CHAPTER I

THERMAL CONDUCTIVITY OF GASEOUS AMMONIA AT DIFFERENT TEMPERATURES
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Abstract.

Thermal conductivity of the polar gas ammonia at a pressure of 18 cm of Hg has been measured over the temperature range 38 - 200°C by the hot-wire method. With the help of a theory recently put forward by Mason and Monchick, the collision numbers for rotational relaxation $Z_{rot}$ have been determined from the experimental data. The values thus obtained show that $Z_{rot}$ increases with rise of temperature.

Introduction.

The problem of heat transfer in polar gases has received considerable interest in recent years. The coefficient of thermal conductivity for monatomic gases and gas mixtures may be calculated on the basis of rigorous Chapman-Enskog theory. But the heat conductivity of polyatomic gases (nonpolar or polar), which involves inelastic collisions between the molecules, cannot be explained with the help of the classical theory. Eucken was the first to take into consideration the contribution of internal degrees of freedom to the heat transfer. According to him this can be expressed in the following way:
classical formula of Wang Chang and Uhlenbeck, they have derived an expression for $f$, which contains an approximation term involving relaxation times for various internal degrees of freedom. In extending their calculation to polar gases they have assumed that in such cases the resonant exchange of rotational energy becomes important. This type of energy exchange may also occur in the case of nonpolar polyatomic gases, but its cross section is large for polar gases on account of their long range dipole interactions. They have suggested that a correction is to be made for this resonant collision by replacing $D$ by $D_{\text{int}}$, where

$$D_{\text{int}} = D \left[ 1 + \left( \frac{Z'}{Z_0} \right) \right]^{-1}.$$  \hspace{1cm} \ldots (2)

Expressions for $Z'/Z_0$ have been formulated by them for various types of polar molecules. Thus for polar molecules the expression for $f$ becomes

$$f_{M-M} = \frac{1}{C_v} \left[ \frac{5}{2} C_{v,\text{trans}} + \frac{P_{\text{Dint}}}{\gamma} C_{v,\text{int}} \right. \left. - \frac{2}{\gamma} \left( \frac{5}{2} - \frac{P_{\text{Dint}}}{\gamma} \right)^2 \sum \frac{c_k}{Z_k} \right], \hspace{1cm} \ldots (3)$$

where $c_k$ is the specific heat for the $k$th mode and $Z_k$ is the corresponding collision number. In the present case we have considered only the rotational modes since $Z$ is large for other modes. It is further assumed that the specific heat $C_{v,\text{rot}}$ corresponding to the rotational mode
In this paper the values of $Z_{\text{rot}}$ for ammonia at different temperatures have been calculated using the above relation and setting $f = f_{\text{exp}}^2 = \frac{\rho_{\text{int}}}{\eta}$ in a similar way to that of Baker and De Hass\textsuperscript{10} for $\text{SO}_2$. These values of $Z_{\text{rot}}$ have been compared with those obtained from a recent theory of Sather and Dahler\textsuperscript{11}. The details of the method have been discussed later.

**Apparatus and Theory.**

The thick wire variant of the hot-wire method has been employed for the measurement of thermal conductivity. The theory and the procedure of the method have already been discussed\textsuperscript{12-14}. The design of the cell is similar to that used by Srivastava and Saxena\textsuperscript{15}. Only the perspex seal has been replaced by a teflon seal. The bore of the cell used is uniform to one thousandth of an inch over the whole effective length of the conductivity cell. Constants of conductivity cell are given in Table 1.

\[
Z_{\text{rot}} = \frac{3}{\eta} \left( \frac{5}{2} - \frac{\rho_{\text{int}}}{\eta} \right)^2 \frac{R}{C_v} \left[ \frac{\rho_{\text{int}}}{\eta} + \frac{3}{2} \left( \frac{5}{2} - \frac{\rho_{\text{int}}}{\eta} \right) \frac{R}{C_v} - f_{M-M} \right]^{-1} \quad \ldots (4)
\]
Table 1. Constants of thermal conductivity cell at different temperatures.

<table>
<thead>
<tr>
<th>Constants</th>
<th>Temperature in °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>38</td>
</tr>
<tr>
<td>Thermal conductivity $\lambda$</td>
<td>0.1672</td>
</tr>
<tr>
<td>of the wire in cal/cm. sec. °C.</td>
<td></td>
</tr>
<tr>
<td>Temperature coefficient of resistance $\alpha$ of the platinum wire in °C$^{-1}$</td>
<td>0.00301</td>
</tr>
<tr>
<td>Resistance of the cell wire in ohms.</td>
<td>0.96045</td>
</tr>
<tr>
<td>Cell Constants (1-C)</td>
<td>...</td>
</tr>
<tr>
<td>Length of the cell wire ($2l$)</td>
<td>.......</td>
</tr>
<tr>
<td>Radius of the cell wire ($r_1$)</td>
<td>.......</td>
</tr>
<tr>
<td>Internal diameter of the tube ($2r_2$)</td>
<td>.......</td>
</tr>
<tr>
<td>Outer diameter of the tube ($2r_3$)</td>
<td>.......</td>
</tr>
</tbody>
</table>
Experimental Results.

