tion should not occur at any pressure below p_c. An analogy might be expected with the behavior of moderately supercooled liquid, in which freezing must be initiated by external causes but, once started, spreads rapidly until the temperature of the mass has been raised to the freezing point. It might be anticipated, therefore, that a breaking-front, if unable to advance further at the pressure of spontaneous cavitation, p_b, would continue to advance at higher pressure p_b' until it encountered a pressure equal to p_c.

Against such an assumption the following objection may be raised. It can be shown that even

on this alternative hypothesis a breaking-front must advance through the liquid at supersonic velocity. But the advance into regions of pressure higher than p_b would necessarily occur, not as a consequence of automatic changes in the unbroken liquid ahead, but as an effect propagated out of the region already cavitated; and it seems unlikely, although certainly not impossible, that such an effect could be propagated at a speed exceeding that of sound.

Which assumption corresponds more nearly with the behavior of actual liquids remains to be discovered by experiment.

Thermal Diffusion with Ammonia

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With a "two-bulb" thermal diffusion experiment in which is used NH_3 having about a 15 percent N^{15} content to increase the accuracy of the mass spectrometer analyses, it has been found that with decreasing temperature the thermal diffusion constant α of ammonia changes from + to − values at about room temperature. The value of α varies linearly with the logarithm of the absolute temperature, the rate of decrease being, however, nearly eight times that for neon and argon. A qualitative discussion is presented, attributing this effect largely to the strong first-order dipole-dipole intermolecular forces which are proportional to $1/R^4$.

IN general the phenomenon of thermal diffusion operates to produce an increased concentration of the heavier component in a binary gas mixture in the colder portion of the apparatus, while the lighter component tends to concentrate in the warmer part. For these cases there is a positive thermal diffusion constant α in the equation $D_T/D = \alpha c_1 c_2$, where D_T is the coefficient of thermal diffusion, D is the coefficient of ordinary diffusion, and c_1 and c_2 are the relative concentrations of the light and heavy components, respectively. In fact, until just recently no instance where thermal diffusion proceeds with a negative thermal diffusion constant had been reported. Grew[1] has now found a reversal in the sign of α with change in the composition of a neon-ammonia mixture. Be-

tween 0 and 75 percent neon, the heavier molecule, neon, tends to concentrate at the upper end of a Clusius-Dickel column. This indicates that the α is negative. Above 75 percent neon, the neon concentrates at the lower end, so that in this range α is positive. The theoretical possibility of such a reversal had been pointed out by Chapman.[2]

A definite temperature variation of the positive α for neon was found by Nier,[3] the value of α decreasing with the lowering of the mean temperature. Jones[4] has shown theoretically that a variation similar to that reported by Nier is to be expected for either the Sutherland or the Lennard-Jones 9,5 molecular models. This theoretical investigation indicated that, for tem-

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[1] K. E. Grew, Nature 150, 320 (1942).

[2] S. Chapman, Proc. Roy. Soc. A177, 38 (1940).
[3] A. O. Nier, Phys. Rev. 57, 338 (1940).
[4] R. Clark Jones, Phys. Rev. 59, 1019 (1941).

peratures near the critical temperature for a gas whose molecules are spherically symmetrical, the thermal diffusion constant might be negative. Recently Stier[5] has made measurements for α for argon over a number of temperature ranges in the two lowest of which α should be negative according to the Lennard-Jones 9,5 model. The observed α's are positive, however.

The present investigation with ammonia was initiated with the object of finding an experimental case where, with decreasing temperature, a reversal in the sign of the thermal diffusion effect occurs. Ammonia was considered to be a good possibility because (1) predictions from viscosity data indicate that α should be negative in the lower temperature ranges,[6] (2) it is possible to work well below the critical temperature, 132°C, and (3) it is known that long-range intermolecular forces are particularly strong where the molecules are symmetrical tops with a relatively large dipole moment.[7] Since the ammonia molecule is not spherically symmetrical and since there is the possibility of an interchange of energy between the external and internal degrees of freedom, most of the theoretical equations which have been developed for the thermal diffusion effect do not strictly apply. But thermal diffusion depends strongly on the intermolecular forces between the molecules involved, and hence any measurements of controlled variations of this phenomenon should contribute to our better understanding of these forces.

