Heat conductivity of the nonpolar-polar gas mixtures Ar-CH$_3$Cl and Xe-CH$_3$Cl

Heat conductivity of the nonpolar–polar gas mixtures Ar–CH₃Cl and Xe–CH₃Cl

S. K. BHATTACHARYYA, P. K. BANDOPADHYAY and
A. K. BARUA
Indian Association for the Cultivation of Science, Calcutta-32, India
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Abstract. The heat conductivity of the nonpolar–polar gas mixtures, Ar–CH₃Cl and Xe–CH₃Cl has been measured as a function of composition at different temperatures. The conductivity–composition curves for both systems show minima and in some cases maxima also. Such minima and also points of inflexion have recently been observed by Gray *et al.* for some binary mixtures of inert gases with polar gases. The results indicate the limitations of the present theory for the heat conductivity of gas mixtures particularly for some specific systems. The need for a more sophisticated theory is stressed.

1. Introduction

The recent advances made in obtaining a successful kinetic theory of polyatomic gases have regenerated the interest in accurate measurements of the transport properties of gases which are affected by the inelastic collisions. Among the first-order transport properties, the heat conductivity is influenced significantly by such collisions, whereas viscosity and diffusion are unaffected in the first approximation (Monchick *et al.* 1963). The intuitive correction of Eucken for the effect of internal energy transfer on the heat conductivity has been put on a rigorous basis by Hirschfelder (1957a) who assumed that molecules in different quantum states are separate chemical species which are in local chemical equilibrium. However, in general, it is necessary to consider the effects of relaxation of internal energy. These effects have been included in the treatment of Monchick and Mason (1961) for the heat conductivity of polyatomic gases (including polar molecules) which is based on the kinetic theory of polyatomic gases formulated by Wang Chang *et al.* (1964). This theory has been found to be fairly successful in interpreting the heat conductivity of such gases. The approach of Monchick and Mason (1961) for pure gases has been extended to the polyatomic gas mixtures by Monchick *et al.* (1965). Chiefly to provide accurate and extensive data for testing and developing the theories, the following workers have measured heat conductivities of many polyatomic gas mixtures: Mukhopadhyay and Barua (1967a), Mukhopadhyay and Barua (1967b), Srivastava and Das Gupta (1967), Gray *et al.* (1969), Maczek and Gray (1970). For most of the gas mixtures studied, the theory of Monchick *et al.* (1965) fails to improve upon the results obtained by using the Hirschfelder–Eucken expression (Hirschfelder 1957b) which does not include the relaxation effects in the unlike interactions. The probable reasons for this failure have been discussed elsewhere (Gray *et al.* 1969, Barua *et al.* 1970).

A number of polyatomic gas mixtures have shown maxima in the heat conductivity–composition plots, the conditions for the existence of which have been discussed by Gray *et al.* (1970). Some simple binary mixtures have also been found to show either dips or minima as well as points of inflexion (Hansen *et al.* 1964, Neal *et al.*

1966, Mukhopadhyay and Barua 1967a). Mukhopadhyay and Barua (1967a) suggested that the observed dip for the H_2–He system as due to the inability of the existing theory to take into consideration the relaxation effects for the mixture. Van Dael and Cauwenwagh (1970) have attempted to prove that the dip observed for the H_2–HD and H–He system can be explained in terms of the Hirschfelder–Eucken expression (1957b). However, the existence of minima and points of inflexion for some nonpolar–polar gas mixtures shows that these effects cannot be explained away in such a simple way. The probable reason for minima, suggested by Gray *et al.* (1970), is the impedance of energy transfer from a bulky, heavy molecule to a compact, less heavy molecule in a specific manner. The experimental data for a sufficienctly large number of systems showing these effects are scanty. To fulfil this requirement, in the present paper we have measured the heat conductivities of the nonpolar systems Ar–CH_3Cl and Xe–CH_3Cl as functions of composition at different temperatures. For Ar–CH_3Cl, the polar component which is larger in size is heavier than the other component and for Xe–CH_3Cl the sizes are approximately the same and the polar component is the lighter one.

2. Experimental

For the heat conductivity measurements, the hot-wire cell method was used which has been described in detail elsewhere (Kannuluik and Carman 1952, Srivastava and Barua 1960). Argon and xenon gases were supplied by the British Oxygen Co., UK. The argon was spectroscopically pure; the xenon contained 2% of krypton as an impurity. CH_3Cl was obtained from the commercial variety after distillation and drying. Its purity, as tested in a mass spectrometer, was better than 99%.

