

# **CHAPTER 4**

## **Estimation of Theoretical and Experimental Thermal Diffusion factor**

# Estimation of Theoretical and Experimental Thermal Diffusion Factor

## 4.1 Introduction

Theoretical  $\alpha_T$  of any binary gas mixture is derived from the Chapman-Enskog<sup>1)</sup> gas kinetic theory. The theory is based on the elastic collisions among the molecules associated with the distribution function. The distribution function gives the number of molecules with position coordinates and translational velocities in a particular range at a given time. The theory is, therefore, suitable for a gas mixture of monatomic molecules colliding each other elastically.

For polyatomic molecules such a distribution function is inadequate because it requires a knowledge of the number of molecules in a particular internal state. The classical theory for such molecules has been given by Taxman<sup>2)</sup>. A semiclassical theory has further been developed by Wang-Chang, Uhlenbeck and de Boer<sup>3)</sup>. Based on such theories Monchick et al<sup>4)</sup> derived the theoretical  $\alpha_T$  for molecules with inelastic collisions among them.

## 4.2. Theoretical $\alpha_T$ Due to Elastic Collisions Among Molecules

$\alpha_T$  due to Chapman-Enskog<sup>1)</sup> gas kinetic theory is derived as the solution of an infinite set of coupled algebraic equations whose coefficients are functions of molefractions, molecular masses and collision integrals. For convenience, in numerical calculations it is customary to select some molecular diameter  $\sigma$  and define the dimensionless collision integrals as :

$$\Omega^{(l,s)*} = \frac{4}{\sigma^2(s+1)!} \left[ 1 - \frac{1+(-1)^l}{2(1+l)} \right]^{-1} \left( \frac{\mu}{2\pi kT} \right)^{1/2} \Omega^{(l)}(s) \quad \dots\dots(4.1)$$

The reduced collision integrals are so defined as to be unity for rigid elastic spheres of molecular diameter  $\sigma$ . The solution of the infinite set of equations can formally be written as the ratio of two infinite determinants. In Chapman-Cowling<sup>1)</sup> procedure this is replaced by the ratio of two finite determinants.

The coefficients  $a_{ij}$  in these determinants can be expressed in terms of the collision integrals. But explicit expressions are available only to the third order of approximation.

Another successive approximation procedure has been derived by Kihara<sup>5)</sup> and extended by Mason<sup>6)</sup>. Although Kihara's approximation for the transport coefficients are usually simpler than the Chapman-Cowling<sup>1)</sup> expression, they may not be more accurate depending on the specific system under consideration. Following Chapman-Enskog<sup>1)</sup> procedure the expression for  $\alpha_T$  of a binary gas mixture can be given by :

$$\alpha_T = \frac{1}{6[\lambda_{ij}]_1} \frac{S_i^{(1)}x_i - S_j^{(1)}x_j}{X_\lambda + Y_\lambda} (6C_{ij}^* - 5) \quad \dots\dots\dots (4.2)$$

where  $C_{ij}^*$  is the ratio of the collision integral and it strongly depends on the temperature of the gas mixture.  $\lambda_{ij}$  is the coefficient of thermal conductivity,  $x_i$  and  $x_j$  are respectively the molefractions of the lighter (i) and heavier (j) components of the mixture.  $S_i^{(1)}$  is given by :

$$S_i^{(1)} = \frac{M_i + M_j}{2M_j} \left( \frac{\lambda_{ij}}{\lambda_i} \right)_1 - \frac{15}{4 A_{ij}^*} \left( \frac{M_j - M_i}{2M_i} \right) - 1 \quad \dots\dots\dots (4.3)$$

where  $A_{ij}^*$  is the collision integral which depends upon  $\epsilon_{ij}/k$  of the binary mixture.  $M_i$  and  $M_j$  are the masses of the lighter and the heavier components of the molecules of thermal conductivities  $(\lambda_i)_1$  and  $(\lambda_j)_1$  respectively. The usual values of thermal conductivities are computed by the relation :

$$[\lambda_{ij}]_1 = \frac{15}{4} \frac{R}{M_i} [\eta_{ij}]_1 \quad \dots\dots\dots (4.4)$$

instead of  $[\lambda_{ij}]_1 = 1989.1 \times 10^{-7} \frac{[T (M_i + M_j) / 2 M_i M_j]^{1/2}}{\sigma^2 \Omega_{ij}^{(2,2)*} (T_{ij}^*)}$

