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Heat transfer in polar organic vapours

A. MANNA, A. DAS GUPTA and B. N. SRIVASTAVA

Indian Association for the Cultivation of Science, Calcutta, India

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Abstract. The thermal conductivity of several polar organic vapours has been measured over the temperature range of 38 °C to 200 °C by the thick-wire variant of the hot-wire method. An attempt has been made to interpret the observed data with the help of a theory recently developed by Mason and Monchick.

1. Introduction

A very accurate measurement of the thermal conductivity of gases and gas mixtures may serve as one of the best sources of information on the exchange of energy between the external and the internal degrees of freedom during like and unlike encounters. Various theories so far developed have been able to explain the thermal conductivity data of non-polar gases reasonably well. In the case of polar gases, however, owing to the existence of long-range dipole forces the theoretical treatment becomes more complicated for thermal conductivity than for other transport properties.

Recently Mason and Monchick (1962) have tried to explain the thermal conductivity of polyatomic gases by introducing the idea of relaxation in the exchange of energy between translational and internal degrees of freedom. Starting from the semi-classical theory of Wang Chang and Uhlenbeck and making a few simplifying assumptions, they have derived the following explicit expressions for the thermal conductivity of non-polar polyatomic gases:

$$\frac{\lambda M}{\eta} = \frac{5}{2} C_{V \text{ trans}} + \frac{\rho D}{\eta} C_{V \text{ int}} - \frac{2}{\pi} \left(\frac{5}{2} - \frac{\rho D}{\eta} \right)^2 \sum \frac{C_k}{Z_k} \quad (1)$$

where C_k is the heat capacity for the k th mode and Z_k is the corresponding collision number. In extending their calculation to polar gases Mason and Monchick have assumed that in such cases internal energy may be transferred in resonant collisions without affecting the translational energy. This type of energy exchange may also occur in the case of non-polar gases, but it is significant only in the case of polar gases for which the cross section for resonant exchange of rotational energy is large owing to the long-range dipole forces. The net result of this type of energy transfer is to lower the effective diffusion coefficient for internal transfer and thus the thermal conductivity. For polar gases, therefore, the diffusion coefficient D is replaced by D_{int} where

$$D_{\text{int}} = D(1 + \delta)^{-1}. \quad (2)$$

Expressions for δ have been formulated by Mason and Monchick (1962) for various types of polar molecules. Thus the expression for the thermal conductivity of polar gases becomes

$$\frac{\lambda M}{\eta} = f_{\text{MM}} C_V$$

where

$$f_{\text{MM}} = \frac{1}{C_V} \left\{ \frac{5}{2} C_{V \text{ trans}} + \frac{\rho D_{\text{int}}}{\eta} C_{V \text{ int}} - \frac{2}{\pi} \left(\frac{5}{2} - \frac{\rho D_{\text{int}}}{\eta} \right)^2 \sum \frac{C_k}{Z_k} \right\}. \quad (3)$$

In the application of equation (3) to various polar gases only the rotational modes are generally considered since Z_k is large for other modes. Consequently the expression for the thermal conductivity of polar gases becomes

$$\frac{\lambda M}{\eta C_V} = \frac{1}{C_V} \left\{ \frac{5}{2} C_{V \text{ trans}} + \frac{\rho D_{\text{int}}}{\eta} C_{V \text{ int}} - \frac{2}{\pi} \left(\frac{5}{2} - \frac{\rho D_{\text{int}}}{\eta} \right)^2 \frac{C_{\text{rot}}}{Z_{\text{rot}}} \right\}. \quad (4)$$

This paper reports the results of measurements of the thermal conductivities of various organic polar gases over the temperature range 40–200 °C. The observed data have been interpreted with the aid of the theory developed by Mason and Monchick (1962).

2. Experimental details

The thick-wire variant of the hot-wire method has been employed for the measurement of thermal conductivity. The theory and experimental procedure have already been discussed (Kannuluik and Martin 1933, Kannuluik and Carman 1952, Srivastava and Barua 1960). The design of the cell is similar to that used by Srivastava and Das Gupta (1966). The bore of the cell used is uniform to one thousandth of an inch over the whole effective length of the conductivity cell. The various constants of the cell are recorded in table 1.

During the experiment the cell was placed in an oil bath, the temperature control of which was in general within ± 0.05 degC. Gases used in this experiment were obtained by vaporizing chemically pure liquids.

Table 1. Constants of the thermal conductivity cell at different temperatures

(1)	(2)	(3)	(4)	(5)
35.8	0.1672	0.00308	0.972	0.986
59.8	0.1690	0.00289	1.0382	0.985
100	0.1718	0.00260	1.155	0.985
120	0.1730	0.00247	1.2125	0.984
140	0.1738	0.00236	1.273	0.986
160	0.1746	0.00226	1.328	0.987
180	0.1750	0.00216	1.391	0.989
200	0.1753	0.00207	1.446	0.985
Length of the cell wire ($2l$)			6.29 cm	
Radius of the cell wire (r_1)			0.00506 cm	
Internal diameter of the tube ($2r_2$)			0.301 cm	
Outer diameter of the tube ($2r_3$)			0.590 cm	

(1) Temperature (°C); (2) thermal conductivity of the wire ($\text{cal cm}^{-1} \text{ degC}^{-1} \text{ s}^{-1}$); (3) temperature coefficient of resistance α of the platinum wire (degC^{-1}); (4) resistance of the cell wire (ohms); (5) cell constant $1 - C$.

