

# **APPENDIX**

## Column Calibration Factor to Study the Composition Dependence of the Thermal Diffusion Factors of Inert Gas Mixtures

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The experimental thermal diffusion factors  $\alpha_T$  of He<sup>4</sup>-Ar<sup>40</sup> and Ne<sup>20</sup>-Xe<sup>132</sup> gas mixtures at different compositions of the lighter components and an isotopic natural mixture of Ne<sup>20</sup>-Ne<sup>22</sup> are estimated at the mean temperature  $\bar{T}=340$  K by the column calibration factor method from the available values of  $\ln q_e$  ( $q_e$  being the equilibrium separation factor) for those mixtures at different pressures in atmosphere for each composition, measured by J. M. Saviron *et al.* in a thermal diffusion column with the column calibration factor  $F_s=3.946$ , the value (at  $\bar{T}=340$  K) derived from the formula  $F_s=68.94796-0.3174514\bar{T}+3.71383\times 10^{-4}\bar{T}^2$  as obtained by S. Acharyya *et al.* It is shown that the experimental  $\alpha_T$ 's, thus estimated with the help of  $F_s$  and  $\ln q_{\max}$ , agree excellently with those due to the existing methods using molecular models as well as with those due to Sliker's model-independent method, so far as their magnitudes and the trends of their variation with the mole fraction of the lighter components are concerned. This suggests that the present method is a unique one which can safely be used to study the composition dependence of  $\alpha_T$  in both the isotopic and nonisotopic cases.

### §1. Introduction

Nowadays the study of thermal diffusion is mostly directed to measuring the equilibrium separation factor  $q_e$ , defined by

$$q_e = (c_i/c_j)_{\text{top}} / (c_i/c_j)_{\text{bottom}}, \quad (1)$$

for isotopic and nonisotopic binary gas mixtures of different compositions at a fixed temperature, or for a binary gas mixture of fixed composition at different temperatures, in a thermal diffusion (TD) column first introduced by Clusius and Dickel.<sup>1)</sup> Here  $c_i$  and  $c_j$  are the mass fractions of the lighter and heavier components of a gas mixture, respectively, and the subscripts top and bottom denote the values at the top and bottom of a TD column. The experimental values of  $q_e$  are measured usually at different pressures below and around one atmosphere with the help of a precision type mass spectrometer, and hence the TD factor  $\alpha_T$  of a binary gas mixture as a function of the composition or the temperature is estimated by using various molecular models such as those of Maxwell and Lenn-

ard-Jones<sup>2)</sup> and sometimes by using Sliker's model-independent method,<sup>3)</sup> which is, however, a crude one. In an attempt to get the actual  $\alpha_T$ , we,<sup>4-6)</sup> however, introduced a factor  $F_s$ , called the column calibration factor of a TD column, by the relation

$$\ln q_{\max} = \alpha_T F_s(r_c, r_h, L, \bar{T}), \quad (2)$$

where  $q_{\max}$  is the maximum value of  $q_e$  measured experimentally in a TD column,  $r_c$  and  $r_h$  are the cold wall and hot wall radii of the column of geometrical length  $L$ , and  $\bar{T}$  is the mean temperature in K of the gas mixture in the column, defined by  $\bar{T}=(T_h+T_c)/2$ ,  $T_h$  and  $T_c$  being the temperatures of the hot and cold walls of the column, respectively. The column calibration factor  $F_s$ , which is purely an apparatus quantity, is supposed to be independent of a molecular interaction model and depends only on the geometry of the column at any mean temperature  $\bar{T}$ .

The column calibration factor  $F_s$  of a column with  $L=149$  cm,  $r_c=1.37$  cm and  $r_h=0.6$  cm has already been studied elsewhere,<sup>5)</sup> and the empirical relation of  $F_s$  to  $\bar{T}$  has been

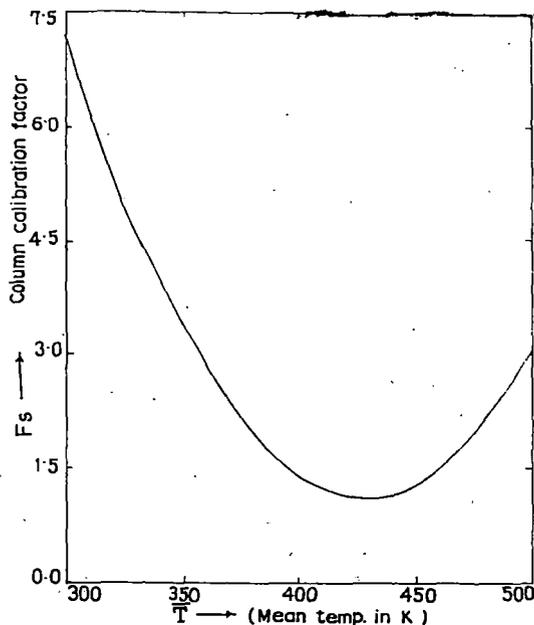


Fig. 1. Plot of the column calibration factor against  $\bar{T}$ , the mean temperature in K.

found to be

$$F_s = 68.94796 - 0.3174514 \bar{T} + 3.71383 \times 10^{-4} \bar{T}^2,$$

yielding the value of  $F_s = 3.946$  at  $\bar{T} = 340$  K. The  $F_s$  for this column is plotted against  $\bar{T}$  in Fig. 1. Fortunately J. M. Saviron *et al.*<sup>7)</sup> have recently studied the pressure dependence of the reduced logarithmic separation factors,  $\ln \bar{Q}_{\text{exp}}$ , for two binary inert gas mixtures of  $\text{He}^4\text{-Ar}^{40}$  and  $\text{Ne}^{20}\text{-Xe}^{132}$  and also an isotopic natural mixture of  $\text{Ne}^{20}\text{-Ne}^{22}$  for different compositions of the lighter components in the respective mixtures, in this column, at the experimental mean temperature  $\bar{T} = 340$  K, the hot wall and cold wall temperatures being  $T_h = 380$  K and  $T_c = 300$  K, respectively. From these results we estimate  $\ln q_c$  of the mixtures for different concentrations of the lighter components at different pressures in atmosphere, and the data thus obtained are found to satisfy the hydrodynamical part of the column theory, as developed by Furry and Jones<sup>6)</sup> and Furry, Jones and Onsager,<sup>9)</sup> so excellently as shown in Figs. 2 and 3 that we have at once the following relations of  $p^2/\ln q_c$  to  $p^4$  for these mixtures at different concentrations:

