494
300	765	15.79	.436	.564
350	897	15.87	.410	.590
450	1159	15.96	.369	.631
550	1423	16.02	.337	.663
600	1556	16.06	.323	.677
650	1689	16.10	.311	.689
700	1821	16.11	.300	.700
	Equilibrium at 45°			
300	613	13.51	0.698	0.302
350	722	13.63	.671	.329
450	948	13.93	.625	.375
550	1172	14.08	.587	.413
600	1284	14.14	.570	.430
650	1396	14.19	.554	.446
700	1509	14.25	.540	.460
	Equilibrium at 70°			
300	476	11.31	0.893	0.107
350	558	11.36	.879	.121
450	731	11.58	.854	.146
550	904	11.72	.830	.170
600	992	11.79	.820	.180
650	1078	11.83	.810	.190
700	1166	11.87	.800	.200
	Equilibrium at 95°			
300	388	9.894	0.967	0.033
350	454	9.923	.962	.038
450	588	9.990	.952	.048
550	724	10.07	.943	.057
600	794	10.12	.938	.062
650	863	10.15	.933	.067
700	932	10.18	.929	.071
	Equilibrium at 125°			
300	330	9.095	0.991	0.009
350	386	9.124	.990	.010
450	495	9.102	.987	.013
550	606	9.117	.984	.016
600	661	9.117	.983	.017
650	716	9.109	.981	.019
700	771	9.109	.980	.020

$$P_{\text{molar}} = \frac{\epsilon - 1}{3} \times \frac{760}{p} \times \frac{T}{273} \times 22{,}400$$

n_1 = mole fraction of NO_2
n_2 = mole fraction of N_2O_4

Since at each temperature the observations were made at a number of pressures, it is now possible to evaluate for each temperature the contribution

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(10) Verhoek and Daniels, THIS JOURNAL, **53**, 1250 (1931).

(11) Bodenstein, *Z. physik. Chem.*, **100**, 78 (1922).

of each molecule to the total molar polarization. The procedure will be evident from the graph given here as Fig. 3, in which is plotted the change of total molar polarization of the mixture P against mole fraction of nitrogen dioxide. Thus by making use of the optical data of Cuthbertson it is possible to evaluate the electric moment of the nitrogen dioxide molecule at the several temperatures. Since, within the accuracy with which our extrapolations can be made, the molar polarization for nitrogen tetroxide is independent of temperature and only very slightly greater than the electron polarization which has been estimated by using the optical data, our observations are consistent with the conclusion that the electric moment of nitrogen tetroxide cannot differ greatly from zero. The results of the calculations are summarized in Table III.

TABLE III

SUMMARY OF RESULTS

I. N_2O_4

At n_1 = 0 (1.0 mole fraction N_2O_4)

P_{molar} = 16.87 cc., independent of temperature over interval 25 to 125°

P_D = 16.73 cc.[a]

Molecule N_2O_4 has moment which cannot differ greatly, if at all, from zero.

II. NO_2

At n_1 = 1.0 (1.0 mole fraction NO_2)

T	$1/T \times 10^3$	P_{molar}	[a]P_D	P_0	$\mu \times 10^{18}$ e. s. u.
298.1	3.355	14.68	7.616	7.06	0.58
318.1	3.144	12.24	7.616	4.62	.49
343.1	2.915	10.69	7.616	3.07	.41
368.1	2.717	9.65	7.616	2.03	.35
398.1	2.512	9.03	7.616	1.41	.30

[a] Cuthbertson and Cuthbertson, *Proc. Roy. Soc.* (London), **A89**, 361 (1913).

Discussion

As mentioned above our electric moment values do not agree with those reported by Zahn not so much because of inconsistencies in the two sets of data as because of differences in the methods of calculation and interpretation. Thus, using the data published by Zahn and the method of calculation outlined above we obtain the following polarization and electric moment values for nitrogen dioxide.

TABLE IV

POLARIZATION AND ELECTRIC MOMENT DATA, CALCULATED FROM EXPERIMENTAL OBSERVATIONS OF ZAHN

T	P_{molar}	P_0	$\mu \times 10^{18}$ e. s. u.
296.51	13.05	5.43	0.51
320.85	11.80	4.18	.47
359.48	10.51	2.89	.41
397.42	9.89	2.27	.38

The method of calculation used by Zahn is based upon the assumption that the total electrical polarization of the mixture, P, is given by an expression of the form

$$P = n_1\left(A_1 + \frac{B_1}{T}\right) + n_2\left(A_2 + \frac{B_2}{T}\right)$$

in which the subscripts 1 and 2 refer to nitrogen dioxide and nitrogen tetroxide, respectively. The optical constants A_1 and A_2 are known from the Cuthbertson data and the concentrations n_1 and n_2 are evaluated from the equilibrium constants for the mixture at the several temperatures, thus there may be obtained values for the quantities B_1 and B_2, assumed constant and proportional to the squares of the electric moments of two molecules.

