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TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENTS FOR GASEOUS AMMONIA

by Charles E. Baker
Lewis Research Center
Cleveland, Ohio

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16. Abstract

Diffusion measurements were made in a stainless-steel Loschmidt-type cell; temperature ranged between 301.3 and 445.6 K, and pressures varied between 408 and 729 torr. Ammonia-N-15 was used as the tracer gas with concentrations determined by mass spectrometry. The experimental results are in excellent agreement with theoretical values calculated from rigorous kinetic theory using the Stockmayer potential parameters obtained from recent viscosity data and with values obtained directly from experimental viscosities. These results suggest that simplifying assumptions made in the calculation of collision integrals for strongly orientation-dependent potentials such as the Stockmayer potential are valid.

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TEMPERATURE DEPENDENCE OF SELF-DIFFUSION COEFFICIENTS FOR GASEOUS AMMONIA

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SUMMARY

The collision integrals necessary for theoretical calculation of the transport properties of polar gases have been available since the early part of this decade. However, the validity of simplifying assumptions needed to make mathematically tractable calculation of collision integrals for strongly orientation-dependent potentials (such as the Stockmayer potential) has not been adequately tested because of the scarcity of reliable transport-property data. Measurement of the self-diffusion coefficient D_{11} of a strongly polar gas over a range of temperatures should provide such a test. This report gives results of recent measurements of D_{11} for gaseous ammonia between 301.3 and 445.6 K with pressures varying between 408 and 729 torr.

Measurements were made in a stainless-steel Loschmidt-type diffusion cell with a shear interface. The cell was mounted in a large oil bath maintained to within $\pm 0.02^{\circ}$ C. Ammonia-N-15 $\left({}^{15}NH_3\right)$ was used as the tracer gas, and the ${}^{15}NH_3$ concentrations following diffusion were determined by mass spectrometry.

The experimental values for D_{11} are in excellent agreement with theoretical values calculated from rigorous kinetic theory using the Stockmayer potential parameters obtained from recent viscosity data. The only measurments of D_{11} for ammonia reported previously were in marked disagreement with calculated values at low temperatures. Values of D_{11} which are effectively independent of any molecular model may be calculated directly from experimental viscosities. Diffusion coefficients obtained by this method are also in good agreement with the experimental results reported herein.

This research was undertaken to test the validity of the simplifying assumptions needed to make feasible calculation of collision integrals for strongly orientation-dependent potentials. For the case of highly polar ammonia over the indicated temperature range, the results reported herein strongly suggest that the present theory is indeed adequate even though simplifying assumptions were needed in its development.

INTRODUCTION

Even though polar gases play an important role in modern technology, relatively little study has been devoted to their transport properties. In particular, diffusion-coefficient data, which offer an excellent means for the determination of intermolecular forces, are in short supply. There are several reasons for this lack of data. Polar gases are generally difficult to handle experimentally; many are corrosive and react with, and/or are adsorbed on, the surfaces of the apparatus. They also may react with themselves (to form dimers or polymers) or with other polar gases. In addition, until the early part of this decade the experimentalist had no reliable theoretical values with which to compare his results because the necessary collision integrals based on a realistic potential model were not available. Monchick and Mason (ref. 1) provided the needed incentive by calculating these integrals for a modified (angle-independent) Stockmayer potential. This potential is a superposition of a dipole-dipole inverse r^3 interaction on the familiar Lennard-Jones (12:6) potential. It may be written as

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \delta\left(\frac{\sigma}{r}\right)^{3}\right] \tag{1}$$

where r is the molecular separation, ϵ the depth of the potential well and σ the molecular separation at zero interaction energy in the absence of dipole forces, and $\delta = (\mu^2/4\epsilon\sigma^3)\zeta$. Here, μ is the dipole moment and ζ is a function of the relative orientation of the colliding molecules.

In order to make the analysis of the dynamics involved in binary collisions between polar molecules mathematically tractable, Monchick and Mason (ref. 1) made two important assumptions. The first is that inelastic collisions, even though they may occur frequently, have little effect on the trajectories. Their justification for this assumption is based on the argument that most inelastic collisions involve the transfer of only a few quanta of rotational energy. For most molecules at ordinary temperatures this amount of energy is small compared to the translational energy, which is of the order of kT. Thus, they expect inelastic collisions to have only a small effect on the trajectories, and they neglect them.