$$p^2/\ln q_c = 3.09752 + 177.30496 p^4,$$

$$p^2/\ln q_c = 8.52467 + 66.65334 p^4,$$

$$p^2/\ln q_c = 17.20000 + 41.70213 p^4,$$

$$p^2/\ln q_c = 19.65238 + 16.78669 p^4,$$

$$p^2/\ln q_c = 18.74249 + 12.92235 p^4,$$

for the  $\text{He}^4\text{-Ar}^{40}$  mixture for the concentrations 8.76, 21.63, 30.14, 49.30 and 64.46% of  $\text{He}^4$ , respectively;

$$p^2/\ln q_c = 0.59848 + 3156.6 p^4,$$

$$p^2/\ln q_c = 2.39745 + 327.3 p^4,$$

$$p^2/\ln q_c = 3.03368 + 133.3 p^4,$$

for the  $\text{Ne}^{20}\text{-Xe}^{132}$  mixture for 15, 66 and 90% of  $\text{Ne}^{20}$ ; and finally

$$p^2/\ln q_c = 13.3 + 89.06 p^4,$$

for the  $\text{Ne}^{20}\text{-Ne}^{22}$  mixture. These establish that the graph of  $p^2/\ln q_c$  against  $p^4$  is always a straight line as predicted by the FJO theory.<sup>9)</sup> Rutherford and Kaminski<sup>10)</sup> have recently shown that the FJO theory<sup>9)</sup> is applicable mainly in the case of an isotopic binary gas mixture and also in the case of a mixture in which one of the components is in trace concentrations.

In the thermal diffusion phenomena of isotopic gas mixtures, the elastic collisions are supposed to play a prominent role between the interacting molecules. Again, the thermal diffusion phenomenon is very sensitive to intermolecular interactions of the binary gas molecules; therefore, the study of the composition dependence of the TD factors  $\alpha_T$  of any gas mixture is necessary to throw much light on the interactions between like molecules and those between unlike molecules of a gas mixture. The temperature dependence of  $\alpha_T$  is, however, entirely governed by the factor  $(6C_{ij}^* - 5)$ , where  $C_{ij}^*$  is the ratio of the collision integrals. Moreover, the effect of inelastic collisions on the thermal diffusion, if any, is practically negligible in gas mixtures containing inert gases. All the facts mentioned above inspired us to study  $\text{He}^4\text{-Ar}^{40}$  and  $\text{Ne}^{20}\text{-Xe}^{132}$  mixtures at different compositions of the lighter components at a given experimental mean temperature  $\bar{T} = 340$  K and also the isotopic mixture  $\text{Ne}^{20}\text{-Ne}^{22}$  with its natural isotopic abun-

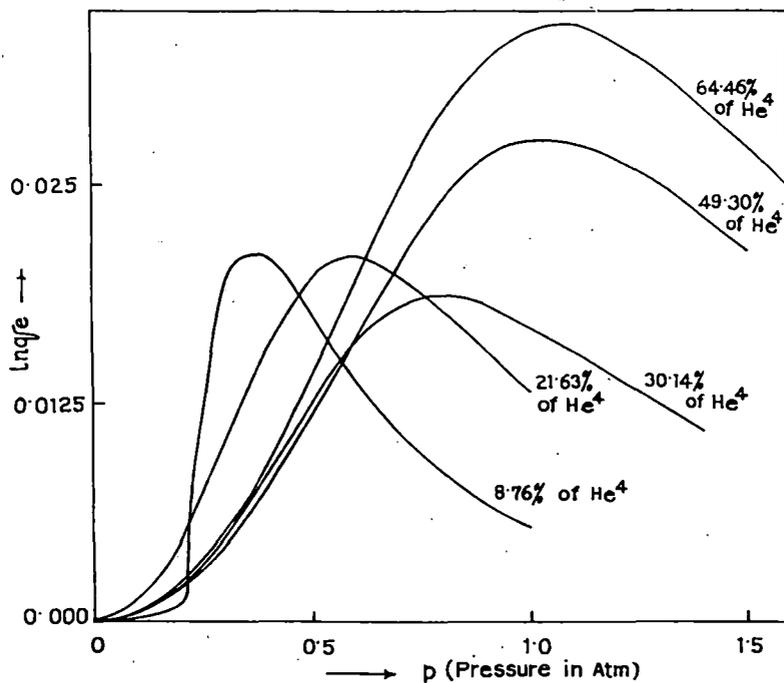


Fig. 2. Plot of  $\ln q_e$  of  $\text{He}^4$ - $\text{Ar}^{40}$  (binary inert gas mixture) against pressure  $p$  in atm. at different concentrations of  $\text{He}^4$  at temperature  $\bar{T} = 340$  K.

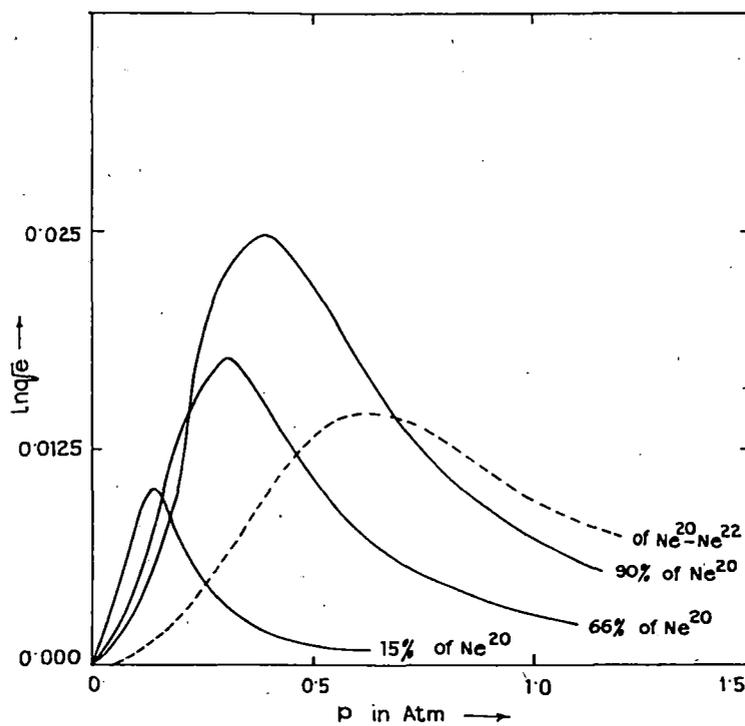


Fig. 3. Plot of  $\ln q_e$  of  $\text{Ne}^{20}$ - $\text{Xe}^{132}$  (binary inert gas mixture) against pressure  $p$  in atm. at different concentrations of  $\text{Ne}^{20}$  at temperature  $\bar{T} = 340$  K. The dotted curve represents that of  $\text{Ne}^{20}$ - $\text{Ne}^{22}$ .