Table 2. Observations taken for the thermal conductivity of chloroform in $\text{cal cm}^{-1} \text{ degC}^{-1} \text{ s}^{-1}$

T (°C)	I (mA)	$R - R_0$ (Ω)	$K_u \times 10^5$	$K' \times 10^5$	$K'_{\text{mean}} \times 10^5$	$\lambda \times 10^5$
59.8	128.67	0.041010	2.161	2.058	2.063	2.033
	129.37	0.041389	2.164	2.061		
	130.48	0.041892	2.173	2.069		
120	126.53	0.035753	2.818	2.683	2.698	2.655
	128.34	0.036527	2.839	2.703		
	130.07	0.037357	2.844	2.708		
160	127.63	0.034456	3.287	3.130	3.137	3.096
	128.40	0.034863	3.289	3.132		
	129.44	0.035173	3.306	3.148		

In table 2 a typical set of observations for chloroform taken at 59.8 °C, 120 °C and 160 °C have been recorded. In this table K_u is the apparent thermal conductivity and K' is that obtained after reducing to the bath temperature and making corrections for non-radial flow, radiation loss, temperature jump and wall effects. λ 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 35.8 °C, 59.8 °C, 100 °C, 120 °C, 140 °C, 160 °C, 180 °C and 200 °C, taking the thermal

conductivity values calculated from viscosity data as standard. At every temperature the conductivity has been measured for three different currents, and the K_u values are found to agree within less than 1% on the average. The thermal conductivity values thus obtained are recorded in table 3. The variation of thermal conductivity with temperature has been shown graphically in figures 1 and 2. The results obtained are found to be in good agreement within 1–3% with those obtained by certain workers (Moser 1913, Vines and Bennett 1954).

Table 3. Thermal conductivity and rotational collision number of organic vapours at different temperatures

System	Temperature (°C)	$\lambda \times 10^5$ (cal cm ⁻¹ degc ⁻¹ s ⁻¹)	Z_{rot} (from smoothed out values)
Chloroform	35.8	1.896	1.1
	59.8	2.033	2.2
	100.0	2.404	2.5
	120.0	2.656	3.1
	140.0	2.877	4.1
	160.0	3.096	10.2
	180.0	3.253	13.1
	200.0	3.458	—
Methelene chloride	35.8	2.028	3.4
	60.6	2.239	2.5
	100.0	2.645	2.4
	139.8	3.105	2.3
	179.1	3.582	2.2
	199.2	3.810	2.0
Ethyl chloride	35.8	2.883	2.0
	60.5	3.308	2.7
	100.0	4.138	4.2
	119.3	4.363	5.2
	140.7	4.872	4.4
	160.9	5.414	4.3
	180.7	5.649	4.8
	200.0	6.183	15.1
Acetone	35.3	2.898	—
	60.6	3.303	0.5
	100.9	4.148	0.8
	120.8	4.679	1.0
	140.9	5.038	1.0
	160.8	5.593	1.0
	180.6	6.050	0.9
	201.0	6.559	0.9
Ethyl alcohol	100.9	5.167	1.2
	120.8	5.444	1.0
	140.6	5.929	0.8
	160.9	6.262	0.6
	180.1	6.538	0.5
	200.9	6.886	0.4
Methyl alcohol	35.8	3.603	0.8
	61.9	4.356	0.8
	100.9	5.256	0.9
	120.5	5.766	0.9
	140.8	6.280	0.9
	160.9	6.876	0.9
	180.3	7.508	1.0
200.0	8.212	1.1	

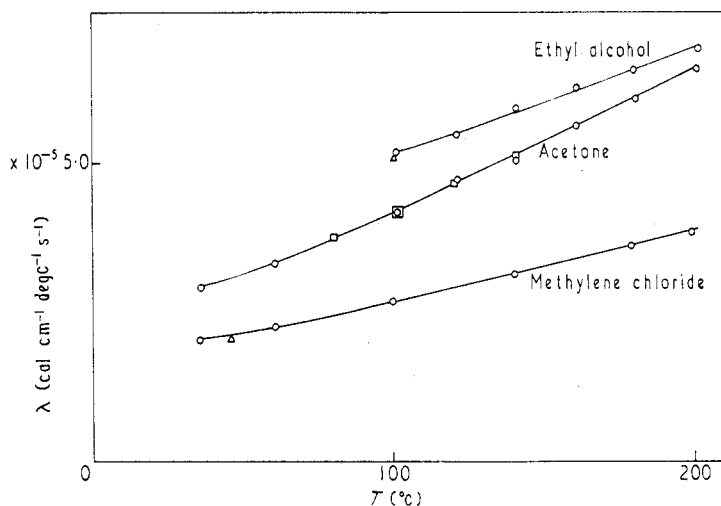


Figure 1. Thermal conductivity of organic vapours at different temperatures: ○ present work; □ Vines and Bennett 1954; △ Moser.