Their second assumption concerns the effect of the orientation-dependent potential on the angle of deflection χ in a collision. They argue that although the orientation-dependent forces act along the whole trajectory, the angle of deflection is determined primarily by the interaction in the vicinity of the distance of closest approach. Because the average time required to complete a collision is of the same order of magnitude as the average rotation time, over a small range near the distance of closest approach, it seems unlikely that the relative orientation would change much. The result is that in each collision χ is determined largely by only one relative orientation, and they evaluate χ as if the orientation were fixed at one value throughout the entire collision. Thus, different collisions will correspond to different fixed orientations.

These two assumptions change the analysis of orientation-dependent forces from a difficult collision dynamics problem to one that is mathematically manageable. However, the kinetic-theory problem now corresponds to a gas in which collisions follow not one intermolecular force law, but any one of a very large number of force laws, one for each relative orientation. The formal kinetic-theory expressions for the transport coefficients which result from the solution of this problem are the same as for a single interaction potential, but the collision integrals appearing in these expressions are averages over all possible force laws. In these averages, equal weight has been assigned to each orientation or force law.

How well do the results of this somewhat simplified theoretical treatment agree with experiment? Monchick and Mason (ref. 1) concluded that the 12-6-3 potential model worked about as well for polar gases as the 12-6 potential model does for nonpolar gases, as far as they could tell from the available data. However, we have already emphasized that there is a general paucity of data for the transport properties of polar gases. In addition to the intrinsic value of the data itself, measurement of the self-diffusion coefficient of a strongly polar gas over a range of temperatures should provide a test of the validity of the simplifying assumptions necessary for calculation of the collision integrals for strongly orientation-dependent potentials. Furthermore, these measurements should also test the ability of the Stockmayer potential (which represents a polar molecule simply as a spherical potential with a point dipole embedded at the center) to describe the interaction of polar gases. This report gives results of recent measurements of the self-diffusion coefficient for gaseous ammonia over the temperature range 301.3 to 445.6 K.

EXPERIMENTAL APPARATUS AND PROCEDURE

Of all the methods that have been used to measure diffusion coefficients, the Loschmidt method is generally recognized as the most suitable for accurate work in the gaseous phase (ref. 2). For this reason, this method was chosen for the work reported herein. Briefly, the Loschmidt method involves placing the gases to be studied in separate, but identical, tubes of uniform cross section. Diffusion is started by joining the two tubes in such a way that the boundary between them is not unduly disturbed, and is terminated after a suitable time by separating the two half-cells. The average concentration of the reference substance in each half-cell is then determined. With this information and a knowledge of the geometry of the apparatus, it is then possible to calculate the diffusion coefficient for the particular temperature and pressure of the experiment.

The Loschmidt-type diffusion cell used in this work is shown schematically in figure 1. The cell was constructed of hardened 17-4-PH stainless steel, which permits its use with corrosive gases. Each half-cell consists basically of a 6-inch-diameter plate of 1-inch thickness to which a tube of uniform inside diameter (1.129±0.0005 in.) is welded. A hole with a diameter equal to the inside diameter of the tube was cut through the plate and the mating surface of the half-cell carefully ground and lapped. A system