$X_\lambda$  and  $Y_\lambda$  of eq (4.2) are calculated using the relations :

$$X_\lambda = \frac{x_i^2}{(\lambda_i)_1} + \frac{2x_i x_j}{(\lambda_{ij})_1} + \frac{x_j^2}{(\lambda_j)_1} \quad \dots\dots\dots (4.5)$$

$$\text{and } Y_\lambda = \frac{x_i^2}{(\lambda_i)_1} U^{(1)} + \frac{2x_i x_j}{(\lambda_{ij})_1} U^{(2)} + \frac{x_j^2}{(\lambda_j)_1} U^{(3)} \quad \dots\dots\dots (4.6)$$

$$\text{where } U^{(1)} = \frac{4}{15} A_{ij}^* - \frac{1}{12} \left( \frac{12}{5} B_{ij}^* + 1 \right) \frac{M_i}{M_j} + \frac{1}{2} \frac{(M_i - M_j)^2}{M_i M_j} \quad \dots\dots\dots (4.7)$$

$$U^{(2)} = \frac{4}{15} A_{ij}^* - \frac{1}{12} \left( \frac{12}{5} B_{ij}^* + 1 \right) \frac{M_j}{M_i} + \frac{1}{2} \frac{(M_j - M_i)^2}{M_i M_j} \quad \dots\dots\dots (4.8)$$

$$\text{and } U^{(3)} = \frac{4}{15} A_{ij}^* \frac{(M_i + M_j)^2}{4 M_i M_j} \frac{(\lambda_{ij}^2)_1}{(\lambda_i)_1 (\lambda_j)_1} - \frac{1}{12} \left( \frac{12}{5} B_{ij}^* + 1 \right) - \frac{5}{32 A_{ij}^*} \left( \frac{12}{5} B_{ij}^* - 5 \right) \frac{(M_i - M_j)^2}{M_i M_j} \quad \dots\dots\dots (4.9)$$

$B_{ij}^*$  is another collision integral. For different binary molecular mixtures  $\alpha_T$ 's can be evaluated using eqs (4.2) to (4.9). The present investigation includes binary gas mixtures like  $\text{CH}_4^{16} - \text{CH}_4^{17}$ ,  $\text{N}_2^{28} - \text{N}_2^{29}$  and  $\text{CO}^{28} - \text{CO}^{29}$ , hydrogenic gases in trace concentration in Helium ( $\text{He}^4$ ) and inert gas molecules. The purpose is to compare the theoretical  $\alpha_T$  with the experimental  $\alpha_T$  obtained by the CCF method and to examine whether elastic or inelastic collisions occur among the experimental molecules. Here, it is to be noted that thermal diffusion is a second order effect in the sense that its existence depends on the nature of molecular collisions, whereas the other transport properties like viscosity, heat conductivity and ordinary diffusion arise due to occurrence of collisions and secondarily on their nature.

### 4.3. Theoretical $\alpha_T$ Due to Inelastic Collisions Among Molecules

The most satisfactory theory of  $\alpha_T$  based on inelastic collisions among the molecules was given by Monchick, Munn and Mason<sup>7</sup>. It is as follows :

$$\alpha_T = \frac{\mu_{ij} (6C_{ij}^* - 5)}{5nk (D_{ij})_1} \left( \frac{\lambda_{ij}}{x_j M_j} - \frac{\lambda_{ij}}{x_i M_i} \right) \quad \dots\dots\dots (4.10)$$

where  $x_i$  and  $M_i$  are the molefraction and molecular mass of the component  $i$ ,  $\mu_{ij}$  is the reduced mass of the molecules and  $n$  is the number density of the mixture. For the polyatomic gas molecules the standard ratio of the collision integral  $C_{ij}^*$  is given by<sup>8)</sup>

$$(6 C_{ij}^* - 5) = \frac{2 \langle (\gamma'^2 - 5/2)(\gamma^2 - \gamma\gamma' \cos \chi) \rangle_{ij}}{\langle (\gamma^2 - \gamma\gamma' \cos \chi) \rangle_{ij}}$$

where the angle bracket notation  $\langle \dots \rangle_{ij}$  is the standard notation for a collision integral. Primed and unprimed quantities are used after and before collisions of the colliding molecules and  $\chi$  is a dynamic variable for the scattering angle.