The experimental heat conductivity data (modified by the necessary corrections) are shown in table 1 and graphically in figures 1–4. For the pure components,
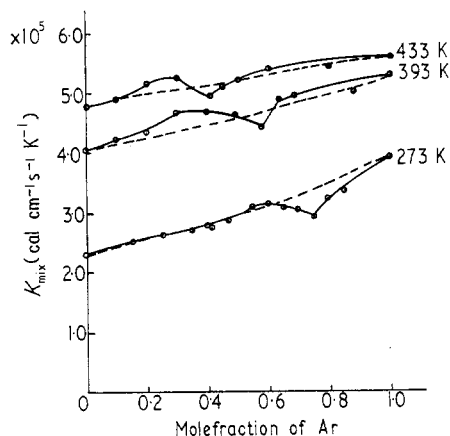

Figure 1. Heat conductivity of the system Ar–CH_3Cl as a function of composition at different temperatures. Experimental points $\bigcirc$; experimental curve ——; theoretical curves - - - .
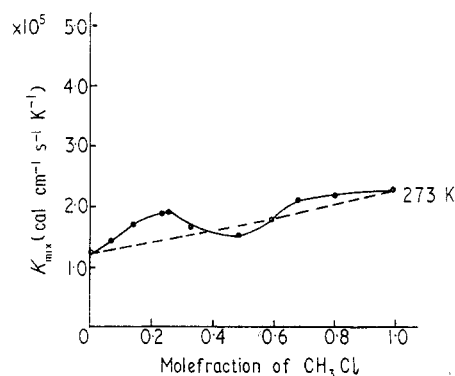
Figure 2. Heat conductivity of the system Xe–CH_3Cl as a function of composition at 273 K. Experimental points $\bigcirc$; experimental curve ——; theoretical curve - - - .

Table 1. Heat conductivity of the system Ar–CH₃Cl and Xe–CH₃Cl at different temperatures

System	Temperature (K)	Mole fraction of lighter component	$(K_{mix})_{exp}$	$(K'_{mix})_H$	ΔK
				$(10^{-5}\,cal\,cm^{-1}\,s^{-1}\,K^{-1})$	
		0·000	2·32	—	—
		0·154	2·55	2·51	−0·04
		0·254	2·63	2·64	−0·07
		0·350	2·72	2·76	−0·09
		0·397	2·81	2·83	−0·10
		0·416	2·77	2·87	−0·10
		0·470	2·88	2·95	−0·11
Ar–CH₃Cl	273	0·550	3·11	3·07	−0·12
		0·600	3·16	3·20	−0·12
		0·650	3·11	3·24	−0·12
		0·700	3·06	3·32	−0·11
		0·750	2·96	3·42	−0·11
		0·800	3·25	3·51	−0·10
		0·850	3·37	3·61	−0·08
		1·000	3·95	—	—
		0·000	4·06	—	—
		0·100	4·22	4·16	−0·04
		0·200	4·36	4·26	−0·08
		0·300	4·67	4·37	−0·12
		0·398	4·68	4·48	−0·14
Ar–CH₃Cl	393	0·489	4·63	4·58	−0·16
		0·580	4·44	4·70	−0·16
		0·635	4·89	4·76	−0·16
		0·685	4·95	4·82	−0·16
		0·880	5·01	5·05	−0·09
		1·000	5·24	—	—
		0·000	4·80	—	—
		0·100	4·91	4·88	−0·04
		0·200	5·17	4·97	−0·09
		0·300	5·26	5·05	−0·13
Ar–CH₃Cl	433	0·410	4·95	5·15	−0·16
		0·450	5·11	5·19	−0·17
		0·500	5·23	5·23	−0·17
		0·600	5·40	5·32	−0·18
		0·800	5·45	5·49	−0·14
		1·000	5·62	—	—
		0·000	1·26	—	—
		0·075	1·44	1·32	—
		0·145	1·73	1·39	—
		0·240	1·90	1·47	—
		0·260	1·93	1·49	—
		0·334	1·69	1·57	—
Xe–CH₃Cl	273	0·382	1·61	1·62	—
		0·490	1·55	1·73	—
		0·600	1·81	1·85	—
		0·684	2·17	1·94	—
		0·805	2·23	2·04	—
		0·895	2·28	2·23	—
		1·000	2·32	—	—

Table 1 (cont.)