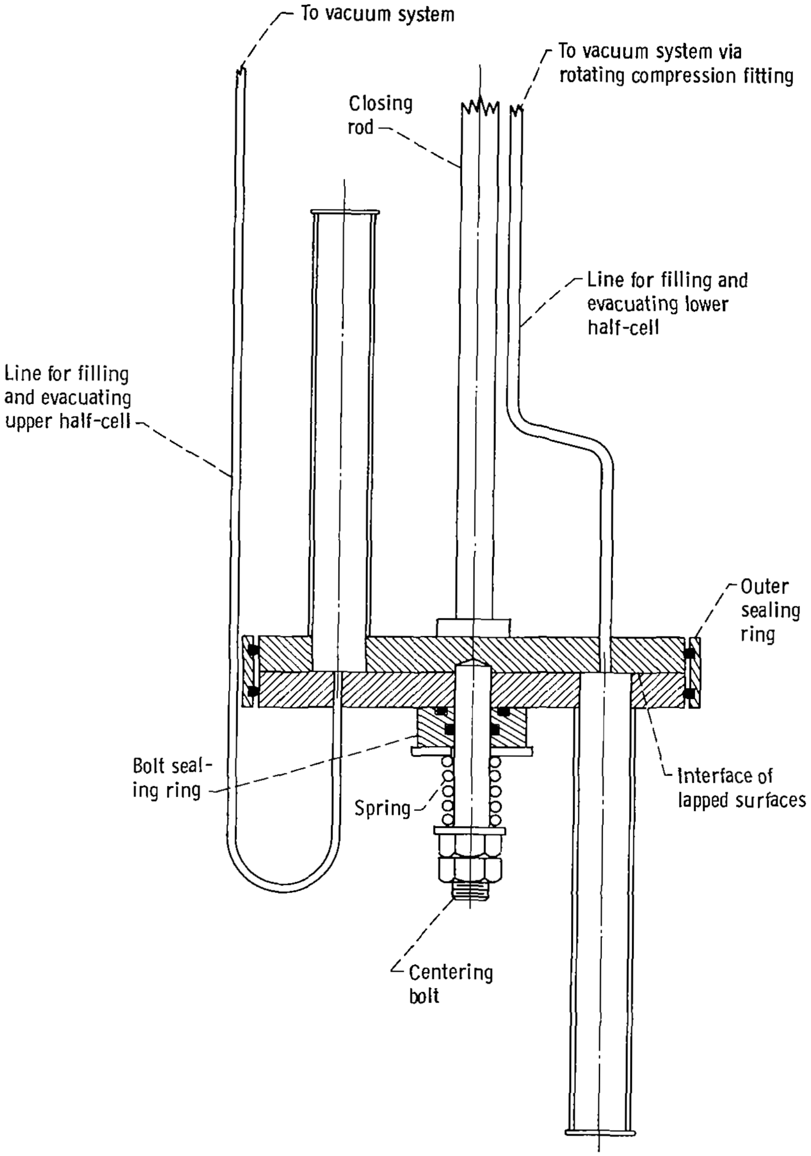

Figure 1. - Schematic of diffusion cell.

of stops allows the two half-cells to be placed in any one of three positions relative to each other. The "fill" position is shown in figure 1 and is used when pumping out the half-cells or filling them with the test gases. In the "mid" position none of the tubes are alined, while in the "diffusion" position the two half-cells form one uniform tube. In this position the inside length of the diffusion cell was 60.866 centimeters, originally. However, because several relappings were required, the cell measured only 60.813 centimeters at the conclusion of the work. This change of length following each relapping was accounted for in the diffusion calculations.

In order to ensure a vacuum-tight seal and to prevent damage to the lapped surfaces, a thin layer of high-temperature silicone stopcock grease was used on the metal surfaces and the plates were spring mounted at the centering bolt. The lower half-cell remained fixed during the turning procedure, while the upper half-cell was rotated by means of the closing rod shown in figure 1. A four-O-ring rotating compression fitting mounted above the centerline of the closing rod conveniently solved the problem of movement of the line to the lower half-cell during turning of the upper half-cell.

The original Loschmidt method had the disadvantage of using a diaphragm to separate the gases in the two half-cells. The volume of the diaphragm could not be made equal to zero; when the two half-cells were connected, gas rushed in to fill this volume causing some mixing which was not due to ordinary diffusion. With the present apparatus, the two half-cells are connected by means of a shear interface technique, and turbulence caused by alining the two half-cells is minimized.

The diffusion cell was mounted in a large capacity constant temperature bath which could be controlled to within ±0.02° C. Temperature was measured with a platinum resistance thermometer. A commercially available polyalkylene glycol "synthetic oil" was used as the thermostat fluid. Pressures of the test gases, which ranged between 408 and 729 torr, were measured with a differential precision dial manometer with readability to within 0.25 torr. Diffusion times were measured with a standard electric timer which could be read to within 0.01 second. Since the two half-cells are interconnected by rotating the top half-cell at reasonably constant angular velocity, rather than instantaneously, diffusion actually starts as soon as the two half-cells begin to overlap. Thus, the question arises as to what is zero time for the process. A calculation for zero time similar to the one given in detail by Strehlow (ref. 3) shows that the timing should be started when the angle between the centers of the two half-cells is 17.3°. The diffusion experiments reported herein were timed in this manner.