A typical set of observations taken at 80, 100, and 120°C is given in Table II. In this table $K_u$ is the apparent thermal conductivity, and $K'$ is that obtained after reduction to the bath temperature and making corrections for nonradial flow, radiation loss, temperature jump, and wall effects. $\lambda$ is the thermal conductivity obtained after correcting the mean value of $K'$ for the asymmetry in the cell construction by the relation $\lambda = K' (1 - C)$. The factor $(1 - C)$ was obtained by calibrating the cell with argon at 60, 80, 120, and 180°C taking the data of Kannuluik and Carman as standard. The values of thermal conductivity of argon obtained by interpolation and used for calibrating the cell at the above mentioned temperatures are $4.62 \times 10^{-5}$, $4.32 \times 10^{-5}$, $5.24 \times 10^{-5}$, and $5.81 \times 10^{-5}$ cal/cm sec °C, respectively. The average value of $(1 - C)$ was used over the entire range of temperature as the values showed no systematic change.

Gaseous ammonia used in this experiment was prepared in this laboratory in a similar way to that of Srivastava and Srivastava. The purity of the sample was tested by means of mass spectrometer. The experimental thermal conductivity data thus obtained were smoothed out and are recorded in column 5 of Table III. The maximum
Fig. 1. Comparison of experimental values of Thermal Conductivity obtained from different sources.
<table>
<thead>
<tr>
<th>T °C</th>
<th>I in mA</th>
<th>(R-R₀) in Ω</th>
<th>Kᵤ x 10⁵</th>
<th>K' x 10⁵</th>
<th>Kₘₑᵃₙ x 10⁵</th>
<th>λ x 10⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>111.71</td>
<td>0.00985</td>
<td>7.484</td>
<td>7.359</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>123.45</td>
<td>0.01205</td>
<td>7.491</td>
<td>7.341</td>
<td>7.354</td>
<td>7.317</td>
</tr>
<tr>
<td></td>
<td>135.46</td>
<td>0.01409</td>
<td>7.500</td>
<td>7.362</td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>110.54</td>
<td>0.00831</td>
<td>8.189</td>
<td>8.040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>124.83</td>
<td>0.01188</td>
<td>8.204</td>
<td>8.030</td>
<td>8.033</td>
<td>7.993</td>
</tr>
<tr>
<td></td>
<td>137.35</td>
<td>0.01437</td>
<td>8.230</td>
<td>8.030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>119</td>
<td>119.47</td>
<td>0.01050</td>
<td>8.935</td>
<td>8.750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>124.80</td>
<td>0.01151</td>
<td>8.905</td>
<td>8.730</td>
<td>8.740</td>
<td>8.696</td>
</tr>
<tr>
<td></td>
<td>138.01</td>
<td>0.01405</td>
<td>8.941</td>
<td>8.740</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Table III: Rotational collision number at different temperatures

<table>
<thead>
<tr>
<th>T°C</th>
<th>C_W/R</th>
<th>Z'/Z_o</th>
<th>( \rho \text{D}_{\text{int}} / \eta )</th>
<th>( \lambda_{\text{exp.}} \times 10^5 )</th>
<th>( f_{\text{exp.}} )</th>
<th>( Z_{\text{rot}} ) (calc.)</th>
<th>( Z_{\text{rot}} ) (theor.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>3.310</td>
<td>0.130</td>
<td>1.1690</td>
<td>6.040</td>
<td>1.465</td>
<td>1.665</td>
<td>5.530</td>
</tr>
<tr>
<td>60</td>
<td>3.380</td>
<td>0.117</td>
<td>1.1385</td>
<td>6.697</td>
<td>1.480</td>
<td>1.700</td>
<td>5.974</td>
</tr>
<tr>
<td>80</td>
<td>3.448</td>
<td>0.103</td>
<td>1.2000</td>
<td>7.306</td>
<td>1.494</td>
<td>1.709</td>
<td>6.292</td>
</tr>
<tr>
<td>100</td>
<td>3.520</td>
<td>0.092</td>
<td>1.2125</td>
<td>7.990</td>
<td>1.520</td>
<td>1.866</td>
<td>6.760</td>
</tr>
<tr>
<td>120</td>
<td>3.593</td>
<td>0.082</td>
<td>1.2237</td>
<td>8.684</td>
<td>1.540</td>
<td>2.000</td>
<td>7.038</td>
</tr>
<tr>
<td>140</td>
<td>3.664</td>
<td>0.074</td>
<td>1.2334</td>
<td>9.405</td>
<td>1.550</td>
<td>2.073</td>
<td>7.325</td>
</tr>
<tr>
<td>160</td>
<td>3.740</td>
<td>0.067</td>
<td>1.2442</td>
<td>10.120</td>
<td>1.560</td>
<td>2.144</td>
<td>7.466</td>
</tr>
<tr>
<td>180</td>
<td>3.815</td>
<td>0.061</td>
<td>1.2484</td>
<td>10.895</td>
<td>1.570</td>
<td>2.299</td>
<td>7.582</td>
</tr>
<tr>
<td>200</td>
<td>3.892</td>
<td>0.055</td>
<td>1.2550</td>
<td>11.715</td>
<td>1.590</td>
<td>2.628</td>
<td>7.745</td>
</tr>
</tbody>
</table>
deviation of the smoothed out values from the observed
data is not more than 0.15%. A comparison of the present
data with those obtained by previous workers$^{17-21}$ is
presented in Fig. 1. It is evident from the figure that
the agreement with previous workers is quite good at
ordinary temperatures, but at higher temperatures our
values are slightly higher than the recent values of
Richter and Sage$^{21}$. This difference which is (2 - 3%) more than the experimental errors cannot be resolved
satisfactorily at present.