System	Temperature (K)	Mole fraction of lighter component	$(K_{mix})_{exp}$	$(K'_{mix})_H$ $(10^{-5}$ cal cm^{-1} s^{-1} K$^{-1})$	ΔK
Xe–CH₃Cl	338	0·000	1·52	—	—
		0·050	1·93	1·53	—
		0·135	2·24	1·69	—
		0·150	2·32	1·72	—
		0·222	2·18	1·82	—
		0·347	2·54	2·01	—
		0·464	2·76	2·20	—
		0·564	2·80	2·37	—
		0·782	3·09	2·74	—
		1·000	3·14	—	—
Xe–CH₃Cl	353	0·000	1·60	—	—
		0·050	2·04	1·73	—
		0·175	2·32	1·91	—
		0·222	2·27	1·97	—
		0·344	2·59	2·18	—
		0·464	2·70	2·37	—
		0·564	2·83	2·52	—
		0·676	2·94	2·72	—
		0·782	3·00	2·90	—
		0·845	3·22	3·02	—
		1·000	3·38	—	—
Xe–CH₃Cl	393	0·000	1·77	—	—
		0·050	2·52	1·86	—
		0·135	2·93	2·06	—
		0·150	2·98	2·08	—
		0·220	2·86	2·20	—
		0·240	2·86	2·26	—
		0·270	2·87	2·31	—
		0·344	3·26	2·48	—
		0·464	3·46	2·71	—
		0·565	3·50	2·97	—
		0·780	3·79	3·50	—
		1·000	4·06	—	—
Xe–CH₃Cl	433	0·000	1·91	—	—
		0·050	2·80	2·04	—
		0·135	3·58	2·25	—
		0·222	3·37	2·48	—
		0·247	3·25	2·55	—
		0·300	3·40	2·69	—
		0·344	3·67	2·82	—
		0·464	3·94	3·16	—
		0·564	3·95	3·44	—
		0·676	4·11	3·78	—
		0·780	4·40	4·10	—
		1·000	4·80	—	—

the agreement with the previous data is within 1% (Kannuluik and Carman 1952, Srivastava and Manna 1969). For the gas mixtures under consideration no previous heat conductivity data are available for comparison.

The heat conductivity–composition curves (figure 1) for the system Ar–CH$_3$Cl show undulations, the nature of which change with temperature. At 273 K the curve is concave with a dip at higher concentrations of argon; at higher temperatures there are also humps to the left of the dips. The height of the hump increases with
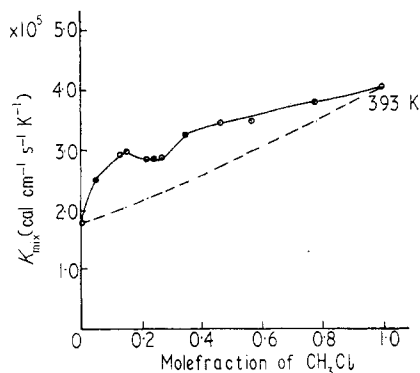

Figure 3. Heat conductivity of the system Xe–CH$_3$Cl as a function of composition at 393 K. Experimental points O; experimental curve ———; theoretical curve - - - .
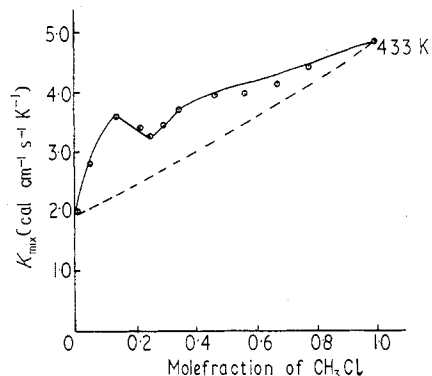
Figure 4. Heat conductivity of the system Xe–CH$_3$Cl as a function of composition at 433 K. Experimental points O; experimental curve ———; theoretical curve - - - .

increasing temperature. The depths of the dips are much larger than the experimental uncertainties. To be more certain about the existence of such dips, a large number of measurements have been made at small intervals of concentration.

The heat conductivity–composition curves for the system Xe–CH$_3$Cl also show some interesting features. At 273 K there is initial increase of the heat conductivity with the addition of CH$_3$Cl which has higher heat conductivity than that of Xe and then a broad dip followed by slow increase. At the higher temperatures more or less the same features are retained although the dips are much narrower and the convex nature of the curve is more pronounced.

3. Comparison with theory

By assuming local chemical equilibrium, the heat conductivity of a monatomic and polyatomic gas mixture can be written (Hirschfelder 1957b):

$$(K_{mix})_H = K_{mix-mon} + (K_1 - K_{1mon})\left(1 + \frac{x_2}{x_1}\frac{D_{11}}{D_{12}}\right)^{-1} \tag{1}$$

where $K_{mix-mon}$ is the heat conductivity of the gas mixture when both the components are treated as monatomic. The expression for $K_{mix-mon}$ based on the Chapman–Enskog theory has been given elsewhere (Hirschfelder et al. 1954). The subscripts 1 and 2 represent the polyatomic and monatomic component respectively. K_1 and K_{1mon} are respectively the heat conductivity of the polyatomic gas and its monatomic part. x are the molefractions, D_{11} and D_{12} are the self- and mutual-diffusion coefficients respectively.