The only parts of the diffusion cell not already discussed are the outer sealing ring and bolt sealing ring shown in figure 1. These became necessary when it was found that, despite the quality of the lapped surfaces, at elevated temperatures the thermostatic fluid found its way into the interface (and thence into the lower half-cell) although the apparatus had been leak-tight in air at room temperature. The outer sealing ring contains two high temperature silicone rubber O-rings; one O-ring contacts the upper plate, and the other the lower plate, so that the interface is isolated from contact with the bath fluid that could have entered from the outer edge. The bolt sealing ring, which also contains two silicone rubber O-rings, prevents fluid from entering the interface via the bolt hole in the lower plate. This system of O-rings completely solved the problem of fluid leakage into the lower half-cell.

The gas-handling system used in these experiments was constructed of glass and was conventional in all respects. Both the ordinary ammonia $\left(^{14}NH_3\right)$ and the isotopically substituted ammonia $\left(^{15}NH_3\right)$ used in this work were of high chemical purity (99.99 percent min.). However, any noncondensibles were removed by freezing the ammonia with liquid nitrogen, pumping on the condensate, then bringing the ammonia to room temperature. This procedure was repeated several times. The mixtures of 85 to 90 percent $^{14}NH_3$ and 10 to 15 percent $^{15}NH_3$ were made up by the method of partial pressures. However, as will be seen later, it was not necessary to know the initial concentration of $^{15}NH_3$ in the mixture in order to calculate the diffusion coefficient.

Attempts to mass analyze the ammonia mixtures obtained after diffusion were unsuccessful. This was probably due to the highly polar nature of ammonia, which causes it to adsorb on the surfaces of the mass spectrometer inlet system. This problem was solved by completely decomposing the ammonia mixture on a heated platinum filament ($\sim 1200^{\circ}$ C). The resulting mixture contained nitrogen molecules of masses 28, 29, and 30, plus hydrogen. By scanning masses 28, 29, and 30 it was possible to calculate the percentage $^{15}NH_3$ in the ammonia mixture prior to decomposition.

A typical diffusion run was carried out according to the following procedure: The nitrogen with which the diffusion cell was filled when the apparatus was not in use was pumped out. Ammonia was then added directly from the storage cylinder, pumped out, and again added to 750 torr. This ammonia was allowed to stand in the cells for at least 1 hour. This procedure was followed to ensure against the presence in the upper half-cell of any $^{15}NH_3$ from an earlier run. (In the subsequent calculation of the diffusion coefficient for a given run, the concentration of $^{15}NH_3$ in the upper half-cell was assumed to be 0.37 percent, which is the natural isotopic abundance of ^{15}N (ref. 4).) This ammonia was then pumped out of the upper half-cell and previously purified ammonia added to the desired diffusion pressure. The lower half-cell was then pumped out and filled to this same pressure with the $^{14}NH_3$-$^{15}NH_3$ mixture. After several minutes the two half-cells were briefly connected externally to make certain that the pressure in both half-cells was identical. The upper half-cell was then rotated to the mid-position. After at least 15 minutes of equilibration, diffusion was started by rotating the upper half-cell until the half-cells were alined. During the diffusion period several determinations of the bath temperature were made and recorded. After the desired diffusion time, the half-cells were put back into midposition, both filling lines evacuated, and the half-cells put into fill position. The entire contents of each half-cell was then frozen into sample bottles via separate glass lines. Later, a portion of each sample was decomposed over the heated platinum filament, and the resulting mixtures of $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$ (as well as hydrogen which does not interfere with the analysis) were mass analyzed.

EXPERIMENTAL RESULTS

The first part of this section will describe the steps required to obtain self-diffusion coefficients D_{11} from the experimental data. These steps are (1) to determine the percent ^{15}N in the diffusion samples from the mass spectrometer peak heights, (2) to get the mutual-diffusion coefficient D_{12} from the results of mass analysis, and (3) to calculate D_{11} from D_{12}.

For step (1), the following equation is used:

$$\text{Percent } {}^{15}N = \frac{h_{30} + \frac{1}{2} h_{29}}{h_{28} + h_{29} + h_{30}} \times 100 \qquad (2)$$

where h is the peak height at the mass given by the subscript. Because this analysis is concerned with isotopes of the same chemical species, it is not necessary to bring instrument sensitivity (which varies from day to day) into the calculation. Thus, the accuracy of the concentration determination is enhanced.

