Effect of inelastic collisions on thermal diffusion in polyatomic gas mixtures : N_2—CO and N_2O—CO_2 mixtures.

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The temperature and composition dependence of thermal diffusion factor α_T for the system N_2-CO and N_2O-CO_2 have been studied by an *effective* four-tube swing separator. These systems have the special features that the components have the same molecular mass and the nearly equal collision diameters. Therefore, the elastic theory for thermal diffusion predict negligible values of $\alpha_T(\sim 10^{-4})$ whereas the experimental values are much higher. This result has to be ascribed to the effects of inelastic collisions and the present data proves conclusively the presence of such effects. The theory of Monchick *et al* for thermal diffusion in polyatomic systems has been found to be fairly successful for the N_2-CO mixture.

1. INTRODUCTION

Recent experimental and theoretical studies (Monchick *et al* 1966, Monchick *et al* 1968, Humphreys & Gray 1970, Humphreys & Gray 1971, Bhattacharyya *et al* 1973, Pal *et al* 1974) on thermal diffusion in polyatomic gas mixtures which have indicated the influence of inelastic collisions have greatly enhanced the interest in this phenomenon. From the experimental side, the position is still confusing and sometimes contradictory evidences (Humphreys & Gray 1971, Bhattacharyya *et al* 1973, Pal *et al* 1974) are available regarding the influence of inelastic collision on thermal diffusion. Thermal diffusion factor in a gas mixture is a function of mass difference, size difference and the collision dynamics of the interacting molecules which include the effects of inelastic collisions. To study specifically, the effects of inelastic collisions it is therefore, best to choose systems having components with very nearly equal masses, sizes and similar molecular force fields but different molecular symmetries. The last factor will influence inelastic collisions only and any significant separation due to thermal duffision in such systems may be ascribed to the effect of inelastic collisions. Two gas mixtures which fulfil these requirements very well are N_2-CO and N_2O-CO_2. For these gas mixtures, till now, thermal diffusion has been studied only by the thermal diffusion column (Leaf & Wall, 1942, de Vries 1956, Muller 1962) which do not yield reliable values of the thermal diffusion factors. In fact, there have .

been contradictory results even regarding the component which goes up and the one which goes down. Srivastava et al (1967) have attempted to estimate the values of α_T of the CO_2-N_2O system from the study of separation in a thermal diffusion column. Amongst the different methods for the measurement of thermal diffusion factors in systems having small separation the tronnschaukel or swing separator is the best.

In view of the above discussions, we have studied the thermal diffusion factor α_T of the system N_2-CO and N_2O-CO_2 by the swing separator method. Attempts have been made to interpret the data in terms of the theories which take into consideration the inelastic collisions.

2. Experimental

The thermal diffusion factors α_T were measured by an *effective* four-tube swing separator which has been described in detail elsewhere (Ghosh et al 1967). The sampling arrangement was improved by taking out simultaneously the samples from the top and bottom bulbs of the swing separator. This method eliminated to a large extent the errors due to the disturbances created by repeated sampling from the swing separator. In the actual experiment, sufficient time was allowed for the system to come to equilibrium based on the relaxation time which is given by (Saxena & Joshi 1962)

$$\tau = \frac{Vt_p}{2A}\left[\frac{n+2(V'/V)}{\pi}\right]^2, \qquad \cdots \ (1)$$

where V is the volume of the main tube, V' is the volume of the gas on either side of the mercury U-tube, t_p the time period of swing, n is the number of tubes and $2A$ is the volume of the gas displaced per half-cycles. α_T value was calculated from the relation

$$\alpha_T = \frac{1}{N}\ \frac{\ln q}{\ln(T_H/T_C)}, \qquad \cdots \ (2)$$

N is the number of stage and q being the separation factor. T_H, T_C are the temperatures of the hot and cold bulbs respectively. q is given by

$$q = \frac{(x_1/x_2)_{\text{top}}}{(x_1/x_2)_{\text{bot}}}, \qquad \cdots \ (3)$$

where x's are the molefractions of the components and the subscripts 1 and 2 indicate respectively the heavier and lighter component. The temperature assignment was made by the formula (Brown 1940)

$$\overline{T} = \frac{T_H.T_C}{T_H-T_C}\ln(T_H/T_C). \qquad \cdots \ (4)$$

The temperatuie difference between the top and bottom bulbs was kept within 50°C and therefore, error in temperature assignment due to the use of eq. (4) is not likely to be significant.

