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Thermal conductivity of methyl chloride–hydrogen sulphide gas mixtures

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Abstract. The thermal conductivity of binary polar gas mixtures $\text{CH}_3\text{Cl}-\text{H}_2\text{S}$ has been measured over the temperature range 0–200 °C for various compositions by applying the thick-wire variant of the hot-wire method. From the analysis of the data it is concluded that the Hirschfelder–Eucken expression for the thermal conductivity of the mixture is in fair agreement with the experimental data, provided the pure-component thermal conductivities are replaced by their corresponding experimental values. The effect of inelastic collision and resonant exchange of energy is investigated in detail and found to be not negligible.

1. Introduction

The theory of heat conductivity of polar gases is very complicated since it has to include the effects of polyatomicity as well as the polarity of gases. Besides the relaxation effect, another effect, known as resonant exchange of internal energy during collisions, has to be taken into account. Resonant exchange may also be present in non-polar polyatomic gases but its contribution is negligible. In polar gases, however, the effect is important owing to the large cross section for resonant exchange collisions due to long-range dipole forces. Recently Mason and Monchick (1962) derived explicit expressions for the heat conductivity of polar gases considering inelastic collisions and exchange effects. This has been generally considered satisfactory, though it involves relaxation times which are often not known independently.

In the case of mixtures of polar gases there is a further complication due to the presence of inelastic collision between unlike molecules. Monchick *et al.* (1965) have derived an expression for the thermal conductivity of the mixture which takes into account the effects of inelastic collision between like and unlike molecules and also resonant exchanges of internal energy between all molecules. According to them, using the Chapman–Enskog first approximation,

$$\lambda_{\text{mix}} = \lambda_{\text{HE}}' + \Delta\lambda \quad (1)$$

where λ_{HE}' is the modified Hirschfelder–Eucken expression for the thermal conductivity of the mixture, with D and λ replaced by D_{int} and λ_{exp} respectively, and $\Delta\lambda$ is a first-order correction term. Monchick *et al.* (1965) concluded that for the polar gas mixture $\text{H}_2\text{O}-\text{D}_2\text{O}$ the exchange correction between all molecules is important and, in general, the use of correct internal diffusion coefficients is at least as important as the inclusion of a correction for inelastic collisions.

Tests of this theory require thermal conductivity measurements for polar–polar mixtures, but at present such measurements are few (Bennett and Vines 1955, Baker and Brokaw 1964, 1965, Srivastava and Das Gupta 1967, Gutweiler and Raw 1968, Manna and Srivastava 1969, Gray and Maczek 1968). Baker and Brokaw (1964, 1965) concluded from their measurements on the isotopic mixtures $\text{HCl}-\text{DCl}$, $^{14}\text{NH}_3-^{15}\text{NH}_3$ and others that resonant or near-resonant exchange of rotational quanta is important in determining the thermal conductivity of pure polar gases and their mixtures. They further concluded that exact resonance is not necessary for the rotational exchange process between HCl and DCl and that this exchange makes a significant contribution of 2–4% in the mixture conductivity, while the contribution of $\Delta\lambda$ is less than 1%. They found satisfactory agreement with theory whether the modified Hirschfelder–Eucken formula or equation (1) was used. For the non-isotopic mixtures ammonia–diethyl ether (Srivastava and Das Gupta 1967), ammonia–methylamine (Gutweiler and Raw 1968) and methyl chloride–sulphur dioxide

(Gray and Maczek 1968, Manna and Srivastava 1969), dimethyl ether-sulphur dioxide (Gray and Maczek 1968) and dimethyl ether-methyl chloride (Gray and Maczek 1968) it was generally concluded that the contribution of $\Delta\lambda$ is negligible but the determination of a correct value of the mutual diffusion coefficient D_{12} is important and probably the resonant exchange effect between unlike molecules is small.

In the present paper the thermal conductivity of binary mixtures of methyl chloride-hydrogen sulphide have been reported for different compositions over the temperature range 0–200 °C and the importance of the various contributory factors has been examined in detail.