Once the concentration of $^{15}NH_3$ (which is the same as the concentration of ^{15}N) in both half-cells after a given diffusion time is determined, D_{12} at the experimental pressure is calculated from the following relation (ref. 5):

$$\left(D_{12}\right)_p = -\frac{L^2}{\pi^2 t} \ln\left[\frac{\pi^2}{8}\left(\frac{n_B - n_T}{n_B + n_T - 2n_T^o}\right)\right] \qquad (3)$$

where L is the length of the diffusion tube in centimeters, t is the time of diffusion in seconds, n_T and n_B are the average concentrations of $^{15}NH_3$ in the top and bottom half-cells after diffusion, and n_T^o is the concentration of $^{15}NH_3$ in the top half-cell before diffusion, which is taken to be 0.37 percent as previously noted. This equation is accurate to better than 1 part per thousand as long as the dimensionless quantity $\left(D_{12}\right)_p t\pi^2/L^2$ is kept equal to, or greater than, 0.6. In these experiments the diffusion time and pressure were always adjusted so that this requirement was satisfied. Equation (3) gives D_{12} at the experimental pressure which usually varies from run to run. Thus, it is convenient to convert the $(D_{12})_p$ values to $(D_{12})_{atm}$ using the relation: $(D_{12})_{atm} = p(D_{12})_p/760$ where p is in millimeters of mercury (torr).

Since the experiment actually measures the diffusion of $^{15}NH_3$ into $^{14}NH_3$, whereas the self-diffusion coefficient of ammonia refers to the diffusion of $^{14}NH_3$ into itself, an isotopic correction must be applied to the D_{12} values. This correction is obtained by dividing the rigorous kinetic-theory expression for D_{11} by the similar expression for D_{12} (ref. 6) and is as follows:

$$D_{11} = \left(\frac{2M_2}{M_1 + M_2}\right)^{1/2} \cdot D_{12} \tag{4}$$

where M_1 is the molecular weight of $^{14}NH_3$ (17.032) and M_2 is the molecular weight of $^{15}NH_3$ (18.033). For the $^{14}NH_3$-$^{15}NH_3$ system the ratio of D_{11} to D_{12} is 1.01417.

At the time the current research was initiated, no measurements of D_{11} for ammonia had been reported. Because of the difficulties encountered when working with polar gases, it seemed desirable to checkout the apparatus by measuring the mutual diffusion coefficient of a nonpolar gas pair for which diffusion data was available. The carbon dioxide - nitrous oxide system satisfies these requirements; moreover, diffusion experiments on this gas pair give a close approximation to self-diffusion because of their striking physical similarity (ref. 7).

The mutual diffusion coefficients obtained for this gas pair between 325.0 and 475.5 K are listed in table I and shown graphically in figure 2. The current results are

TABLE I. - EXPERIMENTAL MUTUAL-DIFFUSION COEFFICIENTS

FOR CARBON DIOXIDE - NITROUS OXIDE SYSTEM

Temperature, K	Mutual-diffusion coefficient, D_{12}, cm^2/sec (referred to 1 atm)	Temperature, K	Mutual-diffusion coefficient, D_{12}, cm^2/sec (referred to 1 atm)
325.0	0.139	403.5	0.209
327.3	.141	422.7	.233
347.7	.157	432.1	.240
374.3	.184	433.5	.237
382.9	.194	443.2	.251
383.0	.192	444.0	.256
393.5	.201	475.5	.284