Assuming the entrance and the exit channels are not the same except for an angle independent factor equal to the probability of a change in the internal energy state, Monchick, Sandler and Mason<sup>9)</sup> removed certain approximations of the previous work<sup>8)</sup>. Under this assumption the partial thermal conductivity  $\lambda_{ij}$  becomes the steady state translational thermal conductivity  $\lambda_i^\alpha$  of species  $i$  in the mixture. Using the relations of  $\lambda_i^\alpha$  and  $\lambda_i^{\alpha_{int}}$  and retaining the spin isotropic approximations it is found that

$$\alpha_T = \frac{(6C_{ij}^* - 5)\mu_{ij}}{5nk (D_{ij})_1} \left[ \frac{\lambda_j^\alpha}{x_j m_j} - \frac{\lambda_i^\alpha}{x_i m_i} \right] + \frac{1}{5nk (D_{ij})_1} \left[ \frac{(6\tilde{C}_{ij} - 5)\lambda_j^{int}}{x_j} - \frac{(6\tilde{C}_{ij} - 5)\lambda_i^{int}}{x_i} \right]$$

The collision integral ratio  $\tilde{C}_{ij}$  is not symmetric with respect to interchanges of the indices  $i$  and  $j$  and is very sensitive to inelastic collisions among molecules.  $\lambda_i^\alpha$  and  $\lambda_j^\alpha$  are also influenced by inelastic collisions and they are expressed as<sup>10)</sup>:

$$\lambda_{i,trans}^{\alpha} = \frac{\eta}{M} \left[ \left( \frac{5}{2} C_{v,trans} + \frac{\rho D_{int}}{\eta} C_{int} \right) - \left( \frac{2}{\pi} \frac{C_{int}}{Z_{rot}} \right) \left( \frac{5}{2} - \frac{\rho D_{int}}{\eta} \right)^2 \left\{ 1 + \frac{2}{\pi Z_{rot}} \left( \frac{5}{3} \frac{C_{int}}{R} + \frac{\rho D_{int}}{\eta} \right) \right\}^{-1} \right]$$

Partial internal thermal conductivity is given as below<sup>11)</sup>

$$\lambda_{i,trans}^{\alpha} = \frac{n (D_{ij})_1 C_{i,int}}{1 + (x_i / x_j) (D_{ii} / D_{ij})_1}$$

It is observed by many workers<sup>12,13)</sup> that this theory is successful in predicting both temperature and composition dependence of  $\alpha_T$  in such system where one of the components of the binary mixtures is eccentrically loaded sphere molecule. In other cases the theory fails to explain the experimental results. However, Chattopadhyay and Acharyya<sup>14)</sup> extended this part of the theory with the nonspherical part of the potential in the following way :

$$(6 \tilde{C}_{ij} - 5) = \frac{5}{2} \left( \frac{W_j^{(1)} - W_j^{(2)}}{W_j^{(1)}} \right) \dots \dots \dots (4.11)$$

where  $W_j^{(1)} = 2 \epsilon_j^{-1/2} \sin^{-1} \left( \frac{\epsilon_j}{1 + \epsilon_j} \right)^{1/2} \dots \dots \dots (4.12)$

and  $W_j^{(2)} = \frac{2}{(1 + \epsilon_j)} \dots \dots \dots (4.13)$

$\epsilon_j$  is the molecular eccentricity given by

$$\epsilon_j = \frac{m \xi_j^2}{2 I_j}$$

the subscript  $j$  refers to the eccentrically loaded sphere molecule,  $\xi_j$  is the distance between the centre of mass of the molecule from its centre of symmetry and  $I_j$  is the moment of inertia about the centre of mass of the molecule.

However, the rotational translational collision number  $Z_{rot}$  is approximately inversely proportional to  $(6 \tilde{C}_{ij} - 5)$ . Thus from eqs (4.11) to (4.13) we have

$$\sin \frac{5K^{1/2}}{(K+1) [5-2(C_{ji}-5)]} = \frac{1}{(K+1)^{1/2}}$$

Since  $\xi_j = \frac{C}{T}$  then  $K = I_j / C$ . This K can be found out from the method of successive approximation. The distance  $\xi_j$  is calculated from the knowledge of structure and bond lengths of different types of molecules of varying sizes and shapes.