2. Experimental details

The thick-wire variant of the hot-wire method has been utilized in these measurements. The experimental procedure and the theory have been described earlier (Kannuluik and Martin 1933, Kannuluik and Carman 1952, Srivastava and Barua 1960). The description of the cell is the same as that used by Srivastava and Das Gupta (1966). For the range 80–200 °C the cell was placed in an oil bath where temperature control was within ± 0.05 degc. For 0 °C the cell was placed in a Dewar containing ice. Methyl chloride was collected from cylinders after proper distillation. Preparation of H₂S has already been described (Barua *et al.* 1968). The smoothed-out experimental values of λ are shown in column (3) of table 1, the observed deviation from the smoothed-out value being nowhere greater than 0.5%.

3. Comparison with theory

The expression for λ_{HE}' obtained by Monchick *et al.* (1965) is

$$\lambda_{HE}' = \lambda_{mix\ mon} + \frac{\lambda_{1\ exp} - \lambda_{1\ mon}}{1 + (x_2/x_1)(D_{1\ int\ 1}/D_{1\ int\ 2})} + \frac{\lambda_{2\ exp} - \lambda_{2\ mon}}{1 + (x_1/x_2)(D_{2\ int\ 2}/D_{1\ int\ 2})} \quad (2)$$

where $\lambda_{mix\ mon}$ is the thermal conductivity of the mixture when both components are assumed to possess no internal degrees of freedom. $\lambda_{1\ mon}$ and $\lambda_{2\ mon}$ are the thermal conductivities of methyl chloride and hydrogen sulphide (referred to as components 1 and 2 respectively) when they are devoid of internal degrees of freedom and x_1 and x_2 are the mole fractions of methyl chloride and hydrogen sulphide. $D_{1\ int\ 1}$ and $D_{2\ int\ 2}$ are the self-diffusion coefficients corrected for resonant exchange of rotational energy as given by the general formula

$$D_{i\ int\ i} = \frac{D_{ii}}{1 + \delta_{ii}} \quad (3)$$

where the δ_{ii} are the correction factors due to resonant exchange of rotational energy. The mutual diffusion coefficient $D_{1\ int\ 2}$ is given by

$$D_{1\ int\ 2} = \frac{D_{12}}{1 + \delta_{12}} \quad (4)$$

where the δ_{12} term is due to the resonant exchange between unlike molecules. Generally we put $\delta_{12} = \frac{1}{2}(\delta_{11} + \delta_{22})$, the arithmetic mean value, because of the absence of any theoretical justification for a particular way of treating the resonant exchange correction for a polar-gas mixture. If, however, there are no resonant exchanges between unlike molecules, δ_{12} would be zero.

The calculations of $\lambda_{mix\ mon}$, $\lambda_{1\ mon}$, $\lambda_{2\ mon}$, D_{11} , D_{22} and D_{12} have been done according to the expressions given by Hirschfelder *et al.* (1954). The values for δ_{11} and δ_{22} were taken from Manna and Srivastava (1969) and Barua *et al.* (1968), respectively. In order to calculate the elements in equation (2) force parameters are taken from Monchick and Mason (1961). For the unlike interaction terms in D_{12} and $\lambda_{mix\ mon}$ the usual combination rules have been employed. The results are given in table 1.