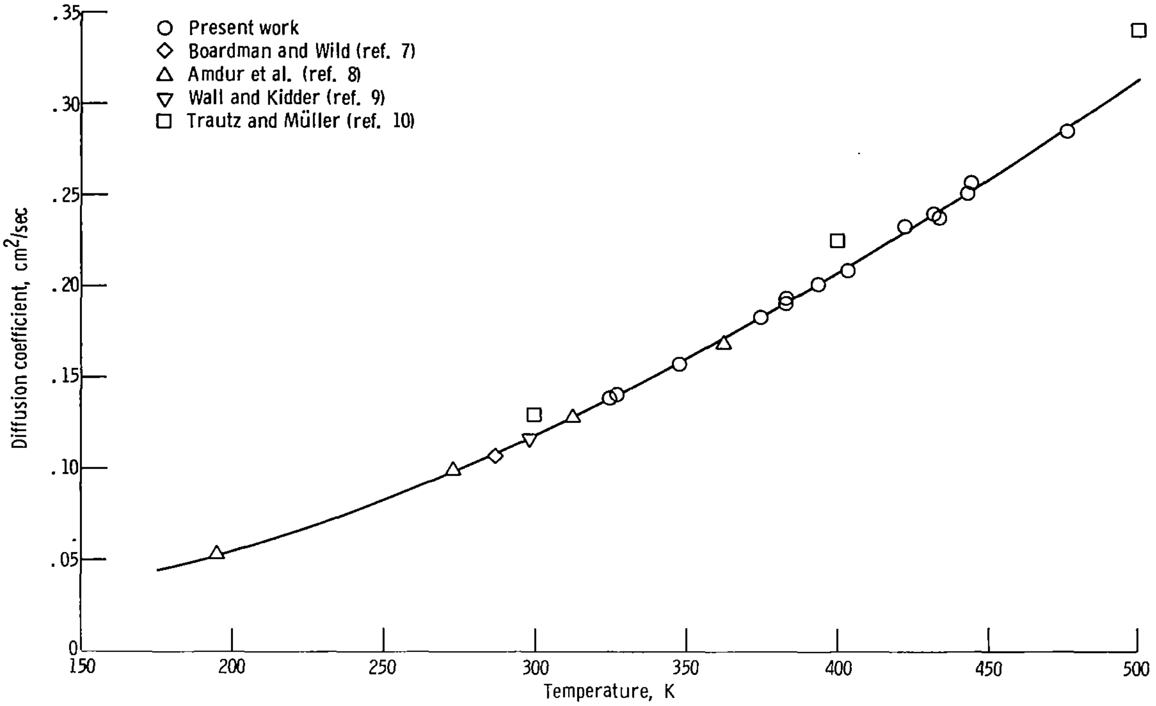

Figure 2. - Diffusion coefficients for carbon dioxide - nitrous oxide system as function of temperature.

in excellent agreement with the available data (refs. 7 to 10) with the exception of the three points obtained by Trautz and Müller (ref. 10). Their values are 9 to 10 percent higher than the values obtained from a smooth curve drawn through the rest of the data, and this suggests a systematic error in their work. Trautz and Müller's diffusion data for the ammonia-nitrogen and ammonia-hydrogen gas pairs were also found to be much higher (about 11 percent) than the careful measurements of Bunde (ref. 11) for these same two systems. Thus, it seems very likely that there was a systematic error in their experiments reported in reference 10, and their data for CO_2-N_2O can be disregarded. The agreement between the results reported herein and the remaining data indicates that the apparatus used in this work is capable of producing reliable diffusion data over a useful temperature range.

The experimental results for the ammonia diffusion are presented in table II. All the data necessary for calculating $\left(D_{12}\right)_p$ for each run are also included. The average value for D_{11} at each temperature is listed in the last column of table II, and these results are plotted against temperature in figure 3. The only measurements of D_{11} for ammonia reported previously are those of Paul and Watson (ref. 12) using the two-bulb modification of the Loschmidt method. Their results (published after the checkout of this apparatus) are also shown on figure 3.