EXPERIMENTAL PROCEDURE

The experiments have been performed with an all-glass "two-bulb" apparatus, both bulbs being of large volume, 2 liters, in order to have a sufficient amount of gas for a number of cycles of operation in spite of the low initial pressure of 4.6 cm of Hg set by the temperature of the cold bulb, −76°C. The two bulbs were connected by a 1-cm bore tube 34 cm long, containing a three-way stopcock also of 1-cm bore. Appropriate temperature baths maintained the bulbs at the required constant temperatures during each experiment. After some trials good data were

obtained for the temperature intervals 197°K–298°K, 197°K–373°K, and 298°K–457°K. These results are presented below.

Both to overwhelm any residual $N^{14}H$ mass peak (all NH_3 samples were converted to N_2 and analyzed for the N^{15}/N^{14} ratio) in the mass spectrometer and to develop larger changes in concentration in the thermal diffusion experiments, ammonia gas was prepared from samples of NH_4NO_3 in which the N of the ammonium radical was enriched in the N^{15} isotope. This "heavy" NH_4NO_3 was obtained from the Eastman Kodak Company and was diluted in every case with ordinary ammonium nitrate so that the prepared ammonia contained from 13 to 15 atom percent N^{15}. The NH_3 was obtained by slowly adding a concentrated solution of NaOH, the reaction taking place in a vacuum. The gas was condensed in a dry-ice trap and then thoroughly dried by vacuum distillations and drying agents. A sample of this ammonia was then taken for mass spectrometer analysis, and the two-bulb apparatus filled with the gas to a pressure of 4.6 cm of Hg. The hot and cold bulbs were then interconnected and allowed to come to equilibrium.

It can be shown that the relaxation time τ for this process is

$$\tau \cong (Vl/DA)[T_c/(T_h+T_c)], \qquad (1)$$

where V is the volume of one of the bulbs, l is the length, and A the cross section of the connecting tube, D is the coefficient of ordinary diffusion, and T_c and T_h are the temperatures of the cold and hot bulbs, respectively. For $T_c=197°$ and $T_h=373°$, τ is 3.2 hours. To insure that equilibrium was reached, the first thermal diffusion was continued for about five times this value of τ. The cold bulb was then isolated, and the ammonia pumped out of the hot bulb. Next, the connection between the two bulbs was reestablished and the process repeated. Since D is inversely proportional to the density, τ decreases

[5] L. G. Stier, Phys. Rev. 62, 548 (1942).
[6] H. Brown, Phys. Rev. 57, 242 (1940).
[7] H. Margenau and D. T. Warren, Phys. Rev. 51, 748 (1937).

TABLE I. Values of α and R_T for ammonia.

T_c °K	T_h °K	$c_2{}^0$	$c_1{}^0$	$c_2-c_2{}^0$	α	R_T
298	457	0.1379	0.8621	+0.0017	+0.0105±0.0051	+0.41±0.20
197	373	0.1525	0.8475	−0.0009	−0.0039±0.0035	−0.15±0.14
197	298	0.1419	0.8581	−0.0016	−0.0100±0.0063	−0.39±0.25
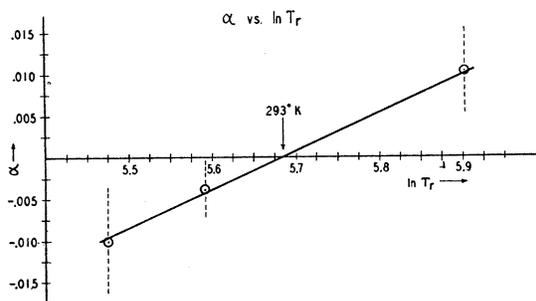
Fig. 1. Variation of the thermal diffusion constant α for ammonia with the logarithm of the absolute temperature.