The gases were prepared by following standard laboratory procedures and their purity as tested in mass spectrometer (Associated Electrical Industries, U.K., MS3 Model) was better than 99.5%. The temperature control of the bath in which the lower tubes were placed was within ±0.2°C and that of oven which was placed at the top was within ±1°C. The samples drawn out from the swing separator were analysed in a mass spectrometer. For N_2-CO and N_2O-CO_2 gas mixtures N_2 and N_2O were taken respectively, as the component 1. The values of q obtained are estimated to be accurate within a few parts in 10^3 whereas the corresponding errors in α_T are much larger due to the sensitivity of the logarithmic table at such small values of q. The α_T values of N_2-CO system for a mixture containing 70.5% CO in the temperature from 290°K to 350°K are shown in table 1 and the composition dependence of α_T at 299°K is shown in table 2. The corresponding results for the N_2O-CO_2 system are given in tables 3 and 4 and figures 3 and 4. For the N_2-CO system, all the previous thermal diffusion studies have been made with columns (de Vries 1956, Srivastava *et al* 1967). The values of α_T estimated were $\sim 10^{-3}$ at 350°K (de Vries 1956) and 1.6×10^{-3} at 425°K (Srivastava *et al* 1967). These values are about one

Temperature and composition dependence of thermal diffusion factor
for (CO-N_2) mixture

Table 1

Table 2

Mole fraction of CO = 0.705 Mole fraction of N_2 = 0.295		$\bar{T} = 299°K$	
Temperature (°K)	α_T	Mole fraction of CO	α_T
274.0	−0.022±0.008	0.100	−0.042±0.006
275.5	−0.027±0.007	0.210	−0.032±0.004
276.0	−0.025±0.008	0.310	−0.020±0.004
280.0	−0.028±0.009	0.395	−0.009±0.003
285.0	0 ±0.006	0.500	0.004±0.005
*299.0	0.020	0.620	0.011±0.005
310.0	0.006±0.006	0.750	0.030±0.010
328.2	0.029±0.009	0.855	0.044±0.007
343.5	0.037±0.008		

* Smoothed values obtained from composition dependence of thermal diffusion factor (table 2).

Temperature and composition dependence of thermal diffusion factor
for (CO$_2$-N$_2$O) mixture

Table 3		Table 4	
Mole fraction of CO$_2$ = 0.328 Mole fraction of N$_2$O = 0.672		$\bar{T}$ = 296°K	
Temperature (°K)	α_T	Mole fraction of CO$_2$	α_T
*296.0	0.015±0.006	0.120	0.042±0.005
304.0	0.025±0.005	0.220	0.036±0.004
317.5	0.039±0.010	0.326	0.015±0.006
324.8	0.048±0.006	0.420	0.012±0.005
338.5	0.054±0.006	0.520	−0.004±0.006
347.5	0.063±0.008	0.620	0.004±0.004
		0.734	0.030±0.005
		0.840	0.052±0.007

* Smoothed values obtained from composition dependence of thermal
diffusion factor (table 4).

order of magnitude lower than the values obtained by us. It has recently been
shown (Rutherford 1973) for some systems that reliable values for α_T can be
obtained by the thermal diffusion colum method provided the column is cons-
tructed with a very accurate geometry. Since emphasis was not laid in the
earlier studies on this aspect, the values of α_T thus obtained are probably not
quite accurate. It may also be pointed out that in a column the separation
due to thermal diffusion is mixed with other effects and for systems involving
small separations the swing separator is the best method for obtaining α_T values.
In the studies with column there was, however, controversy regarding which
component was enriched at the top or the bottom. Our results for both the
composition and temperature dependence of α_T show that there is inversion in
α_T values and the sign is determined by the temperature and composition range.
For CO$_2$-N$_2$O the sign of α_T with N$_2$O taken as the heavier component is positive
which is in agreement with the result obtained by Srivastava et al (1967) by the
thermal diffusion column method. The present values of α_T are, however, much
higher than the values obtained from column experiment. The α_T vs composition
curve (figure 4) for this system show a pronounced concave nature.

3. COMPARISON WITH THEORY

The expression for α_T by including elastic collisions only can be expressed
in the first approximation as (Hirschfelder et al 1964),

$$[\alpha_T]_1 = B(6C^*_{12}-5), \qquad \qquad \dots (5)$$

where C^*_{12} is a ratio of collision integrals and is a function of $T^* = kT/\epsilon$, ϵ being the depth of the potential well. The quantity B is a function of the masses and other molecular parameters and is a slowly varying function of temperature.