Table I. Composition dependence of thermal diffusion factors  $\alpha_T$  of inert gas mixture at  $\bar{T}=340$  K in a column of  $L$ =geometrical length=149 cm,  $r_c$ =the cold wall radius=1.37 cm and  $r_h$ =the hot wall radius=0.6 cm.

System	$T_h$ K	$T_c$ K	$\bar{T}$ K	% of lighter component.	$a' \times 10^3$ (atm) <sup>2</sup>	$b' \times 10^3$ (atm) <sup>4</sup>	$\ln q_{\max}$	$F_s$	Expt. $\alpha_T \times 10^3$ present method	Expt. $\alpha_T \times 10^3$ based on models			Theo. $\alpha_T$ (elastic)
										Maxwell	L-J	Sliker	
He-Ar	380	300	340	8.76	5.64	17.47	0.0213		5.40	4.20	1.60	3.80	0.226
				21.63	15.00	127.87	0.0210	5.30	3.00	1.20	2.40	0.253	
				30.14	23.98	412.46	0.0187	3.946	4.70	2.70	1.00	2.10	0.273
				49.30	59.57	1170.72	0.0275		7.10	3.60	1.40	2.90	0.327
				64.46	77.39	1295.62	0.0340		8.60	7.20	2.50	5.80	0.340
Ne-Xe	380	300	340	15.00	0.32	0.19	0.0115		2.90	4.20	4.50	3.40	0.247
				66.00	3.06	7.32	0.0178	3.946	4.50	7.30	7.50	5.40	0.218
				90.00	7.50	22.76	0.0249		6.30	13.70	15.50	11.00	0.236
Ne <sup>20</sup> -Ne <sup>22</sup>	380	300	340	10.00	11.23	148.87	0.0146	3.946	3.70	5.40	1.70	4.40	0.0248

dances. The purpose of this work is to observe how far the TD factors  $\alpha_T$  as estimated by our column calibration factor method agree with those obtained by the existing methods, using the column shape factors involved in the molecular models, and by Sliker's model-independent method.<sup>3)</sup> The comparison is presented in Table I, and shown graphically in Figs. 4 and 5 for He<sup>4</sup>-Ar<sup>40</sup> and Ne<sup>20</sup>-Xe<sup>132</sup> mixtures, respectively. The molecular parameters as well as the column shape factors used to calculate the experimental  $\alpha_T$ 's by the existing method are shown in Table II. The theoretical  $\alpha_T$ 's as functions of the mole fractions of the lighter components are also calculated from the formula derived from the Chapman-Enskog kinetic theory<sup>11)</sup> based upon the elastic collisions between the interacting molecules. These  $\alpha_T$ 's are also shown in Table I and in Figs. 4 and 5 for comparison.

## §2. Mathematical Formulations to Estimate the Experimental $\alpha_T$ 's of the Mixtures

For a TD column with both ends closed, the hydrodynamical part of the column theory related with the transport of the lighter component up the tube, so far developed by Furry, Jones and Onsager,<sup>9)</sup> yields that the net transport of the  $i$ th component of a binary gas mixture up the column tube is zero, i.e.

$$\tau_i = Hc_i c_j - (K_c + K_d) \frac{\partial c_i}{\partial z} = 0, \quad (3)$$

where  $z$  is the coordinate along the column,

and  $H$ ,  $K_c$  and  $K_d$  are called the transport coefficient, the convective remixing coefficient and the diffusive remixing coefficient, respec-

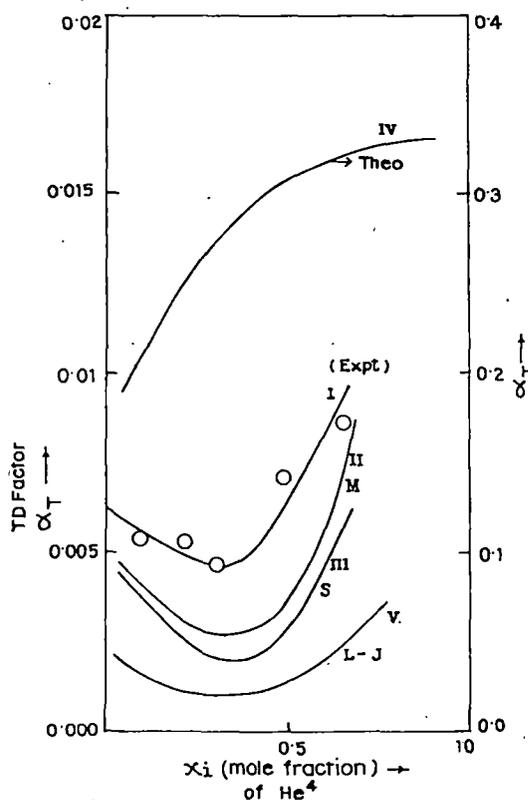


Fig. 4. Experimental  $\alpha_T$  against mole fraction of He<sup>4</sup> of He<sup>4</sup>-Ar<sup>40</sup> mixture at mean temperature  $\bar{T}=340$  K. I Expt.  $\alpha_T$  (our calibration factor method), II Expt.  $\alpha_T$  (Maxwell's model), III Expt.  $\alpha_T$  (Sliker), IV Theoretical  $\alpha_T$  (elastic), V Expt.  $\alpha_T$  (L-J model).