proportionally with the pressure drop each time. This cycle of operations was repeated eight times in each experiment. For greater accuracy it would have been desirable to have repeated this process more than eight times, but there was a limitation on the initial amount of gas set by the vapor pressure of NH_3 at $-76°C$, and in the conversion to N_2 before analysis the pressure of the N_2 is only half that of the NH_3 converted. Before analysis we found it necessary to have this nitrogen in contact with a liquid-air trap for about 12 hours in order to condense all water vapor evolved in the conversion and any remaining non-oxidized ammonia.

The N^{15}/N^{14} ratios in the original and changed samples of gas were obtained by identical procedures using a modified Nier-type 60° mass spectrometer. Our modifications of Nier's original specifications[8] have been made to increase the stability of the instrument and to facilitate its operation. In order to be able to replace a burned-out filament more quickly, the filament stem is introduced into the side of the ion source. The electrometer tube is placed in a metal case in the evacuated system, with the ion collector placed at the top of the grid of the tube. The connections to the elements of the electrometer tube are brought into the case through the base of a 6L6 tube soldered into the metal case. Since this case may not be raised to as high a temperature as the other parts of the system during the preliminary baking out, its walls are cooled with water, ice, or dry ice to a constant lower temperature while in operation.

RESULTS

The experimental values of α may be calculated from the equilibrium concentrations of the two isotopic molecules in such a two-bulb experiment from the relation

$$\alpha = \frac{c_2 - c_2^0}{c_2^0 c_1^0 n} \times \frac{T_h/T_c + 1}{\ln (T_h/T_c)}, \qquad (2)$$

where c_2 is the concentration of N^{15} in the cold bulb, c_2^0 and c_1^0 are the concentrations of N^{15} and N^{14}, respectively, in the gas before the thermal diffusion began, n is the number of cycles of operation, and T_h and T_c are the temperatures of hot and cold bulbs, respectively. R_T, the index of intermolecular force, is taken to be the ratio of this experimental α to the hard sphere value $(105/118)[(m_1 - m_2)/(m_1 + m_2)]$. The latter is 0.0254 for this $N^{15}H_3$, $N^{14}H_3$ mixture. The measured concentrations and calculated α and R_T values are given in Table I.

The magnitude of the maximum possible error assigned to each of these α's needs explanation. For each temperature range only one thermal diffusion experiment is represented; the concentrations given are the average of at least ten determinations of the N^{15}/N^{14} abundance ratio in each case. The average deviation from the mean for this ratio in each case is about 0.0004, which makes the possible error for each $c_2 - c_2^0$ difference ± 0.0008. Improvement in this accuracy could have been made by averaging in data from additional runs, of course, but we feel that our values of α are considerably more accurate than would seem to be indicated by these tabulated possible errors. For in Fig. 1 in which these α's are plotted against $\ln T_r$, where

$$T_r = \frac{T_h T_c}{T_h - T_c} \ln \frac{T_h}{T_c} \qquad (3)$$

is the correct mean temperature[9] for the temperature interval $T_h - T_c$, it is evident that a linear relationship holds just as for neon and argon.[5] If Fig. 1 is changed into a R_T vs. $\ln T_r$ plot, the equation fitting the resulting straight line is

$$R_T = 1.9 \ln (T_r/293). \qquad (4)$$

[8] A. O. Nier, Rev. Sci. Inst. 11, 212 (1940).

[9] H. Brown, Phys. Rev. 58, 661 (1940).

TABLE II. Comparison of R_T values.