TABLE II. - EXPERIMENTAL SELF-DIFFUSION COEFFICIENTS FOR AMMONIA

Temperature, K	Pressure, p, mm Hg	Diffusion time, sec	Percent $^{15}NH_3$ after diffusion		Mutual-diffusion coefficient, D_{12}, cm^2/sec		Self-diffusion coefficient, D_{11}, cm^2/sec	
			Lower half-cell	Upper half-cell	At pressure, p	At atmospheric pressure	At atmospheric pressure	Mean
301.3	580.0	901.73	8.497	3.559	0.257_6	0.196_6	0.199_4	0.200±0.001
	551.0	901.98	7.759	3.400	$.275_0$	$.199_4$	$.202_2$	
	408.0	632.39	7.838	3.308	$.368_6$	$.197_9$	$.200_7$	
	492.0	731.93	7.131	2.945	$.303_4$	$.196_4$	$.199_2$	
326.4	649.5	834.57	11.830	4.773	0.269_4	0.230_3	0.233_5	0.233±0.002
	650.5	833.78	11.522	4.631	$.267_5$	$.228_9$	$.232_2$	
	729.0	934.96	9.310	3.823	$.242_4$	$.232_5$	$.235_8$	
	699.5	903.96	8.112	3.327	$.246_6$	$.226_9$	$.230_2$	
348.7	648.75	743.18	6.539	2.773	0.308_9	0.263_6	0.267_4	0.268±0.001
	648.75	684.03	6.008	2.454	$.310_1$	$.264_7$	$.268_5$	
	698.5	783.58	8.867	3.671	$.291_8$	$.268_2$	$.272_0$	
	697.5	784.68	8.645	3.553	$.287_1$	$.263_5$	$.267_2$	
373.8	700.5	682.46	7.498	3.138	0.334_8	0.308_6	0.313_0	0.308±0.003
	700.5	683.00	7.335	3.059	$.331_6$	$.305_6$	$.310_0$	
	651.5	632.54	7.452	3.053	$.348_0$	$.298_3$	$.302_5$	
	653.0	633.28	7.241	3.000	$.353_1$	$.303_4$	$.307_7$	
397.3	651.0	563.01	8.783	3.563	0.392_0	0.335_7	0.340_5	0.343±0.002
	651.0	563.05	8.539	3.486	$.395_0$	$.338_3$	$.343_1$	
	700.5	603.44	8.295	3.401	$.370_1$	$.341_1$	$.346_0$	
422.9	651.0	503.49	8.343	3.505	0.462_3	0.396_0	0.401_6	0.399±0.003
	651.5	503.25	8.214	3.457	$.463_1$	$.397_0$	$.402_6$	
	700.5	543.00	8.100	3.333	$.419_9$	$.387_1$	$.392_6$	
	700.0	543.15	7.857	3.307	$.427_1$	$.393_4$	$.399_0$	
445.6	701.5	454.73	7.971	3.188	0.468_6	0.432_5	0.438_6	0.441±0.001
	700.5	456.65	7.762	3.134	$.472_6$	$.435_6$	$.441_7$	
	700.0	513.75	7.482	3.246	$.472_4$	$.435_1$	$.441_3$	

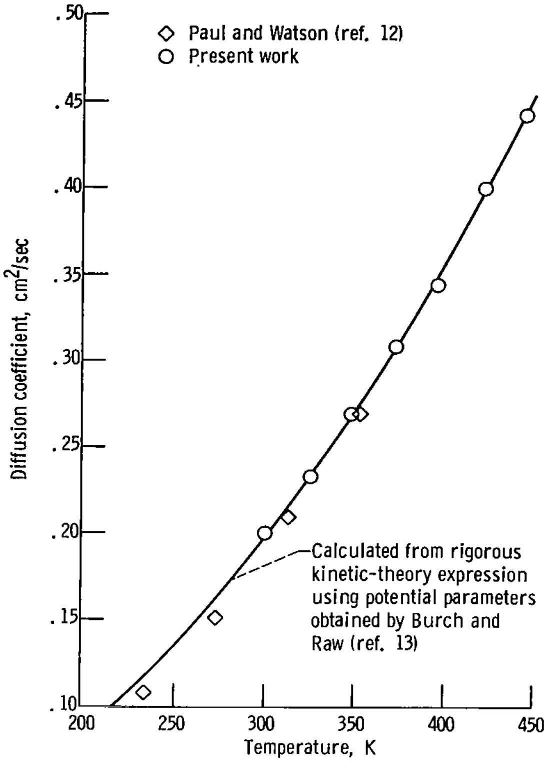

Figure 3. - Comparison of experimental self-diffusion coefficients for ammonia with theory and with literature values.

ANALYSIS AND DISCUSSION

Theoretical values of the self-diffusion coefficient of polar gases may be obtained from the rigorous kinetic-theory expression for D_{11} using collision integrals calculated for the modified (angle-independent) Stockmayer potential (ref. 1). The parameters for this potential, which must be known in order to obtain the appropriate collision integrals, are generally obtained by fitting experimental viscosity data. Viscosity data are more available and are usually more accurate and precise than the other transport property data. Self-diffusion coefficients may also be obtained directly from viscosity data using the well-known relation (ref. 6):

$$\frac{\rho D_{11}}{\eta_{11}} = \frac{6}{5}\langle A_{11}^{*}\rangle \tag{5}$$

where ρ is the density, η_{11} is the viscosity, and $\langle A_{11}^{*}\rangle$ is a ratio of collision integrals (essentially the ratio of the viscosity and diffusion cross sections). Because $\langle A^*_{11} \rangle$ is quite insensitive to temperature and the details of the intermolecular force law, at least for spherically symmetric potentials, equation (5) yields D_{11} from experimental viscosity which is effectively independent of any molecular model.