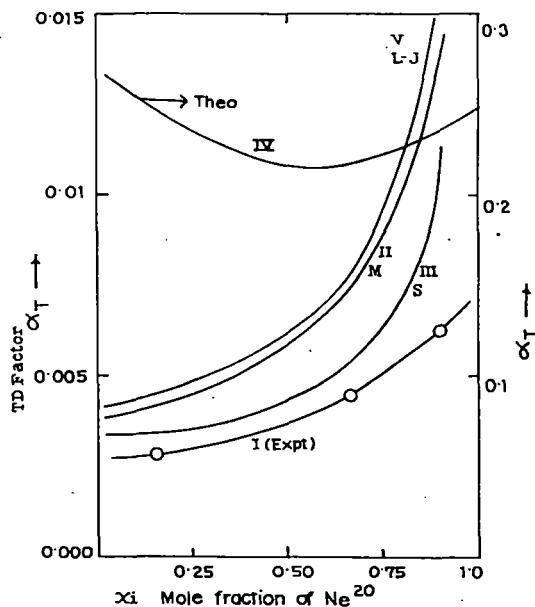


Fig. 5. Experimental  $\alpha_T$  against mole fraction of  $\text{Ne}^{20}$  of  $\text{Ne}^{20}\text{-Xe}^{132}$  mixture at mean temperature  $\bar{T}=340$  K. I Expt.  $\alpha_T$  (our calibration factor method), II Expt.  $\alpha_T$  (Maxwell's model), III Expt.  $\alpha_T$  (Sliker), IV Theoretical  $\alpha_T$  (elastic), V Expt.  $\alpha_T$  ( $L-J$  model).

tively; they are complicated functions of the wall temperatures, the geometry of the column and also the transport properties of the binary gas mixture, and are given by

$$H = \frac{2\pi}{Q^3} \int_{T_c}^{T_h} \frac{\rho D_{ij}}{\lambda} \alpha_T \frac{G(T)}{T} dT, \quad (4)$$

$$K_c = \frac{2\pi}{Q^2} \int_{T_c}^{T_h} \frac{\rho D_{ij}}{\lambda} G^2(T) dT, \quad (5)$$

$$K_d = \frac{2\pi}{Q} \int_{T_c}^{T_h} r^2 \lambda \rho D_{ij} dT, \quad (6)$$

where  $\rho$  is the density,  $r$  is the radial coordinate,  $\lambda$  and  $D_{ij}$  are the thermal conductivity and diffusion coefficient of the gas mixtures, respectively,  $T_h$  and  $T_c$  are the hot and cold wall temperatures, and  $2\pi Q$  denotes the radial heat flow per unit length of the column. The function  $G(T)$  is the solution of the fourth-order differential equation

$$\frac{d}{dT} \left( \frac{1}{\lambda r^2} \right) \frac{d}{dT} \left( \frac{\eta}{\lambda} \right) \frac{d}{dT} \left( \frac{1}{\lambda \rho r^2} \right) \frac{d}{dT} \left( \frac{\rho D_{ij}}{\lambda} G(T) \right) = -g \frac{dp}{dT}, \quad (7)$$

with the boundary conditions

$$G(T_c) = G(T_h) = G'(T_c) = G'(T_h) = 0. \quad (8)$$

Here  $\eta$  and  $g$  denote the coefficient viscosity of the gas mixture and the acceleration of gravity, respectively.

Integrating eq. (3) between the column ends  $z=0$  and  $z=L$ , where  $L$  is the geometrical length of the column, one gets

$$\ln q_c = \frac{HL}{K_c + K_d}. \quad (9)$$

The coefficients  $H$ ,  $K_c$  and  $K_d$  for an ideal column are proportional to the 2nd, the 4th and the 0th powers of the pressure  $p$  in at-

Table II. Column shape factors and other molecular parameters used to calculate  $\alpha_T$  of  $\text{He}^4\text{-Ar}^{40}$ ,  $\text{Ne}^{20}\text{-Xe}^{132}$  and  $\text{Ne}^{20}\text{-Ne}^{22}$  mixtures at  $\bar{T}=340$  K and the  $L-J$  potential  $\epsilon_{12}$  in erg.

Systems	$\epsilon_{12}/kK$	$\sigma_{12} \text{ \AA}$	Shape factors due to Maxwell's model		Sliker's shape factors	
			$h'$	$k'_d$	$[SF]_1$	$\pi(1-a^2)$
$\text{He}^4\text{-Ar}^{40}$	34.95	3.191				
$\text{Ne}^{20}\text{-Xe}^{132}$	79.36	3.457	0.99425	0.97734	$\frac{0.7041}{6!}$	1.7647
$\text{Ne}^{20}\text{-Ne}^{22}$	27.50	2.858				
Lennard-Jones' shape factors						
			$h$	$k_c$	$k_d$	
$\text{He}^4\text{-Ar}^{40}$	34.95	3.191	0.00750	0.00224	0.41875	
$\text{Ne}^{20}\text{-Xe}^{132}$	79.36	3.457	0.00250	0.00180	0.40700	
$\text{Ne}^{20}\text{-Ne}^{22}$	27.50	2.858	0.00975	0.00240	0.42310	

mosphere, respectively, for a binary gas mixture, and hence eq. (9) reduces to

$$\ln q_c = \frac{ap^2}{b+p^4}. \quad (10)$$

However, in a practically constructed column, parasitic remixing of the components of the mixture always occurs. This can be taken into consideration by adding a term  $K_p$ , proportional to  $p^4$ , in the denominator of eq. (9), so that eq. (9) becomes

$$\ln q_c = \frac{a'p^2}{b'+p^4},$$

or

$$p^2/\ln q_c = \frac{b'}{a'} + \frac{1}{a'} p^4. \quad (11)$$

The  $a'$  and  $b'$  in eq. (11) are related to  $a$  and  $b$  in eq. (10) by  $a = a'(1 + K_p/K_c)$  and  $b = b'(1 + K_p/K_c)$ , respectively. The  $a$  and  $b$  in eq. (10) again are expressed in terms of the column coefficients and the pressure of the binary gas mixture as

$$a = (HL/K_c)p^2 \quad \text{and} \quad b = (K_d/K_c)p^4.$$

Further, since  $(1 + K_p/K_c) = K_d/b'K_c$ , we have

$$H = a'K_d/b'L = K_d/LC, \quad (12)$$

where  $C = b'/a'$  is given by the straight line expressing eq. (11) for  $p^2/\ln q_c$  against  $p^4$ , demanded by the FJO column theory.<sup>9)</sup>