Moments of inertia of different molecules from inelastic theory of thermal diffusion has been shown elsewhere<sup>11)</sup>. On comparison with experimental values of moment of inertia it reveals that for molecules like HT, DT, HD, CH<sub>3</sub>Cl, NH<sub>3</sub> etc, there is a good agreement while in case of other molecules like NO, CO, HCl, HBr, N<sub>2</sub>O, H<sub>2</sub>O etc wide disagreement occurs. It is thus obvious that experimental  $\alpha_T$  for molecules like HT, DT, HD, CH<sub>3</sub>Cl etc as one of the components in a binary mixture will give reasonable good agreement with theoretical  $\alpha_T$  due to inelastic collision.

In case of NO, CO molecules with very small eccentricity and N<sub>2</sub>O whose eccentricity is comparable to that of HT there is wide disagreement between theoretical and experimental  $\alpha_T$ 's. Also disagreement are there for other molecules whose eccentricities are larger. Thus the eccentricity parameter does not appear to be an important factor in determining the validity of this theory. Any rationalisation of the disagreement or any inference regarding the types of molecules for which the theory is valid can not be made at present<sup>14)</sup>.

However, the composition dependence of  $\alpha_T$  due to elastic collision theory of He<sup>4</sup> - Ar<sup>40</sup>, Ne<sup>20</sup>-Xe<sup>132</sup> and Ne<sup>20</sup>-Ne<sup>22</sup> binary molecular mixtures have been determined theoretically and discussed in chapter 5 of the thesis. Theoretical  $\alpha_T$  due to elastic collision theory for different experimental molecules are presented in different tables as well as in different graphical plots of  $\alpha_T$  against  $\bar{T}$  curves in the thesis chapterwise.  $\alpha_T$  for He-HT, He-HD, He-T<sub>2</sub>, CH<sub>4</sub><sup>16</sup>-CH<sub>4</sub><sup>17</sup>, N<sub>2</sub><sup>28</sup>-N<sub>2</sub><sup>29</sup> and CO<sup>28</sup>-CO<sup>29</sup> molecules based on elastic collision theory fails to explain experimental  $\alpha_T$ 's. Consequently,  $\alpha_T$  based on inelastic collision theory for these molecules are worked out and

compared with their respective experimental  $\alpha_T$ . It reveals that inelastic collision plays an important role in case of binary molecular mixtures like He-HT, He-HD and He-T<sub>2</sub> molecules.

#### 4.4. Experimental $\alpha_T$ by the Existing and the Present Method

For an ideal column of length L with a gas mixture at any mean temperature  $\bar{T}$  the separation factor  $q_e$  is given by the relation<sup>11)</sup>

$$\ln q_e = \frac{HL}{K_c + K_d}$$

where H,  $K_c$  and  $K_d$  are proportional to  $p^2$ ,  $p^4$  and  $p^0$  respectively, p being the pressure in atmosphere of the gas mixture. It is obvious that as pressure p increases  $\ln q_e$  increases and eventually becomes maximum at  $K_c = K_d$  for which the maximum separation factor  $q_{\max}$  is given by the relation :

$$\ln q_{\max} = \frac{HL}{2(K_c K_d)^{1/2}} \dots\dots\dots(4.14)$$

Writing  $(HL/K_c) = a'/p^2$  and  $(K_d / K_c) = b' / p^4$  we have

$$\ln q_{\max} = \frac{a'}{2\sqrt{b'}} \dots\dots\dots(4.15)$$

where  $a'$  and  $b'$  are the parameters governing the nature of experimental  $\ln q_e$  against pressure p at any constant temperature or composition. Experimental  $\ln q_{\max}$  in terms of  $a'$  and  $b'$  can thus be obtained from eq (4.15).