Values of D_{11} obtained from the rigorous kinetic-theory expression and from equation (5) are given in table III along with the experimental values. The third column of table III gives the results obtained using the Stockmayer potential parameters determined by Burch and Raw from their recent viscosity data (ref. 13). The solid curve shown in figure 3 is the result of plotting these D_{11} values against temperature. The fourth column gives results obtained by this same method using the potential parameters determined by Monchick and Mason (ref. 1) from earlier viscosity data.

With the exception of the point at 397.3 K (see fig. 3), the experimental D_{11} values reported herein are in excellent agreement with the theoretical values obtained using Burch and Raw's potential parameters. The experimental values of Paul and Watson are lower than the current results and the theoretical values. Paul and Watson (ref. 12) state that there is marked disagreement between observed and calculated val-

TABLE III. - COMPARISON OF EXPERIMENTAL SELF-DIFFUSION COEFFICIENTS FOR AMMONIA WITH THOSE CALCULATED FROM VISCOSITY DATA AND FROM RIGOROUS KINETIC THEORY

[Pressure, 1 atm.]

Temperature, K	Self-diffusion coefficients, D_{11}, cm^2/sec			
	Experimental	Calculated[a]	Calculated[b]	Calculated (eq. (5))[c]
301.3	0.200±0.001	0.200	0.198	0.195
326.4	.233±0.002	.235	.233	.230
348.7	.268±0.001	.269	.266	.264
373.8	.308±0.003	.309	.305	.305
397.3	.343±0.002	.350	.345	.346
422.9	.399±0.003	.397	.391	.393
445.6	.441±0.001	.441	.434	.438

[a] Calculated by using the Stockmayer potential parameters obtained by Burch and Raw: $\delta_{max} = 0.68$, $\epsilon/k = 431$ K, $\sigma = 2.99$ Å.

[b] Calculated by using the Stockmayer potential parameters obtained by Monchick and Mason: $\delta_{max} = 0.70$, $\epsilon/k = 358$ K, $\sigma = 3.15$ Å.

[c] Values of $\langle A^*_{11} \rangle$ used in eq. (5) were taken from ref. 1 using the Stockmayer potential parameters obtained by Burch and Raw (ref. 13).

ues at low temperatures, and they explain this discrepancy in terms of dimerization. However, the diffusion coefficients obtained in this work show no tendency toward being low in the temperature range where the data overlap.

It is interesting to observe in table III that, with the exception of the results at 397.3 and 422.9 K, the experimental coefficients are equal to or lie between the two theoretical values. The value at 397.3 K definitely appears inconsistent with both theory and the other experimental points from this work. The low results for the several different determinations at this temperature were probably caused by instability of the mass spectrometer during these particular analyses.

The last column of table III lists the diffusion coefficients obtained directly from the viscosity data of Burch and Raw (ref. 13) using equation (5), which effectively gives D_{11} without any assumption as to the nature of the molecular interactions. These values are only slightly lower than the other values below 326.4 K, and are in excellent agreement above this temperature. Thus, the experimental results are generally in excellent agreement with values obtained theoretically using viscosity data and assuming a Stockmayer potential, as well as with values obtained directly from viscosity data.

CONCLUDING REMARKS

In addition to obtaining data which is important in its own right, the purpose of this research was to test the validity of the simplifying assumptions that Monchick and Mason found it necessary to make in order to calculate the collision integrals for strongly orientation-dependent potentials. If these assumptions are valid, and if the Stockmayer potential adequately describes the interaction of strongly polar gases, it should be possible to calculate reliable diffusion coefficients using existing rigorous kinetic-theory and potential parameters obtained from another transport property, such as viscosity. For the case of highly polar ammonia, the excellent agreement between the experimental self-diffusion coefficients obtained in this research and those calculated from different sets of viscosity data strongly suggests that the theory is indeed adequate even though simplifying assumptions were necessary in the course of its development.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 19, 1969,
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