The possible values of  $H$ ,  $K_c$  and  $K_d$  can be obtained by the following equations:

i) Maxwell's<sup>8)</sup> model of binary interaction ( $\alpha_T$  being assumed to be temperature-independent and  $n=1$ , for Maxwellian molecules),

$$H = \frac{2\pi}{6!} \left( \frac{\alpha_T \rho^2 g}{\eta} \right)_1 \frac{1}{2} (r_c + r_h)(r_c - r_h)^3 (2u)^2 h',$$

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

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

ii) Sliker's<sup>3)</sup> model-independent method,

$$C_1 = H = [SF]_1 r_c^4 \left( \frac{\rho^2 g \alpha_T}{\eta} \right)_1 \left( \frac{\Delta T}{\bar{T}} \right)^2,$$

$$C_2 = K_d = \pi(1 - a^2) r_c^2 (\rho D)_1,$$

$$C_3 = K'_c = [SF]_3 r_c^8 (\rho^3 g^2 / \eta^2 D)_1 \left( \frac{\Delta T}{\bar{T}} \right)^2,$$

iii) Lennard-Jones' molecular model of binary interaction,

$$H = \frac{2\pi}{6!} \left( \frac{\alpha_T \rho^2 g}{\eta} \right)_1 r_c^4 h,$$

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

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

The dimensionless quantities  $h'$ ,  $k'_c$  and  $k'_d$ ,  $[SF]_1$ ,  $[SF]_3$  and  $\pi(1 - a^2)$  and  $h$ ,  $k_c$ , and  $k_d$ , called the column shape factors due to Maxwell, Sliker and Lennard-Jones, respectively, are presented in Table II; the factors in (ii) are free from a molecular interaction model;  $u = (T_h - T_c)/(T_h + T_c)$ ,  $a = r_h/r_c$  and  $\Delta T = T_h - T_c$ . The experimental  $\alpha_T$ 's 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> can thus be evaluated by three methods, the former two at the mean temperature  $\bar{T} = (T_h + T_c)/2$  and the last one using  $L - J$  model at the cold wall temperature  $T_c$  of the column. Equation (12) is usually employed to calculate the experimental  $\alpha_T$ 's, in terms of  $H$ ,  $K_d$ ,  $L$  and the experimentally observed intercept  $C (= b'/a')$  for a given experimental temperature by the existing three methods. The experimental values, thus obtained, are presented in Table I and shown graphically in Figs. 4 and 5 for comparison with the experimental  $\alpha_T$ 's due to our method and the theoretical  $\alpha_T$ 's also.

Now, the parameters  $a'$  and  $b'$  in eq. (11) influence the manner of variation of  $\ln q_c$  for any binary gas mixture with the pressure at any experimental temperature. The graph of  $\ln q_c$  against the pressure for He<sup>4</sup>-Ar<sup>40</sup> and Ne<sup>20</sup>-Xe<sup>132</sup> mixtures are shown in Figs. 2 and 3, respectively, at different compositions of the lighter components, along with that for Ne<sup>20</sup>-Ne<sup>22</sup> isotopic mixture. As in most cases of experimental observation, Figs. 2 and 3 show that, as the pressure increases,  $\ln q_c$  increases for a given composition of the binary mixtures mentioned above and becomes maximum at the pressure  $p = (b')^{1/4}$ , where  $\partial \ln q_c / \partial p = 0$ . From eq. (11) the value of  $\ln q_c$  at the point of maximum is

$$\ln q_{\max} = a' / 2 + b' \quad (13)$$

The reliable value of  $\ln q_{\max}$  of the inert gas mixture of a certain composition and at a given temperature can thus be measured from eq. (13), in terms of the experimental parameters  $a'$  and  $b'$  which are obtained by fitting the experimental data of  $\ln q_e$  and pressure  $p$  in atmosphere. Using eqs. (2) and (13) with the knowledge of the value of the column calibration factor, the TD factors  $\alpha_T$  of the inert gas mixtures at different concentrations of the lighter components are then estimated, and shown in Table I and in Figs. 4 and 5.

### §3. Theoretical Formulations

The theoretical  $\alpha_T$ 's can be calculated from

$$\alpha_T = \frac{1}{6[\lambda_{ij}]_1} \frac{S^{(i)}x_i - S^{(j)}x_j}{[X_i + Y_i]} (6C_{ij}^* - 5), \quad (14)$$

where the symbols are defined by Chapman and Enskog.<sup>11,2)</sup> Here,  $(6C_{ij}^* - 5)$  depends strongly on the temperature alone, and the other factor in eq. (14) is not only a function of the temperature but also a complicated function of the compositions and the thermal conductivities of gases and gas mixtures. The  $\alpha_T$ 's thus computed from eq. (14) are presented in the last column of Table I, and shown graphically in Figs. 4 and 5, respectively, for the gas mixtures He<sup>4</sup>-Ar<sup>40</sup> and Ne<sup>20</sup>-Xe<sup>132</sup>. A sample calculation was also made from

$$\alpha_{ij} = \frac{(6C_{ij}^* - 5)\mu_{ij}}{5nk[D_{ij}]_1} \left( \frac{\lambda_{j\text{trans}}^\infty}{x_j m_j} - \frac{\lambda_{i\text{trans}}^\infty}{x_i m_i} \right), \quad (15)$$

as deduced by Monchik, Munn and Mason<sup>12)</sup> by assuming elastic collisions between the molecules; and the results obtained are found to be much higher than those computed from eq. (14).

### §4. Results and Discussions

The Chapman-Enskog kinetic theory of gases<sup>11)</sup> is strictly applicable only to spherically symmetric molecules like noble gases, and give a good account of the viscosity, diffusion and heat conductivity of gases so excellently that it has often been used with fair success to interpret the experimental thermal diffusion fac-

tors of isotopic mixtures of noble gases.<sup>14)</sup> But it has been found that for binary mixtures of spherically symmetric molecules the theory is quite unable to explain the composition dependence and probably the temperature dependence of the experimental thermal diffusion factors  $\alpha_T$  for mixtures of different noble gases. We computed the theoretical  $\alpha_T$ 's from eq. (14) with the available force parameters as presented in Table II, for the mixtures He<sup>4</sup>-Ar<sup>40</sup> and Ne<sup>20</sup>-Xe<sup>132</sup>; the data thus obtained are shown in Table I and in Figs. 4 and 5, only to see that they do not tally with the experimental ones computed by the present as well as the existing methods. The theoretical  $\alpha_T$ 's are found to be two-order higher in magnitude than the experimental  $\alpha_T$ 's estimated, while in the case of Ne<sup>20</sup>-Ne<sup>22</sup> isotopic mixture the theoretical  $\alpha_T$ 's agree fairly well with the experimental ones as shown in Table I. This is the reason why most of the authors, in this field of research, conclude that the FJO column theory is successful in predicting both the temperature and the composition dependence of the experimental  $\alpha_T$ 's for isotopic mixtures as they are reproduced by the theoretical  $\alpha_T$ 's as computed by the Chapman-Enskog theory of monatomic gases.