T_r	R_T obs.	$R_T(n)$ viscosity	R_T(Suth.) $C=500°$	R_T(Suth.) $C=370°$	R_T(L-J 9,5) $\epsilon/k=333°K$
366°	+0.41		−0.15	0	−0.27
268°	−0.15	−0.17	−0.30	−0.13	−0.41
239°	−0.39		−0.33	−0.22	−0.42

Of chief interest are the observed reversal in the sign of R_T at 293°K, the linear variation of R_T with ln T_r even though NH$_3$ is far from being a spherically symmetrical "hard" molecule like neon, and the size of the slope, 1.9, in Eq. (4) as compared to 0.25 for neon and argon.[5] These observations indicate a very rapid "softening" of the NH$_3$ molecule as the temperature decreases.

DISCUSSION

The temperature dependence of R_T as predicted by viscosity data and by the Sutherland and Lennard-Jones 9,5 molecular models has been considered by Jones.[4] Since the predictions on these models have been shown to be rather poor for neon and argon,[5] they could hardly be expected to hold for a polyatomic molecule such as ammonia. There is reason to believe, however, that the 9,5 model might be a fair approximation to the real intermolecular forces existing in ammonia. Comparison of such predicted R_T values with our observed values is made in Table II. For the theoretical relations upon which these calculations are based reference should be made to the paper by R. C. Jones.[4] The exponent n of T to give the coefficient of viscosity is taken to be approximately 1.1 in this entire temperature range.[10] From this a negative value of R_T close to that observed for our intermediate T_r is predicted. The Sutherland constant, $C=500°$, which appears in the equation for the viscosity, is also taken from reference 10, but Edwards'[11] experimental value, $C\cong370°$, for the range 15°C to 184°C yields values of R_T agreeing somewhat better with the observations. As for the Lennard-Jones 9,5 model, the prediction that $R_T=0$ for a temperature of 1.54 T_c or 625°K

[10] M. Trantz and R. Heberling, Ann. d. Physik 10, 155 (1931).
[11] R. S. Edwards and B. Worswick, Proc. Phys. Soc. 38, 16 (1925).

is in marked disagreement with the observed $T_r=293°K$ for the reversal point.

To describe adequately the intermolecular forces between dipole molecules such as ammonia no simple model would suffice. For there are in addition to the attractive forces arising from the dispersion effect which are common to all molecules and which vary as $1/R^7$, R being the distance between interacting molecules, (1) the dipole induction effect ($f\alpha 1/R^7$), (2) the alignment effect which depends on the rotational quantum number and hence on the temperature distribution of the molecules ($f\alpha \pm 1/R^7$ for large R but $\alpha 1/R^4$ for close approach), (3) resonance forces due to the possibility of exchange of a quantum of radiation if the interacting molecules have rotational quantum numbers differing by ± 1($f\alpha \pm 1/R^4$), and (4) the first-order forces between symmetrical top molecules carrying a dipole along their figure axis ($f\alpha \pm 1/R^4$). It has been shown by Margenau and Warren[7] that for NH$_3$ ($\mu=1.5\times 10^{-18}$ e.s.u.) these first-order forces (4) are greater than the second-order effect for linear dipoles over the main part of the range of the latter. And since for the repulsive part of these first-order forces the index is less than the critical value 5 for the Maxwellian case, for which the thermal diffusion effect is zero, they would have the tendency to make the thermal diffusion constant negative. Furthermore, all of these dipole-dipole forces (1)–(4) are temperature dependent, becoming more effective as the temperature is lowered because of lower molecular speeds and the concentration of the molecules into the few lower rotational quantum states.

Qualitatively it is thus clear why the thermal diffusion constant of ammonia becomes negative and why the molecule "softens" at such a rapid rate with decreasing temperature. More such measurements might yield considerable information about certain long-range van der Waals forces. It would be of interest, for example, to have similar data for a linear dipole molecule such as HCN for which the dipole moment is large but for which the symmetrical top effect is missing.