Table 1. Thermal conductivity of CH₃Cl-H₂S gas mixtures in cal cm⁻¹ s⁻¹ degc⁻¹

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
273	0.00	3.200	3.200	3.200	3.200	0.000	3.200
	0.0943	3.080	3.116	3.089	3.110	0.027	3.116
	0.2914	2.840	2.942	2.881	2.928	0.060	2.941
	0.4918	2.620	2.764	2.690	2.748	0.067	2.757
	0.7046	2.435	2.575	2.522	2.563	0.053	2.575
	0.890	2.340	2.411	2.381	2.405	0.024	2.405
	1.00	2.314	2.314	2.314	2.314	0.000	2.314
353	0.00	4.230	4.230	4.230	4.230	0.000	4.230
	0.1012	4.135	4.147	4.119	4.142	0.052	4.171
	0.3048	3.940	3.980	3.919	3.969	0.104	4.023
	0.5063	3.760	3.814	3.748	3.802	0.108	3.856
	0.6364	3.645	3.708	3.649	3.696	0.093	3.742
	0.8952	3.470	3.496	3.474	3.491	0.034	3.508
	1.00	3.410	3.410	3.410	3.410	0.000	3.410
393	0.00	4.800	4.800	4.800	4.800	0.000	4.800
	0.1034	4.745	4.725	4.698	4.724	0.084	4.782
	0.3062	4.640	4.579	4.522	4.575	0.161	4.683
	0.4593	4.540	4.469	4.405	4.463	0.166	4.571
	0.6982	4.380	4.298	4.247	4.291	0.118	4.365
	0.8739	4.230	4.171	4.146	4.168	0.055	4.201
	1.00	4.080	4.080	4.080	4.080	0.000	4.080
433	0.00	5.210	5.210	5.210	5.210	0.000	5.210
	0.10	5.160	5.167	5.147	5.172	0.084	5.231
	0.3079	5.060	5.078	5.059	5.111	0.164	5.223
	0.5095	4.970	4.991	4.944	5.000	0.164	5.108
	0.6872	4.897	4.915	4.876	4.921	0.124	5.000
	0.9023	4.820	4.822	4.826	4.843	0.044	4.870
	1.00	4.780	4.780	4.780	4.780	0.000	4.780
473	0.00	5.810	5.810	5.810	5.810	0.000	5.810
	0.1016	5.790	5.821	5.815	5.843	0.070	5.885
	0.2848	5.765	5.841	5.829	5.886	0.134	5.963
	0.5015	5.750	5.865	5.852	5.915	0.140	5.992
	0.7119	5.780	5.888	5.879	5.926	0.100	5.979
	0.8889	5.850	5.907	5.904	5.925	0.044	5.948
	1.00	5.920	5.920	5.920	5.920	0.000	5.920

(1) Temperature (°K); (2) mole fraction of CH₃Cl; (3) $\lambda_{exp} \times 10^5$, smoothed-out values; (4) $\lambda \times 10^5$ from linear mixing rule (molar average); (5) $\lambda_{HE}' \times 10^5$ with all resonances; (6) $\lambda_{HE}' \times 10^5$ with like resonances; (7) $\Delta\lambda \times 10^5$; (8) $\lambda_{mix} \times 10^5$ with all resonances ((5) + (7)).

4. Discussion

There are no experimental data with which to compare our results of this particular mixture. However, the pure-component conductivities have been discussed elsewhere (Manna and Srivastava 1969, Barua *et al.* 1968). It is found from table 1 that generally speaking the experimental thermal conductivity data are in fair agreement with the values obtained from the Hirschfelder-Eucken expression, provided the pure-component thermal conductivities are replaced by corresponding experimental values (columns (3) and (5)). The discrepancy is within about 3%, while the maximum contribution of the $\Delta\lambda$ term and of the resonant exchange correction is also of the same order. It is, however, felt that the relative experimental error in the smoothed-out values is less than 1%. It was, therefore, considered desirable to examine this in detail by plotting $\{(\lambda - \lambda_{mol\ av})/\lambda_{mol\ av}\} \times 100$ against the percentage of CH₃Cl. Values of $\lambda_{mol\ av}$ have

been calculated by combining the thermal conductivities of the pure gases in the ratio of their mole fractions. The various curves (figures 1 and 2), therefore, give the departure of the conductivity from the molar average as a percentage. It is well to remember that

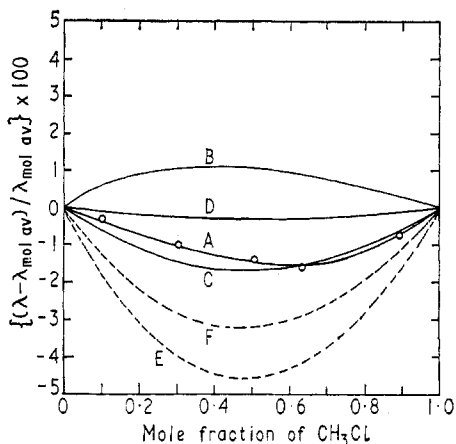


Figure 1. Plot of $\{(\lambda - \lambda_{\text{mol av}}) / \lambda_{\text{mol av}}\} \times 100$ against the mole fraction of CH_3Cl at 353 °K. Curves A, B, C and D represent λ taken from columns (3), (8), (5) and (6), respectively, of table 1. Curves E and F are the same as C and D with σ_{12} increased by 3%.