In the column theory, to estimate the experimental  $\alpha_T$ 's for binary mixtures, molecular models such as Maxwell's inverse fifth power and Lennard-Jones' 12:6 potential model are commonly used. The method based on Lennard-Jones' potential model is applicable to evaluating  $\alpha_T$  at the cold wall temperature  $T_c$  of the column. The column shape factors and other molecular transport parameters also are required to be determined at the cold wall temperature. As evident from Table I, the  $\alpha_T$  values for He<sup>4</sup>-Ar<sup>40</sup> mixture due to the  $L-J$  molecular model shape factor as shown in Table II, are very low compared with our  $\alpha_T$ 's from the column calibration factor ( $F_s$ ) method as well as with those due to Maxwell's molecular model and Sliker's model-independent method. For He<sup>4</sup>-Ar<sup>40</sup> mixture, as the percentage of the lighter component, say He<sup>4</sup>, increases, the experimental  $\alpha_T$ 's decrease gradually, attain the minimum values, and then increase again as shown in Fig. 4. This sort of behaviour of the composition de-

pendence of  $\alpha_T$  for He<sup>4</sup>-Ar<sup>40</sup> could not be at all explained by the elastic theoretical  $\alpha_T$ 's obtained from the Chapman-Enskog kinetic theory of monatomic gases. The magnitudes of the values are found to be two-order higher than all the experimental  $\alpha_T$ 's as observed in Table I. The similar situation occurs in the case of Ne<sup>20</sup>-Xe<sup>132</sup> mixture; the theoretical  $\alpha_T$ 's here also could not explain the composition dependence of the experimental  $\alpha_T$ 's, which are also two-order less in magnitude than the theoretical ones, as observed from Table I and Fig. 5.

It is interesting to note that our experimental  $\alpha_T$ 's due to the column calibration factor method, which is simple, straightforward and free from any binary molecular interaction model, is very close to those due to Sliker's method as well as the method using Maxwell's model, so far as the trends of variation of the  $\alpha_T$ 's with mole fraction and their magnitudes are concerned. The existing method using  $L-J$  model yields  $\alpha_T$ 's of less magnitude for He<sup>4</sup>-Ar<sup>40</sup> mixture but, in the case of Ne<sup>20</sup>-Xe<sup>132</sup>, gives  $\alpha_T$ 's of about the same magnitudes as the  $\alpha_T$ 's due to Sliker's and our method.

Thus it is concluded that the present method, with the use of the column calibration factor  $F_s$  and the experimental  $\ln q_{max}$  as obtained from the experimental parameters  $a'$  and  $b'$ , is not only applicable to isotopic gas mixtures, like the existing methods based on molecular models and Sliker's method, but is also a universal method to estimate the experimental  $\alpha_T$ 's of polyatomic gas mixtures. The temperature as well as the composition dependence of the actual and relatively small  $\alpha_T$  of any binary gas mixture can thus be estimated by our present method. This study finally establishes that the column calibration

factor  $F_s$  plays a significant role in column measurements. Thus it is wise to study a large number of columns of different  $r_c$ ,  $r_h$  and  $L$  and to explore the functional relationship of  $F_s$  to  $r_c$ ,  $r_h$ ,  $L$  and  $\bar{T}$ , by choosing the interesting gas pairs forming binary mixtures, so that we can arrive at the unique formulation of the column calibration factor for a given column.

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## Thermal diffusion factors of hydrogenic trace mixtures with helium by column calibration factor

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**Abstract.** Using column calibration factor (CCF)  $F_s$  for a given column, the temperature dependence of experimental thermal diffusion factors  $\alpha_T$  of hydrogenic trace mixtures in helium are accurately determined. This study, however, observes the inelastic collision effect in these trace mixtures when  $\alpha_T$  by our CCF method are compared with those by the existing methods and theoretical ones respectively.

**Keywords.** Column calibration factor; thermal diffusion factor; thermal diffusion column; inelastic and elastic collisions.

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### 1. Introduction

In the existing column theory as developed by Furry and others [1–3] the column geometry plays an important role in determining the exact value of thermal diffusion factor  $\alpha_T$  of a binary gas mixture. The column as such cannot yield the actual  $\alpha_T$  values both in trend and in magnitude with respect to temperature and composition as the binary molecular interactions are often called into play. Thermal diffusion column is still far superior to any other  $\alpha_T$  measuring instruments as the equilibrium separation factor  $q_e$  defined by

$$q_e = \frac{(\chi_i/\chi_j)_{\text{top}}}{(\chi_i/\chi_j)_{\text{bot}}}$$

is very large even in the case of small mass difference between the components of a mixture. Here,  $\chi_i$  and  $\chi_j$  are the mass fractions of the lighter and the heavier components respectively. Hence for a binary mixture of almost identical masses, shapes and sizes a calibrated TD column can safely be used to measure a reliable relative and small  $\alpha_T$  values. For this reason we have calibrated the given column of Slieker and de Vries [4] with known and reliable  $\alpha_T$  of He –  $T_2$  mixture to arrive at the column calibration factor (CCF)  $F_s$  from the relation:

$$\ln q_{\text{max}} = \alpha_T F_s(r_c, r_h, L, \bar{T}) \quad (1)$$

where  $\bar{T}$  is the mean temperature of  $T_h$  and  $T_c$ ,  $T_h$  and  $T_c$  being the hot and cold wall temperatures in K.  $r_c$  and  $r_h$  are the radii of cold and hot wall of a column of geometrical length  $L$ .  $F_s$  is supposed to be an independent molecular model solely dependent on the column geometry at any mean temperature  $\bar{T}$  in K.