For the calculation of α_T from eq. (5) the Lennard-Jones (12 : 6) potential was used for all the gases and the force parameters were taken as those determined from viscosity data. The unlike interactions were approximated by the usual combination rules. The values of α_T thus obtained were of the order of 10^{-4} which was negligible compared with the experimental values. The molecules under consideration have significant quadrupole moments. We therefore calculated α_T from eq. (5) by using the (12 : 6 : 5) potential which includes the elastic effects of quadrupole moment on thermal diffusion. The results were however very close to those obtained for the Lennard-Jones (12 : 6) potential. Thus the comparatively large values of α_T obtained experimentally have to be interpreted in terms of the inelastic theory of thermal diffusion. The expression obtained by Monchick *et al* (1972) for thermal diffusion factor α_T by including the effects of inelastic collision, may be written as

$$\alpha_{ij} = \frac{(6C^*_{ij}-5)}{5nk[D_{ij}]_1} \left(\frac{\lambda_j^\infty{}_{trans}}{x_j m_j} - \frac{\lambda_i^\infty{}_{trans}}{x_i m_i} \right)$$

$$+\{5nk[D_{ij}]_1\}^{-1} \left[\frac{(6\widetilde{C}_{ji}-5)\lambda_j^\infty{}_{int}}{x_i} - \frac{(6\widetilde{C}_{ij}-5)\lambda_i^\infty{}_{int}}{x_i} \right], \quad \dots \ (6)$$

where x_i and m_i are the molefraction and molecular mass of the *i*th component. respectively, M_{ij} is the reduced mass of the *i*th and *j*th components, n the number density and $[D_{ij}]_1$, is the diffusion coefficient λ's have been defined elsewhere (Hirschfelder *et al* 1964). The first term on the r.h.s. of eq. (6) is the expression of α_T when it is assumed that the differential scattering cross section is same for all entrance and exit channels. Under this condition $\widetilde{Q}^{00,10} = 0$ and $\lambda_{ij} = \tilde{\lambda}_{tran}$. The quantity $\widetilde{C}_{ij}$ unlike C_{ij}^* (the ratio of collision integrals) is not symmetric with respect to the indices *i* and *j* and is very sensitive to inelastic collisions.

At present $\widetilde{C}_{ij}$ can only be evaluated for cocentric loaded sphere molecules and for symmetric loaded sphere $(6\widetilde{C}_{ij}-5) = 0$.

For N_2-CO system, N_2 can be taken as a loaded sphere and CO as eccentric loaded sphere. The eccentricity parameter ξ_i for CO was calculated from molecular symmetry and the value of $(6\widetilde{C}_{ij}-5)$ was obtained as 0.0175. The Z_{rot} value, the rotational-translational quantum number for N_2 and CO were taken from Mason & Monchick (1962). The α_{ij} values thus obtained from eq. (6) are shown in figures 1 and 2.
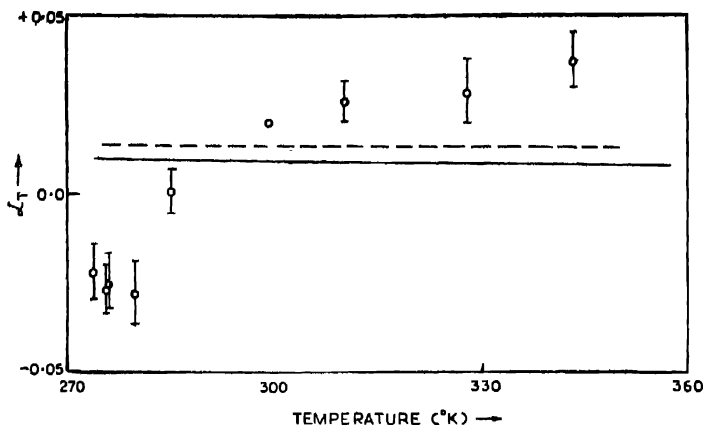
Figure 1. Temperature dependence of thermal diffusion factor (α_T) for (CO–N$_2$) mixture containing 70.5% CO.