Further, the expressions for the column coefficients H,  $K_c$  and  $K_d$  are as the followings<sup>11)</sup> :

(i) Maxwellian case ( $n = 1$ ,  $\alpha_T$  is assumed to be temperature independent)

$$H = \frac{2\pi}{6l} (\alpha_T \rho^2 g / \eta) \frac{1}{2} (r_c + r_h) (r_c - r_h)^3 (2u)^2 h'$$

$$K_c = \frac{2\pi}{9!} (\rho^3 g^2 / \eta^2 D)_1 \frac{1}{2} (r_c + r_h)(r_c - r_h)^7 (2u)^2 k'_c$$

and 
$$K_d = 2\pi (\rho D)_1 \frac{1}{2} (r_c + r_h)(r_c - r_h) k'_d$$

(ii) Sliker's case (Interaction model independent) :

$$H = [S.F.]_1 r_c^4 (\rho^2 g \alpha_T / \eta)_1 \left( \frac{\Delta T}{T} \right)^2$$

$$K_c = [S.F.]_3 r_c^8 (\rho^3 g^2 / \eta^2 D)_1 \left( \frac{\Delta T}{T} \right)^2 \quad \text{and}$$

$$K_d = \pi (1-a^2) r_c^2 (\rho D)_1$$

(iii) Lennard - Jones case (Interaction model dependent)

$$H = \frac{2\pi}{6!} (\alpha_T \rho^2 g / \eta)_1 r_c^2 h,$$

$$K_c = \frac{2\pi}{9!} (\rho^3 g^2 / \eta^2 D)_1 r_c^8 k_c \quad \text{and}$$

$$K_d = 2\pi (\rho D)_1 r_c^2 k_d$$

Here  $\{ h', k'_c, k'_d \}$ ,  $\{ [S.F.]_1, \pi(1-a^2), [S.F.]_3 \}$  and  $\{ h, k_c \text{ and } k_d \}$  are the dimensionless Maxwell, Sliker and Lennard-Jones shape factor (CSF) respectively,  $u = \frac{\Delta T}{T}$  and  $a = r_h / r_c$ . Evaluation of experimental  $\alpha_T$  by the existing methods thus involved with column shape factors. The Lennard-Jones case is, however, inapplicable where the cold wall temperature  $T_c$  is held fixed. The mass density  $\rho$ , the coefficient of viscosity  $\eta$  and the diffusion coefficient  $D$  may be found out from the experimental results or theoretical formulations reported elsewhere<sup>15</sup>. Now, using the expressions for  $H$ ,  $K_c$  and  $K_d$  the experimental  $\alpha_T$  by the existing method can be obtained from eq (4.14). The  $\alpha_T$ 's thus obtained are :

$$\alpha_T (\text{Maxwell model}) = 2.39 \frac{r_c - r_h}{L} \frac{\bar{T}}{\Delta T} \frac{\sqrt{k'_c k'_h}}{h'} \text{In} q_{\max} \quad \dots (4.16)$$

$$\alpha_T (\text{Lennard Jones case}) = 2.39 \frac{r_c}{L} \frac{\bar{T}}{\Delta T} \frac{\sqrt{k_c k_h}}{h} \text{In} q_{\max} \quad \dots (4.17)$$

$$\alpha_T (\text{Sliker model}) = 2.00 \frac{r_c}{L} \frac{\bar{T}}{\Delta T} \frac{\sqrt{\pi(1-a^2) [S.F.]_3}}{[S.F.]_1} \text{In} q_{\max} \quad \dots (4.18)$$

Actually, the column shape factors depends on the geometry of the column. Experimental value of  $\ln q_{\max}$  is obtained from eq (4.15). Thus the  $\alpha_T$  by the existing methods are worked out from eqs (4.16) to (4.18).

The determination of  $\alpha_T$  by the present CCF method deals with the column calibration factor  $F_s$  of the column. The temperature or composition variation of  $\alpha_T$  is simply found out from the relation. :

$$\ln q_{\max} = \alpha_T F_s (r_c, r_h, L \text{ and } \bar{T}) \dots\dots\dots (4.19)$$

where  $F_s$  depends on the geometry of the thermal diffusion column and can be obtained by the calibration method. Determination of  $\alpha_T$  by the CCF method is well discussed in different chapters of this thesis.

We are now in a position to compare the  $\alpha_T$ 's by the CCF method with those by the existing methods as well as with the theoretical  $\alpha_T$ . The comparison is well displayed in different tables and also in different graphs of  $\alpha_T$  against composition or temperature in chapters 5 to 10 of the thesis. Further, estimation of molecular force parameters of the experimental molecules from  $\alpha_T$  by the CCF method have been made in chapters 7 to 9 of the thesis. This is to ensure the reliability of the composition or temperature dependence of  $\alpha_T$  by the present CCF method.

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