A number of studies by Acharyya *et al* [5-7] and Navarro *et al* [8] on  $F_s$  enabled us to study the temperature dependence of  $\alpha_T$  of DT and HT in helium only to explore the fact that the TD column is a reliable relative  $\alpha_T$  measuring instrument and to observe the inelastic collision effects in them. In this study, we estimate the experimental parameters  $a'$  and  $b'$  governing the very nature of variation of the available experimental  $\ln q_e$  against pressure  $p$  of He-DT and He-HT gas mixtures [4], the hydrogenic components were never becoming larger than 5% in helium at three experimental temperatures.

The computed data of  $\ln q_e$  of He-DT and He-HT against pressure in atmosphere are shown in figures 1 and 2 respectively to ensure that the least square fitted curves agree excellently with the experimental ones. For He-HT an interesting feature is that unlike the usual behaviour,  $\ln q_e$  becomes smaller with temperatures, not noticed earlier [7].

The hydrodynamical part of the column theory is excellently obeyed by He-DT and for some selected experimental points of He-HT as their  $p^2/\ln q_e$  against  $p^4$  were found out to be

$$\begin{aligned} p^2/\ln q_e &= 0.7758 + 0.8161 p^4 \text{ at } 338 \text{ K.} \\ &= 0.4938 + 0.7294 p^4 \text{ at } 378 \text{ K} \\ &= 0.3964 + 0.6024 p^4 \text{ at } 423 \text{ K} \end{aligned}$$

and

$$\begin{aligned} p^2/\ln q_e &= 9.0749 + 14.8368 p^4 \text{ at } 338 \text{ K} \\ &= 13.5999 + 64.6412 p^4 \text{ at } 378 \text{ K} \\ &= 14.6461 + 411.5226 p^4 \text{ at } 423 \text{ K respectively.} \end{aligned}$$

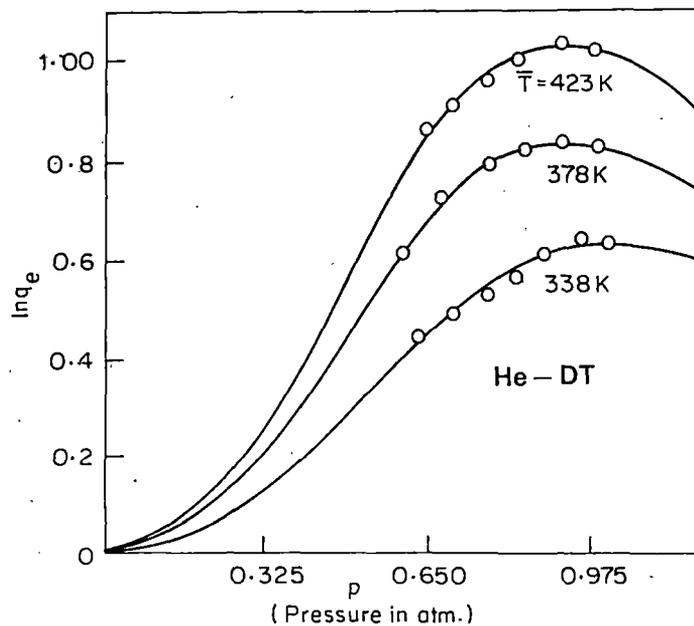


Figure 1.  $\ln q_e$  against pressure  $p$  in atmosphere for He-DT trace mixture, at  $\bar{T} = 338, 378$  and  $423$  K, 'O' experimental points.

Thermal diffusion factors

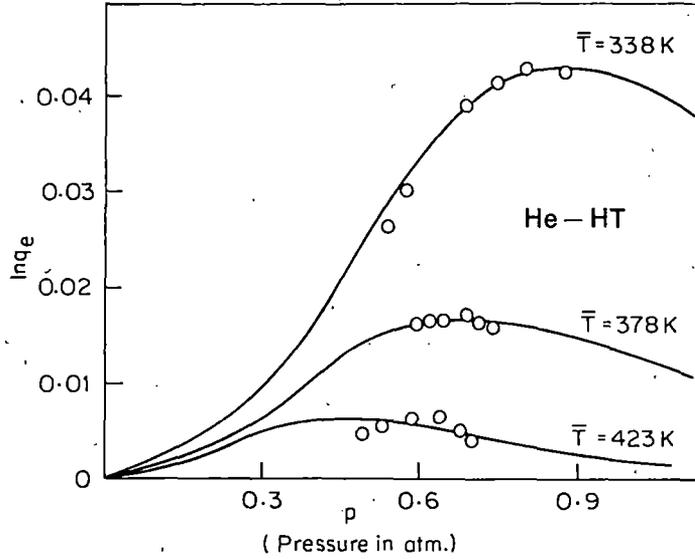


Figure 2.  $\ln q_e$  against pressure  $p$  in atmosphere for He-HT trace mixture at  $\bar{T} = 338, 378$  and  $423$  K, 'O' experimental points.

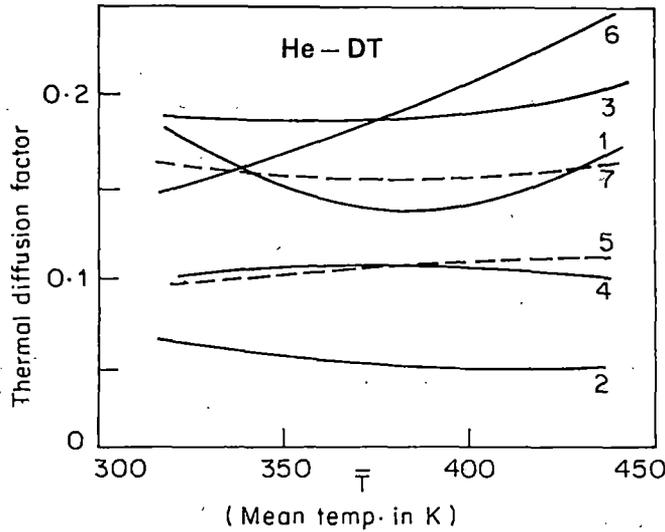


Figure 3. Variation of  $\alpha_T$  with  $\bar{T}$  of He-DT trace mixture, 1. Our expt  $\alpha_T$  from  $\ln q_{max}$  and  $F_s$ ; 2. Expt  $\alpha_T$  (Maxwell case); 3. Expt  $\alpha_T$  (Sliker case); 4. Theor  $\alpha_T$  (elastic) from Eq (7); 5. Theor  $\alpha_T$  (inelastic) with  $Z_{rot} = 300$  from Eq (7); 6. Theor  $\alpha_T$  (inelastic) with  $Z_{rot}$  calculated from Barua *et al* (1970) from Eq (8); 7. Theor  $\alpha_T$  (inelastic) with  $Z_{rot}$  calculated from Parkers [12] formula with adjustable  $Z_{rot}^* = 7.08$  [13].