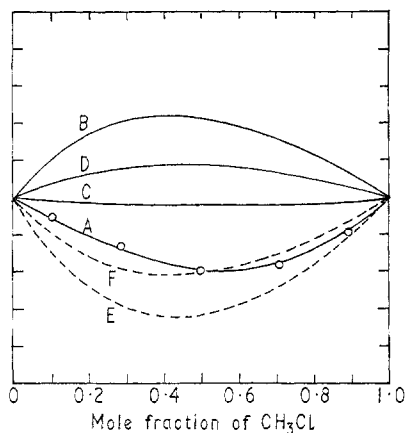


Figure 2. Plot of $\{(\lambda - \lambda_{\text{mol av}}) / \lambda_{\text{mol av}}\} \times 100$ against the mole fraction of CH_3Cl at 473 °K. The labelling on the curves is the same as for figure 1.

these curves do not give a proper idea of the variation of λ with composition as the major part of this variation is already contained in $\lambda_{\text{mol av}}$. We have chosen this way of plotting as this shows, on account of the enlarged scale, most clearly and graphically how the various calculated values differ from the experimental values and what trend this difference shows as a function of composition.

The different curves represent λ obtained in the following ways: A, experimental values; B, values obtained by assuming like and unlike resonances together with $\Delta\lambda$ according to Monchick *et al.* (1965) and $\delta_{12} = \frac{1}{2}(\delta_{11} + \delta_{22})$; C, Hirschfelder–Eucken formula with both like and unlike resonances; D, Hirschfelder–Eucken formula with like resonances only. Curves B, C and D were calculated using the Stockmayer potential, Monchick and Mason's values for the parameters of pure gases and the usual combination rules for unlike interaction.

From the general trend of the curves at the temperatures 353 °K and 473 °K the following conclusions can be drawn.

(i) The deviation of the calculated values from the experimental values seems to be real and more than the experimental errors. It seems also to vary with temperature.

(ii) From a comparison of the curves A, C and D it does not seem safe to draw any definite conclusion about the importance of unlike resonances until the unlike interaction parameters are known with certainty from data on binary diffusion and binary viscosity and the location of curves C and D can be put down with some certainty.

(iii) It seems to us that the force parameters for H_2S are somewhat in error. We have been led to this conclusion by substituting these values for H_2S in the expression for viscosity which then yields values about 5% higher than the experimental data on viscosity of H_2S obtained by Pal and Barua (1967). This would mean that σ for H_2S should be increased by about 2%. This seems to be further corroborated by the fact that the experimental values of λ_{mix} for mixtures of $\text{CH}_3\text{Cl}-\text{H}_2\text{S}$ and $(\text{C}_2\text{H}_5)_2\text{O}-\text{H}_2\text{S}$ are lower than the Hirschfelder–Eucken results while those for $\text{CH}_3\text{Cl}-\text{SO}_2$, $(\text{CH}_3)_2\text{O}-\text{SO}_2$, $(\text{CH}_3)_2\text{O}-\text{CH}_3\text{Cl}$ and $\text{NH}_3-(\text{C}_2\text{H}_5)_2\text{O}$ are higher. Curves E and F are therefore drawn as modifications of curves C and D with σ_{12} increased by 3%.

(iv) The Hirschfelder-Eucken curves with only like resonances and those with all resonances (curves F and E respectively) show minima at nearly the same composition, say about 40% of CH_3Cl , while the experimentally observed minima occur at about 60%. By superposing $\Delta\lambda$ on curve E the minimum would shift to the right and approach the position of the experimental minimum. This shows that $\Delta\lambda$ makes a significant contribution to the composition dependence of λ_{mix} which is mainly due to the cross relaxation terms via Z_{12} and Z_{21} .

The contributions of the term $\Delta\lambda$ and the unlike resonance are seen to be not negligible and certainly the accuracy of the experiment is sufficient to enable us to appreciate their contribution. It is, however, masked by several factors whose exact contribution is not precisely known at present, but if we once determine with certainty the values of the unlike interaction parameters, the contributions of the other possible sources of error could be investigated theoretically and compared with experimental results.

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