The expression for the heat conductivity of gas mixtures (based on the kinetic theory of Wang Chang et al. 1964) as obtained by Monchick et al. (1965) can be

written as

$$K_{\text{mix}} = (K'_{\text{mix}})_{\text{H}} + \Delta K. \tag{2}$$

The expression for $(K'_{\text{mix}})_{\text{H}}$ is given by

$$(K'_{\text{mix}})_{\text{H}} = K_{\text{mix-mon}} + \frac{K_{\text{1exp}} - K_1}{1 + (x_2 D_{\text{1int1}}/x_1 D_{\text{1int2}})} + \frac{K_{\text{2exp}} - K_2}{1 + (x_1 D_{\text{2int2}}/x_2 D_{\text{1int2}})}. \tag{3}$$

ΔK in equation (2) is a correction term due to relaxation effects in the mixture, the detailed expression for which has been given elsewhere (Monchick *et al.* 1965). The internal diffusion coefficients occurring in equation (3) are related to self- and mutual-diffusion coefficients through the following relations:

$$D_{\text{1int1}} = \frac{D_{11}}{1 + \delta_{11}}$$

$$D_{\text{2int2}} = \frac{D_{22}}{1 + \delta_{22}} \tag{3a}$$

$$D_{\text{1int2}} = \frac{D_{12}}{1 + \delta_{12}}$$

where the δ_{11} and δ_{22} are the correction factors due to resonant exchange of rotational energy and δ_{12} is a term due to the resonant exchange between unlike molecules, generally we put $\delta_{12} = \frac{1}{2}(\delta_{11} + \delta_{22})$. In our present case the second component is monatomic, hence $\delta_{22} = 0$ and the expression for $(K'_{\text{mix}})_{\text{H}}$ can be written as

$$(K'_{\text{mix}})_{\text{H}} = K_{\text{mix-mon}} + \frac{K_{\text{1exp}} - K_1}{1 + (x_2 D_{\text{1int1}}/x_1 D_{\text{1int2}})}. \tag{4}$$

The method of calculating δ_{11} for CH_3Cl has been given elsewhere (Srivastava and Manna 1969).

The intermolecular potential for CH_3Cl was represented by the Stockmayer or 12-6-3 potential. The force parameters were taken as those determined from the experimental viscosity data (Monchick and Mason 1961). For Ar and Xe the Lennard–Jones (12:6) model was used and the force parameters as obtained from the viscosity data were used (Hirschfelder *et al.* 1954). The unlike interaction parameters were obtained from the usual combination rules. The values of $(K'_{\text{mix}})_{\text{H}}$ and ΔK (from equations (4) and (2)) are shown in columns 5 and 6 of table 1. For Xe–CH_3Cl system the ΔK values are negligibly small.

4. Discussion of results

For the system Ar–CH_3Cl (figure 1), it is seen that the theoretical curves fail to represent the undulations shown in the experimental heat conductivity–composition curves. At 273 K there is a pronounced dip at the higher concentrations of Ar. The theoretical curve is in reasonable agreement with the experimental one outside the range of the dip. At the higher temperatures, in addition to a dip there is a hump in the conductivity–composition curve which cannot be explained in terms of the existing theories. The addition of ΔK to $(K'_{\text{mix}})_{\text{H}}$ in some cases improves the agreement between experiment and theory but in some cases the agreement becomes worse. However, at all the temperatures the inclusion of ΔK terms does

not help in the explanation of the observed undulations. For the system $Xe-CH_3Cl$ at 273 K there is a broad dip in the middle of the composition range. At the higher temperatures, the overall shape of the conductivity–composition curve is convex with a dip which is less pronounced than that of the $Ar-CH_3Cl$ system. The theoretical curves are, in general, much lower than the experimental ones and do not in any way reproduce their natures. The values of ΔK for this system are negligibly small. Previously, for some binary mixtures of Ar with organic vapours minima and points of inflexion in the conductivity–composition curves have been observed by Gray *et al.* (1970).