Calculation of Rotational Collision Numbers.

For the calculation of $Z_{rot}$ from the expression
(4), we must know the values of $Z'/Z_0$, $C_V$, and $\frac{\rho D}{\eta}$
at different temperatures. The values of $Z'/Z_0$ at
different temperatures were taken from Ref. (8), while
the 12-6-3 potential parameters needed for the calcula-
tion of $\frac{\rho D}{\eta}$ were taken from an earlier paper of
Monchick and Mason$^{22}$. The viscosity values used in the
calculation of $\text{f}_{\exp}$ were obtained by using the same force
parameters. The molar specific heat at constant volume
were calculated from the vibrational frequencies$^{23}$. The
results obtained at different temperatures are shown in
the column 7 of the Table III. It will be seen from the
table that the rotational collision number increases
with the rise of temperature but is much less than the
experimental value of 9 collisions. An attempt was made to check this large discrepancy as well as the temperature variation by applying the recent theory of Sather and Dahler. According to them the rotational relaxation times of gases composed of molecules having rough spherical cores and interacting with square well potential is given by

$$\gamma^{-1}_{\text{rot}} = \frac{16}{3} n \sigma^2 \left( \frac{4 I}{m \sigma^2} \right) \left( 1 + \frac{4 I}{m \sigma^2} \right)^{-2} \left( \frac{n k T}{m} \right)^{\frac{1}{2}} \exp \left( \frac{\epsilon}{kT} \right)$$

\[ \ldots (5) \]

Using Eq. (5), O'Neal and Brokaw derived the following expression for \( Z_{\text{rot}} \):

$$Z^{-1}_{\text{rot}} = \left( \frac{5 \Omega}{12} \right) \left( \frac{4 I}{m \sigma^2} \right) \left( 1 + \frac{4 I}{m \sigma^2} \right)^{-2} \exp \left( \frac{\epsilon}{kT} \right), \ldots (6)$$

where \( \sigma^2 = \sigma^2 \Omega^{(2,2)} \).

According to them the following factors are important in determining the rotational relaxation times for nonpolar molecules.

1. The molecular mass distribution (characterized by the parameter \( 4I/m\sigma^2 \)),
2. the strength of intermolecular forces (characterized by \( \epsilon/kT \)), and
3. the deviation of the molecular force field from spherical symmetry.
This theory is strictly speaking, not applicable to polar molecules with the usual 12-6-3 potential, but we have tentatively applied it to ammonia using the force parameters of ammonia on the square well potential, \( \epsilon/k = 526^\circ K \), \( \sigma = 2.40 \text{ \AA} \), and \( R = 2.5 \) obtained by us from the experimental viscosity data and have calculated \( Z_{\text{rot}} \) theoretically using the above expression (6). The results thus obtained are shown in column 8 of the table III. It will be seen that although the values are not in agreement with those obtained from thermal conductivity data they show a somewhat similar temperature dependence.

**Discussion.**

It is evident from the above analysis of our data that the rotational collision number obtained from thermal conductivity data are rather too low as compared to the experimental value24 or even the values obtained from theoretical treatment of Sather and Dahler11. Mason and Konchick8 also obtained a low value using the data of others. It seems that the low value is due to the neglect of nonresonant exchange collisions which would reduce the value of \( D_{\text{int}} \) and cause an increase in \( Z_{\text{rot}} \). It will, therefore, be worthwhile to calculate the effect of nonresonant exchange collisions in the case of polar molecules in order to test fully the theory given by Mason and Monchick8.
some approximate idea about the rotational collision number for polar molecules. O'Neal and Brokaw\textsuperscript{24} have also applied this theory to several nonpolar polyatomic molecules and found the agreement to be good in case of rough sphere molecules but poor in the case of molecules deviating markedly from sphericity.

References.


