face tensions not differing greatly in magnitude. However, with this method absolute temperature control was found to be difficult when working with solutions of the type studied in this investigation.

LINCOLN, NEBRASKA RECEIVED APRIL 22, 1935

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Dipole Moment of Deuteroammonia[1]

BY J. M. A. DE BRUYNE AND C. P. SMYTH

Because of the accuracy with which the dipole moment of ammonia can be measured, it was selected as a suitable substance for the determination of the effect of the replacement of hydrogen by deuterium upon the dipole moment. The measurement was made possible by the kindness of Dr. J. C. Jungers, who loaned a quantity of pure deuteroammonia which he had prepared. The dielectric constants at different temperatures were measured with an apparatus previously described.[2] This apparatus had, however, been subjected to extensive alterations in the electrical circuits, which were kept at a temperature constant within 0.2° by thermostatic regulation of the air in the large shielding box enclosing them.

Preparation of Materials

Ammonia was prepared from reagent grade ammonium chloride and potassium hydroxide. The gas was passed successively over calcium oxide and potassium hydroxide and condensed in a liquid air trap. By means of liquid air, two fractionations were made on the substance, the system containing the ammonia being pumped out during the process and a small residual quantity being discarded in both fractionations.

Deuteroammonia was prepared by the action of deuterium oxide on magnesium nitride, which had been prepared by passing dry nitrogen through a silica tube containing magnesium turnings heated to about 600°. The gas was sublimed from a tube cooled with a slush of solid carbon dioxide in toluene into a trap cooled with liquid air, the system being pumped out during the sublimation. Any deuterium oxide present would have been retained in the first trap. The triple point of the substance was measured with a copper–constantan thermocouple, which had been calibrated at the boiling point of oxygen, at the freezing point of pure *n*-heptane and at the triple point of ammonia. The temperature at the triple point was found to be −73.6° and the pressure 48.6 mm.

Experimental Results

Although the moment of ammonia had been measured by other investigators, it was determined again at the beginning of this investigation. After the ammonia had been pumped out, the apparatus was rinsed thoroughly by the admission of an impure deuteroammonia and subsequently evacuated before the pure deuteroammonia was run in. The P–V–T relations determined from the equation of state found by Beattie and Lawrence for ammonia[3] were used for both gases in calculating the values of the molar polarization, $P = (\epsilon - 1)M/(\epsilon + 2)d$, where ϵ is the dielectric constant, M the molecular weight, and d the density. These values are given in Table I and are plotted against $1/T$, the reciprocal of the absolute temperature, in Fig. 1. The straight lines thus obtained give the constants a and b of the Debye equation $P = a + b/T$. Table I gives at the bottom the values of a, the induced polarization, and $b = 4\pi N\mu^2/9k$, in which N is the number of molecules per gram molecule, μ the dipole moment, and k the molecular gas constant $= 1.372 \times 10^{-16}$.

TABLE I

POLARIZATIONS OF THE AMMONIAS

Ammonia		Deuteroammonia	
T, °K.	P	T, °K.	P
273.9	53.79	274.1	54.94
309.2	48.30	304.3	49.85
334.9	45.29	333.8	45.85
363.6	41.93	363.8	42.46
394.0	39.05	394.2	39.38
423.1	36.67	425.0	37.04
$a = 5.3$, $b = 13310$, $\mu = 1.46_6 \times 10^{-18}$		$a = 4.4$, $b = 13840$, $\mu = 1.49_6 \times 10^{-18}$	

Discussion of Results

The value of the induced polarization of ordinary ammonia, 5.3, is slightly lower than those

(1) The preliminary part of this work was done while the senior author was a National Research Fellow.

(2) McAlpine and Smyth, THIS JOURNAL, **55**, 453 (1933).