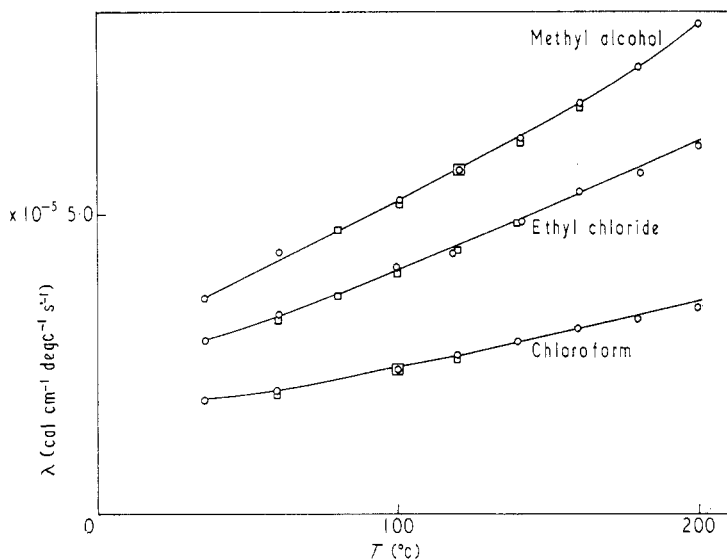


Figure 2. Thermal conductivity of organic vapours at different temperatures: ○ present work; □ Vines and Bennett 1954.

3. Comparison with theory

From equation (4) the expression for Z_{rot} becomes

$$Z_{rot} = \frac{3}{\pi} \left(\frac{5}{2} - \frac{\rho D_{int}}{\eta} \right)^2 \frac{R}{C_V} \left\{ \frac{\rho D_{int}}{\eta} + \frac{3}{2} \left(\frac{5}{2} - \frac{\rho D_{int}}{\eta} \right) \frac{R}{C_V} - f_{MM} \right\}^{-1}. \quad (5)$$

For the calculation of Z_{rot} from the above equation one must know the values of f_{MM} , δ , C_V and $\rho D/\eta$ at different temperatures. f_{MM} in the above expression is replaced by f_{exp} ($= \lambda_{exp} M/\eta C_V$) in the present analysis. The specific heat C_V and viscosity η have been taken from earlier workers (Braune and Linke 1930, Titani 1933, Vold 1935, Collins *et al.* 1949, Craven and Lambert 1951, Barrow 1952, Vines and Bennett 1954). For methyl alcohol and chloroform the δ values calculated from the expression given by the Mason

and Monchick have been used. For other systems, since reliable spectroscopic data for the moment of inertia are not available, the evaluation of δ becomes impossible. It was, however, shown by Mason and Monchick that for bigger molecules having larger moment of inertia the correction for the resonance-exchange effect δ becomes very small; consequently, for these systems D_{int} has been taken to be equal to D , the self-diffusion coefficient. For the calculation of $\rho D/\eta$ the force parameters on the Stockmayer (12 : 6 : 3) potential reported by Monchick and Mason (1961) have been used. The Z_{rot} values for the systems under investigation are recorded in the fourth column of table 3.

4. Discussion

It is evident from the present analysis that the Z_{rot} values obtained from the thermal conductivity data, in general, show an increase with temperature. This is in accordance with the results obtained for SO_2 and NH_3 by Baker and De Haas (1964) and Srivastava and Das Gupta (1966).

Recently, Baker and Brokaw (1965) have shown from thermal conductivity data that Z_{rot} decreases with temperature. Moreover, ultrasonic experiments of Zink *et al.* (1965, 1966) also show a decrease of Z_{rot} with temperature for oxygen and hydrogen-helium systems. In the case of polar gases, however, no such experiments have yet been performed. For a polar gas which involves dipole-dipole interactions it is rather difficult to predict anything regarding the temperature dependence of Z_{rot} . Moreover, the temperature variation of Z_{rot} for repulsive interaction is in the opposite direction to that for an attractive interaction. The different theories so far developed also give conflicting results regarding the temperature dependence of the rotational collision number. Under the present circumstances it appears that for a proper checking of Mason and Monchick's theory, and also for a better understanding of the temperature dependence of rotational-translational energy exchange, direct experiments on the determination of rotational collision numbers of polar molecules should be performed over a wide range of temperature.

The Z_{rot} values for some gases are found to be less than 1, which appears to be physically unrealistic. In the treatment of Mason and Monchick certain types of inelastic collisions (such as rotational-rotational), in which energy is transferred from one internal degree to another, have been ignored. Taking account of these collisions will, however, lower the value of D_{int} . Consequently, this may explain the lowering of Z_{rot} below unity.

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