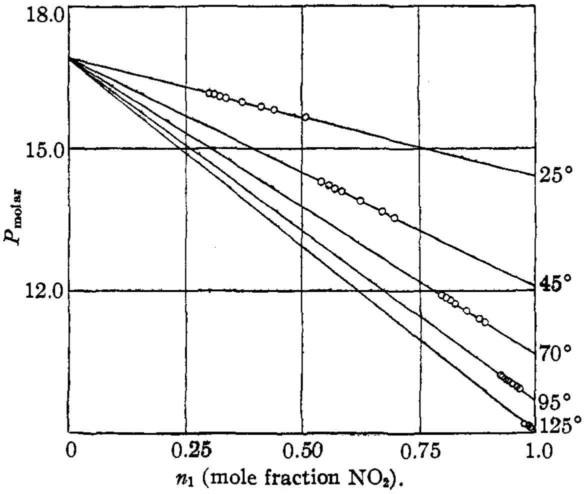

Fig. 3.

Such a formula is valid except in a case where either (or both) of the molecules involved has an electric moment which is variable with temperature. According to our interpretation the nitrogen dioxide molecule does have such a variable moment in the region of temperature in which the investigation was conducted, thus B_1 is not a constant. In this instance there is some reason to believe that we are dealing with a molecule with electric moment dependent upon the vibrational state. Temperature variable moments have been found for several other molecules,[12] but here it always has been possible to explain the variation as being due to differences in the state of rotation of parts of the molecule about single valence bond or bonds.

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[12] (a) Meyer, *Z. physik. Chem.*, **B8**, 27 (1930); (b) Zahn, *Phys. Rev.*, **38**, 521 (1931); **40**, 291 (1932); (c) Greene and Williams, *ibid.*, **42**, 119 (1932).

Some years ago Van Vleck[13] presented a derivation of the classical Debye formula by making use of general quantum-mechanical considerations having to do with the relative values of possible energy transitions within the molecule. It was necessary to assume that the energy levels of the molecule are such that $h\nu$ is never of the order of magnitude of kT, but is either much larger or much smaller. The dipole term would naturally arise from those transitions for which $h\nu \ll kT$. For some of the ordinary vibrational states of non-linear molecules $h\nu$ may become nearly equal to kT, and in such an event an electrical polarization variable with temperature will result.

Assuming nitrogen dioxide to be a triangular molecule, with O–N–O angle of approximately 110°, an electric moment which decreases with increase in temperature can be qualitatively accounted for in the following way. The bending frequency of the molecule,[1] 641 cm.$^{-1}$, is extremely low and of such magnitude that $h\nu \sim kT$. Thus as the temperature is increased over the range in which the observations were made, greater and greater numbers of the molecules are passing into the higher vibrational states. Since the bending of the molecule is of such kind as to increase the valence angle, the activated molecules are more nearly linear in form than the normal ones, in other words they are more nearly electrically symmetrical. Since the moments calculated from the experimental data are average (root-mean-square) values they will decrease in magnitude as more molecules are brought into the higher vibrational states, *i. e.*, as the temperature of the gas is increased.

By means of the Boltzmann distribution law it ought to be possible to calculate the moments of the molecules in the activated states. Thus, in the simplest case where just one activated state is considered, we may assume the presence of n_0 molecules in the normal state with electric moment μ_0 and n_1 molecules in the activated state with moment μ_1, and show that, exclusive of a statistical weight factor

$$\mu^2 = \left[\frac{\mu_1^2 e^{-h\nu/kT} + \mu_0^2}{1 + e^{-h\nu/kT}}\right]$$

The difficulty in the application of such an equation to our data is two-fold:[14]

1. The electric moment of the molecules in the normal state, μ_0, is not known, since our experiments could not be made at temperatures below that of the room.

2. The statistical weight factor cannot as yet be estimated from independent measurements. The most direct and satisfactory method involves the use of specific heat data, but the available figures are hardly accurate and complete enough for the purpose.

The magnitude of the change in polarity, from $\mu = 0.58 \times 10^{-18}$ at 298 °A. to $\mu = 0.30 \times 10^{-18}$ e. s. u. at 398 °A., is larger than might be expected, and actually it is difficult to account for the data by using the equation presented above. If, for practical purposes, the existence of only one activated state is assumed (and this seems reasonable for our temperature interval), then a large statistical weight factor is required.

Several aspects of the problem seem very favorable for future development. The dielectric constant measurements for the nitrogen oxide mixture should now be extended to both lower and higher temperatures. There are several other triatomic molecules, triangular in form, which have low bending frequencies. In these cases one should again obtain polarizations changing exponentially rather than linearly with increasing temperature, and be able to describe the kind of deformation the molecule has undergone in assuming the activated state. In addition the infra-red absorption spectra of such molecules ought to show changes with temperature which are indicative of the passage of some of the molecules into the activated states.