(3) Beattie and Lawrence, *ibid.*, **52**, 6 (1930).

found by other investigators. Keyes and Kirkwood[4] obtained 7.3 and Uhlig, Kirkwood and Keyes[5] found 6.2, while Errera[6] calculated 5.7 from the measurements of Zahn,[7] which should give a more accurate value. Errera's value 5.2 calculated for P_E, the electronic polarization at infinite wave length, gave the atomic polarization $P_A = a - P_E = 0.5$. This difference for the ammonia results in Table I gives $P_A = 0.1$, which is a quite reasonable value for this small molecule. It seems improbable, however, that the polarizability of the deuteroammonia molecule should be so much lower as to give an induced polarization 4.4. In the analogous case of water and deuterium oxide, the molar refraction for the sodium D line was given by Müller as 3.70_5 for the former and 3.67_4 for the latter[8] while Selwood and Frost[9] obtained 3.711 and 3.677. Actually, the difference between the two values of the induced polarization is of the magnitude permitted by the probable error, which is relatively large in these small values.

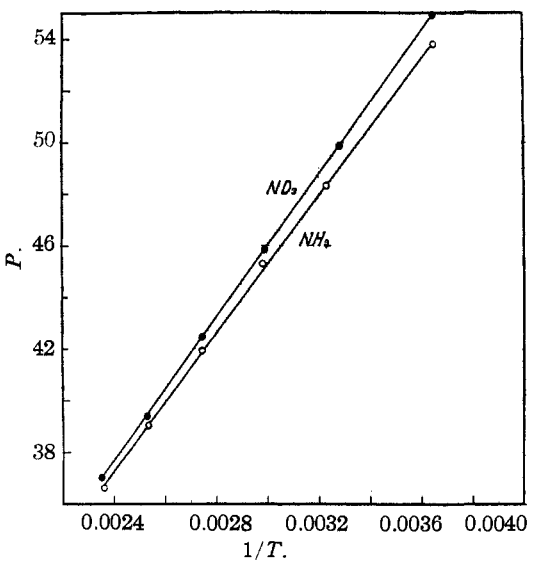

Fig. 1.—The polarizations of the ammonias plotted against the reciprocal of the temperatures.

The greater slope of the line for deuteroammonia in Fig. 1 shows clearly the larger value of b which gives a moment 0.03 ± 0.01 higher for the deuteroammonia molecule. The previously mentioned investigations by Zahn, and Keyes and Kirkwood, gave 1.44 for the moment of ammonia, while that of Uhlig, Kirkwood and Keyes and that of Watson[10] gave 1.48. The mean of these four values 1.46 is indistinguishable experimentally from the value 1.46_6 in Table I.

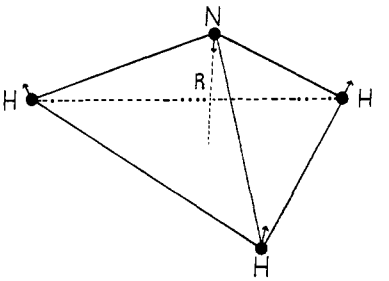

Fig. 2.—Ammonia molecule.

The difference 0.03 between the moments of the two compounds is like that just published for water by Müller,[8] who found that, in solution in benzene, heavy water had a moment 0.02 higher than ordinary water. Any difference in the dipole moments of isotopic molecules is to be traced to differences in the average internuclear distances in the zero point vibrations. For vibrations which are harmonic about the potential minima there will be no such differences. In the ammonia molecule, which consists of a pyramid with the nitrogen at the apex and the hydrogens at the corners of a triangular base (see Fig. 2), the only markedly anharmonic vibration is that in which the nitrogen oscillates with respect to the plane of the three hydrogen atoms. The dependence of the potential energy upon the distance between the nitrogen and the plane of the three hydrogen atoms has been calculated by Manning,[11] and the quantization of the energy so computed as to fit very satisfactorily the energy levels given by the infra-red spectrum. The potential energy curves are identical for the NH_3 and ND_3 molecules having minima when the nitrogen nucleus is 0.37 Å. on either side of the plane of the other three nuclei. Figure 3 gives the curve in the region of one of these minima, the differences of the potential energies from that at the minimum being plotted as ordinates against the corresponding values of the distance R as abscissas. The rise of the curve accompanying increase in this distance beyond 0.37 Å. is steeper than the rise as the distance is diminished so that vibration in these energy troughs causes a swing farther below 0.37 Å. than above it. The greater the vibration, therefore,