As mentioned earlier, the existence of dips in the heat conductivity–composition curves has been observed for the comparatively simple systems H_2-He and H_2-HD. It has been suggested by Mukhopadhyay and Barua (1967) that the appearance of the dips is due to the relaxation effects in internal energy which are not taken into account properly in the theory of Monchick *et al.* (1965). Subsequently, van Dael and Cauwenwagh (1970) have been fairly successful in representing the broad dip for the H_2-HD system by using the Hirschfelder's expression (equation (1)). They have suggested that for a monatomic–polyatomic binary gas mixture which satisfies the condition $(K_2-K_{1mon}) \ll (K_2-K_1)_{expt}$ a minimum in the heat conductivity–composition curve is expected. For the system $Ar-CH_3Cl$, this condition is fulfilled over the whole temperature range of our experiments and for the $Xe-CH_3Cl$ system it does not hold at all although this system also shows dips. Evidence showing that these phenomena cannot be explained away in terms of such a simple condition has been obtained by Gray *et al.* (1970), who have suggested that the condition for minima is that a bulky, heavy molecule should impede the transport of heat by a compact, less heavy molecule in a particular way. Their suggestion means that for certain systems the internal and translational energy exchanges take place in a special way which cannot be accounted for by the existing theories. These effects should be functions of the geometry and other molecular parameters of the system involved and a much more sophisticated theory than those available (Monchick *et al.* 1965) is necessary for a satisfactory explanation of the heat conductivity of all the systems.

It is now well known that for nonpolar–polar interactions, the combination rules for estimating the unlike interactions are subject to larger errors than those for the polar–polar or nonpolar–nonpolar interactions (Rowlinson and Townley 1953). Because of the influence of inelastic collisions which cannot be taken into account accurately, it is not possible to derive the unlike interaction parameters from the heat conductivity data. Some improvement in the agreement between theory and experiment can be achieved by adjustments of the force parameters. However, this will not be able to describe the appearance of dips and other special features observed for the systems under consideration.

References

BARUA, A. K., MANNA, A., MUKHOPADHYAY, P., and DAS GUPTA, A., 1970, *J. Phys.* B: *Atom. molec. Phys.*, **3**, 619–35.
GRAY, P., HOLLAND, S., and MACZEK, A. O. S., 1969, *Trans. Faraday Soc.*, **65**, 1032–43.
—— 1970, *Trans. Faraday Soc.*, **66**, 107–26.
HANSEN, R. S., FROST, R. R., and MURPHY, J. A., 1964, *J. Phys. Chem.*, **68**, 2028–9.
HIRSCHFELDER, J. O., 1957a, *J. chem. Phys.*, **26**, 282–5.
—— 1957b, *Proc. Int. Symp. on Combustion, Yale University* (New York: Reinhold), Pp.251–6.
HIRSCHFELDER, J. O., CURTISS, C. F., and BIRD, R. B., 1954, *Molecular Theory of Gases and Liquids* (New York: Wiley).

KANNULUIK, W. G., and CARMAN, E. H., 1952, *Proc. Phys. Soc.* B, **65,** 701–9.

MACZEK, A. O. S., and GRAY, P., 1970, *Trans. Faraday Soc.*, **66,** 127–41.

MONCHICK, L., and MASON, E. A., 1961, *J. chem. Phys.*, **35,** 1676–97.

—— 1962, *J. chem. Phys.*, **36,** 1622–39.

MONCHICK, L., PEREIRA, A. N. G., and MASON, E. A., 1965, *J. chem. Phys.*, **45,** 3051–8.

MONCHICK, L., YUN, K. S., and MASON, E. A., 1963, *J. chem. Phys.*, **39,** 654–61.

MUKHOPADHYAY, P., and BARUA, A. K., 1967a, *Br. J. appl. Phys.*, **18,** 635–40.

—— 1967b, *Br. J. appl. Phys.*, **18,** 1307–10.

NEAL, W. E. J., GREENWAY, J. E., and COUTTS, P. W., 1966, *Proc. Phys. Soc.* A, **87,** 577–9.

ROWLINSON, J. S., and TOWNLEY, J. R., 1953, *Trans. Faraday Soc.*, **49,** 20–7.

SRIVASTAVA, B. N., and BARUA, A. K., 1960, *J. chem. Phys.*, **35,** 427–35.

SRIVASTAVA, B. N., and DAS GUPTA, A., 1967, *Br. J. appl. Phys.*, **18,** 945–51.

SRIVASTAVA, B. N., and MANNA, A., 1969, *J. Phys.* A: *Gen. Phys.*, **2,** 697–701.

VAN DAEL, J., and CAUWENWAGH, W., 1970, *J. Phys.* A: *Gen. Phys.*, **3,** L29–30.

WANG CHANG, C. S., UHLENBEEK, G. E., and DE BOER, J., 1964, *Studies in Statistical Mechanics*, Vol. 2 (Amsterdam: North-Holland).