For reasons mentioned above, it is our conclusion that the polarity of the nitrogen tetroxide molecule cannot differ greatly from zero. It seems reasonable to expect the polarity of the associated molecule to be smaller than that of the units from which it is formed, especially if, as is believed, the union is through the nitrogen atoms. As far as is known the infra-red spectrum of nitrogen tetroxide can be accounted for if there is assumed a symmetrical molecule in which all the atoms lie in one plane. Harris and King[1d] point out it is possible some of the molecules are not coplanar but have their atoms arranged in two planes at right angles to one another, the rotation having taken place about the N–N bond. Whether or not this is true, it can now be felt that the conclusions drawn from the two types of study, electric moment and infra-red absorption, are mutually consistent with one another.

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(13) Van Vleck, *Phys. Rev.*, **29**, 729 (1927); **30**, 31 (1927).

(14) The Referee has been kind enough to point out to us that the bending vibration is non-degenerate.

The authors desire to express their appreciation to the Wisconsin Alumni Research Foundation for substantial aid in connection with this work. It is also a pleasure to acknowledge our indebtedness to the Civil Works Administration which made it possible for one of us (C. H. S.) to participate in the research.

Summary

1. The dielectric constant of the gaseous equilibrium mixture of nitrogen dioxide and nitrogen tetroxide has been measured at five temperatures between 298 and 398°A. and at seven pressures between 150 and 760 mm.

2. With the aid of density measurements already existent in the literature these data have been utilized to calculate the electric moments of the nitrogen dioxide and nitrogen tetroxide molecules.

3. The polarity of the nitrogen dioxide molecule has been found to decrease with increasing temperature over the interval studied. It is suggested that this decrease is due to the passage of greater and greater numbers of the molecules into more symmetrical higher vibrational states as the temperature is increased.

4. The dipole moment of the nitrogen tetroxide molecule does not differ greatly, if at all, from zero. Thus, there has been removed the apparent inconsistency between the results of infra-red absorption and dielectric constant studies now existent in the literature.

MADISON, WISCONSIN RECEIVED NOVEMBER 4, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Data of State of Phosphine at Low Pressures, and from 190 to 300°A.

BY EARL A. LONG[1] AND EARL A. GULBRANSEN[1]

In conjunction with a research on low temperature heat capacities of gases by the velocity of sound method, which requires accurate corrections for gas imperfection, we have found it expedient to measure the *PVT* behavior of gases whose data of state are unknown. Although it is possible to do this accurately by measuring the velocity of sound in gases as a function of pressure,[2] we have found the methods of gas thermometry more suitable for our purposes.

This communication discusses the apparatus used and the measurements with phosphine.

Phosphine.—Phosphine was obtained from a pure sample prepared for other measurements in this Laboratory.[3] The gas was prepared by the reaction between phosphonium iodide and potassium hydroxide. A detailed description of this preparation will be given in a later communication.[4] From a consideration of the heat capacities of the solidified gas just below the melting point, the amount of solid impurity was estimated to be less than 0.004 of one mole per cent. The method of preparation precluded the presence of any impurities not soluble in the liquefied gas.

Helium.—Purified helium was taken from a supply used for liquefaction purposes in this Laboratory. The helium was passed through a charcoal trap cooled with liquid air. The charcoal had previously been degassed by evacuating to a pressure of 10^{-6} mm. at 400°.

Method and Apparatus

Our method is a modification of that of Johnston and Weimer,[5] and depends on the use of a "double" constant-volume gas thermometer wherein the properties of helium, whose behavior as a real gas is accurately established, are compared directly, in the same apparatus under identical conditions, with those of the gas whose *PVT* behavior is being investigated. The method eliminates errors due to secondary temperature standards.

The apparatus[6] is shown in Fig. 1. The thermometer bulbs A and B were surrounded with lead shot contained within a vacuum-tight copper sheath wound with an electric heater. Pressure corrections for the bulb volumes were eliminated by the compensating effect of a pressure of hydrogen in the sheath.[7] The electric heaters on the "blocks" E and F were wired for separate heating. Copper–constantan thermocouples were soldered at suitable points in the apparatus, including three thermocouples distributed along each of the German silver tubes C and D. A vacuum of better than 10^{-5} mm. provided thermal insulation of the thermometer sheath and "blocks" from the container E. The total temperature drift of the thermometer sheath was about 0.01° per hour at 200°K.

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[2] *Cf.* van Itterbeek and Keesom, *Comm. Phys. Lab. Univ. Leiden*, No. 209-c (1930).

[3] We are indebted to Mr. C. C. Stephenson for supplying us with this quantity of pure phosphine.

[4] Stephenson and Giauque, to be published.

[5] Johnston and Weimer, THIS JOURNAL, **56**, 625 (1934).

[6] *Cf.* also Johnston and Weimer, Ref. 5. and Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927). The latter paper describes the experimental technique employed.

[7] Since these measurements were completed, we have found this precaution unnecessary, as the correction to the bulb volume is negligible for a pressure difference of one atmosphere.