(4) Keyes and Kirkwood, *Phys. Rev.*, **36**, 1570 (1929).
(5) Uhlig, Kirkwood and Keyes, *J. Chem. Phys.*, **1**, 155 (1933).
(6) Errera, "Polarisation Diélectrique," Les Presses Universitaires de France, Paris, 1928, p. 118.
(7) Zahn, *Phys. Rev.*, **27**, 455 (1926).
(8) Müller, *Physik. Z.*, **35**, 1009 (1934).
(9) Selwood and Frost, THIS JOURNAL, **55**, 4335 (1933).
(10) Watson, *Proc. Roy. Soc.* (London), **117**, 43 (1927).
(11) Manning, *J. Chem. Phys.*, **3**, 136 (1935).

the smaller will be the average distance of the base of the pyramid from its apex. More than 95% of the molecules are in the zero energy levels indicated in Fig. 3, the double levels being so close together as to be indicated as one. The average distance of the nitrogen nucleus from the plane of the other three nuclei is given approximately by the abscissa of the mid-point of each zero level in Fig. 3. As the errors resulting from this assumption are nearly the same in the two cases, the difference between the two abscissas should represent fairly accurately the difference between the two average distances which Fig. 3 gives as 0.002_2 Å.

The dipole moment of the molecule depends upon electrical unsymmetry along each of the three N–H or N–D lines, the moment of the molecule as a whole being the sum of the components of the bond moments in the line R in Fig. 2. As the vibration which has been considered is, in the main, a bending of the N–H or N–D bonds, the components of the bond moments in the perpendicular R should be greater the smaller the angles between the bonds and, hence, the greater the length of R. Accordingly, other things being equal, the greater average distance in the ND_3 molecule should give a greater dipole moment as shown in Table I. It is interesting to note that as the ammonia molecules move into higher energy levels, the effective dipole moment should fall off. The consequent decrease in moment with rising temperature would be so gradual that it would not be detected unless measurements were made over a considerably wider range of temperature than that used in the present investigation.

The writers wish to express their indebtedness to Dr. W. S. Benedict for his advice on the interpretation of the results.

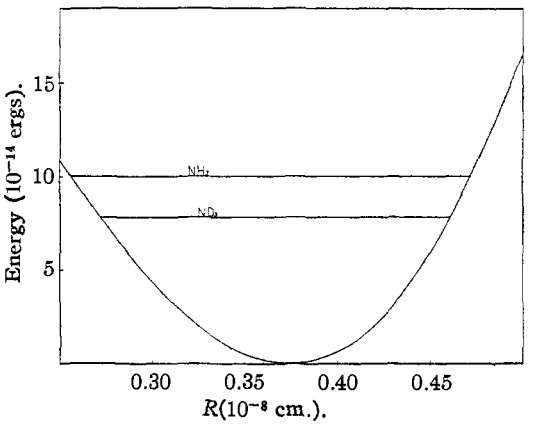

Fig. 3.—The potential energy minimum of the ammonias.

Summary

The triple point of deuteroammonia is found to have a temperature of −73.6° and a pressure of 48.6 mm.

The dielectric constants of ammonia and deuteroammonia have been measured at six temperatures within a range of 150° and used to calculate the dipole moments of the two molecules. The value found for ammonia, $1.46_6 \times 10^{-18}$, agrees with the mean of the four accurate determinations in the literature, 1.46×10^{-18}. Deuteroammonia is found to have a moment 0.03×10^{-18} higher because of the lower energy of the zero level in the vibration of the three deuterons with respect to the nitrogen nucleus, which causes the plane of these three nuclei to have a greater average distance from the nitrogen nucleus than is the case in the ammonia molecule.

PRINCETON, N. J. RECEIVED APRIL 24, 1935