Φ, experimental points; - - -, inelastic curve with $\tilde{Q}_{ij}{}^{00,10} \neq 0$; – · – · –, inelastic curve with $\tilde{Q}_{ik}{}^{00,10} = 0$.
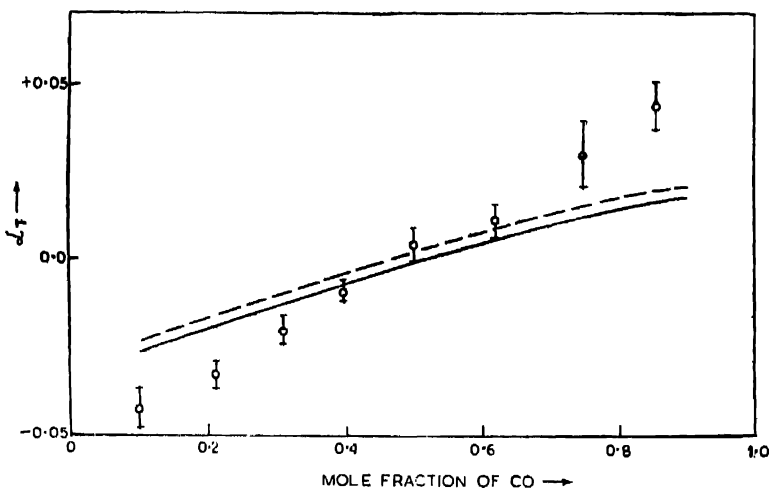

Figure 2. Composition dependence of thermal diffusion factor (α_T) for (CO–N$_2$) mixture at $\overline{T} = 299.0°$K.

Φ, experimental points; - - - -, inelastic curve with $\tilde{Q}_{ij}{}^{00,10} = 0$; ——, inelastic curve with $\tilde{Q}_{ij}{}^{00,10} \neq 0$.

For CO$_2$-N$_2$O, CO$_2$ was taken as loaded sphere. N$_2$O molecule has no centre of symmetry, the configuration being N-N = 0. As an approximation we assume that the centre of symmetry of N$_2$O is at the mid-point of the distance between the centre of N-N bond and the position of the oxygen atom. The centre of mass of the system having masses 28 and 16 at the two ends can be located and
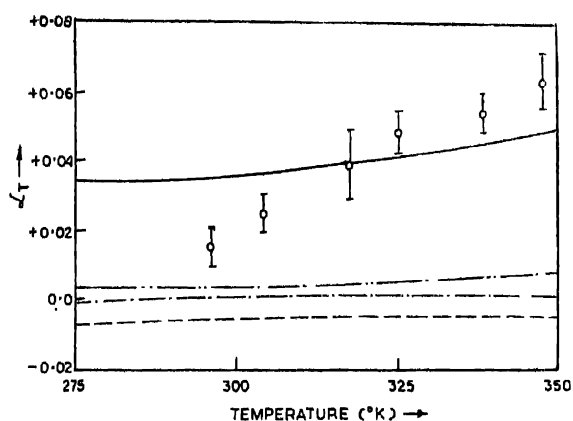
Figure 3. Temperature dependence of thermal diffusion factor (α_T) for $(CO_2$–$N_2O)$ mixture containing 32.8% CO_2.

Φ, experimental points; − · − · −, inelastic curve with $\tilde{Q}_{ij}{}^{00,10} = 0$; · · · ·, inelastic curve with $\tilde{Q}_{ij}{}^{00,10} \neq 0$ and assuming CO_2 as a symmetric linear molecule; − · · − · ·−, inelastic with $O_{ij}{}^{00,10} \neq 0$, taking $(6\tilde{C}_{ij}-5)$ for CO_2 as equal to 0.0296; −−−, inelastic curve taking $(6\tilde{C}_{ij}-5)$ for CO_2 as equal to 0.115 as determined by fitting the experimental α_T data.
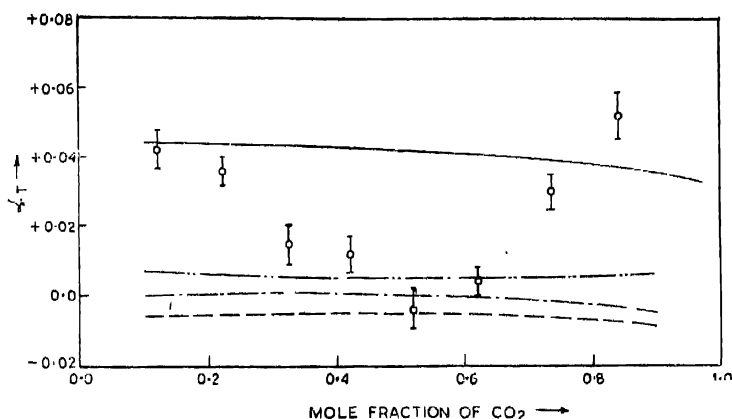

Figure 4. Composition dependence of thermal diffusion factor (α_T) for $(CO_2$–$N_2O)$ mixture at $\overline{T} = 297°K$.

Φ, experimental points; − · − · −, inelastic curve with $\tilde{Q}_{ij}{}^{00,10} = 0$; · · · ·, inelastic curve with $\tilde{Q}_{ij}{}^{00,10} \neq 0$ and assuming CO_2 as a symmetric linear molecule; − · · − · ·−, inelastic curve with $Q_{ij}{}^{00,\varepsilon 0} \neq 0$ and taking $(6\tilde{C}_{ij}-5)$ for CO_2 as equal to 0.0296 −−−, inelastic curve with $Q_{ij}{}^{00,10} \neq 0$ taking $(6\tilde{C}_{ij}-5)$ equal to 0.115 as determined by fitting the experimental α_T values from figure 3.

thus the parameter ξ_l can be located. The moment of inertia of N_2O molecule was taken about the molecular axis. The value of $(6\widetilde{C}_{ij}-5)$ thus obtained was 0.0296. The values of Z_{rot} for CO_2 and N_2O were taken from Mukhopadhyay & Barua (1967). The values of α_{ij} thus obtained from eq. (6) are shown in figures 3 and 4.

4. DISCUSSION OF RESULTS

As mentioned earlier, the elastic Chapman-Enskog theory predicts a negligible value of the thermal diffusion factors for the systems under consideration. The significant values of α_T obtained experimentally have to be ascribed to the effects of inelastic collisions. For the temperature dependence of α_T for N_2-CO system (containing 70.5% of CO) the inelastic curves cross the experimental one. The difference between the two curves for $\widetilde{Q}_{ij}{}^{00,10} = 0$ and $\tilde{Q}_{ij}{}^{00,10} \neq 0$ is small which is probably due to the comparatively small value of the eccentricity parameter. ξ for CO. The theoretical curves however show a much smaller variation with temperature than the experimental one. Unlike the experimental curve, the theoretical curves do not show inversion. For the composition dependence of α_T curve, the agreement between the experimental and calculated value is fairly satisfactory over the whole composition range. This result shows a striking example of the success of the inelastic theory of Mnochick et al (1968). The less satisfactory results obtained for the temperature dependence of α_T may be partially due to the error in the temperature dependence of Z_{rot} values as determined from thermal conductivity data which is not likely to give quantitatively correct values.

For the temperature dependence of α_T curve for CO_2-N_2O system (having 32.8% of CO_2), the theoretical values of α_T as obtained from the inelastic theory are much lower than the experimental values. This may be partially due to the neglect of the effect of $(6\widetilde{C}_{ij}-5)$ term for CO_2 or due to the approximations made in obtaining the asymmetry parameter for N_2O. To test this, we have first assumed the $(6C_{ij}-\tilde{5})$ term for CO_2 to have the same value as that of N_2O, this however does not improve the situation. We have therefore obtained $(6\tilde{C}_{ij}-5)$ value for CO_2 from the experimental α_T value at one temperature and this came out to be 0.115. With this value, the calculated curve passes through the experimental one although the nature of the curve is not reproduced. The situation for the composition dependence of α_T curve at $T = 297°K$ is more or less the same. The experimental α_T curve shows a concave nature when plotted against the increasing concentration of CO_2 whereas the theoretical curve shows a slow decrease of α_T. It may be pointed that for a comparatively simple system like Ar-CO_2 there are certain anomalies which have not been exlplained satisfactorily (Monchick et al 1966). If those discrepanicies are due to some factors

for CO_2, these are likely to influence the CO_2-N_2O system much more as N_2O has many similarities with CO_2 molecule.

5. CONCLUSIONS

The present experimental α_T data for N_2-CO and CO_2-N_2O systems show conclusively the influence of inelastic collisions on thermal diffusion in polyatomic gas mixtures. The inelastic theories of Monchick *et al* have been found to represent the effects of inelastic collisions fairly well for N_2-CO system for which the molecular models used hold well.

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