In the absence of any reliable possibility to estimate the actual experimental  $\alpha_T$  of a mixture through the use of molecular model we used the values of  $F_s$  already obtained for the column [7]:

$$F_s = -66.52202 + 0.3502286 \bar{T} - 4.1879 \times 10^{-4} \bar{T}^2.$$

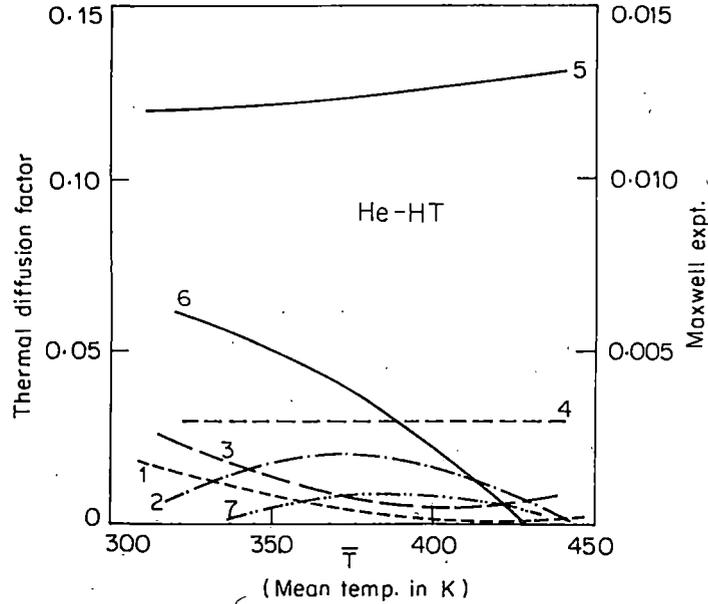


Figure 4. Variation of  $\alpha_T$  with  $\bar{T}$  of He-HT trace mixture

1. Our expt  $\alpha_T$  from  $\ln q_{\max}$  and  $F_s$ ; 2. Expt  $\alpha_T$ (Maxwell); 3. Expt  $\alpha_T$ (Slieker); 4. Theor  $\alpha_T$ (elastic) from Eq (7); 5. Theor  $\alpha_T$ (inelastic) with  $Z_{\text{rot}} = 300$  from Eq (8); 6. Theor  $\alpha_T$ (inelastic) with  $Z_{\text{rot}}$  calculated from Barua *et al* [12] from Eq (8); 7. Theor  $\alpha_T$ (inelastic) with  $Z_{\text{rot}}$  calculated from Parker [13] formula with adjustable  $Z_{\text{rot}}^a = 12-15$ .

Now  $\alpha_T$ 's of He-DT and He-HT were obtained from (1) and compared with those by the existing methods using column theory as well as the theoretical  $\alpha_T$ 's based on elastic and inelastic [9] collisions in figures 3 and 4 respectively in order to reveal the existence of inelastic collisions in these mixtures.

## 2. Theoretical formulation to estimate experimental $\alpha_T$

Both ends being closed for the ideal column of length  $L$ ,  $\ln q_e$  of a gas mixture at any mean temperature  $\bar{T}$  is given by

$$\ln q_e = \frac{HL}{K_c + K_d} \quad (2)$$

where  $H$ ,  $K_c$  and  $K_d$  are the functions of transport coefficients of a gas mixture and proportional to  $p^2$ ,  $p^4$  and  $p^0$  respectively,  $p$  being pressure in atmosphere.

In order to remove parasitic remixing effect, Furry and Jones [2] simply added a term  $K_p$  proportional to  $p^4$  to the denominator when (2) becomes

$$\ln q_e = \frac{a' p^2}{b' + p^4} \quad (3)$$

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which is also written as

$$p^2/\ln q_e = b'/a' + (1/a')p^4 \quad (4)$$

$a'$  and  $b'$  are however related by

$$(HL/K_c)p^2 = a'(1 + K_p/K_c) \text{ and } (K_d/K_c)p^4 = b'(1 + K_p/K_c)$$

$H$ ,  $K_c$ ,  $K_d$  are the functions of the transport coefficient of a mixture and  $K_p$  is the remixing coefficient.

Again if  $c$  represents the intercept of the straight line of (4) we have

$$H = (K_d/Lc) \quad (5)$$

the exact expressions for  $H$ ,  $K_c$  and  $K_d$  are given in our previous publications [5-7].

The estimation of the experimental  $\alpha_T$  through the existing formulations involved the shape factors taking account of the inherent asymmetry of the column geometry. The mass density  $\rho$ , the viscosity coefficient  $\eta$  and the diffusion coefficient  $D$  were calculated from MTGL of Hirschfelder *et al* [10], the column shape factors and the force parameters required had already been reported earlier [7].

It is observed in figures 1-2 that as the pressure increases  $\ln q_e$  increases and becomes maximum when  $p = (b')^{1/4}$  for which  $(\delta \ln q_e / \delta p) = 0$ .

We then have from (3)

$$\ln q_{\max} = (a'/2\sqrt{b'}) \quad (6)$$

It is also observed in He-HT, unlike He-DT, that some experimental data of  $\ln q_e$  are not in fit with the hydrodynamical part of the column theory as they have tendency to yield the negative intercept of  $p^2/\ln q_e$  against  $p^4$  which is absurd unless inversion of  $\alpha_T$  would take place. Hence we are bound to select some six or seven data from the reported graph to fix the values of  $\ln q_{\max}$  from the (6).

Table 1 and the graphs of figures 1-2, revealed that  $\ln q_{\max}$  from (6) in terms of  $a'$  and  $b'$  are in good agreement with the graphically determined values earlier [7]. This establishes the fact that our choice of the  $\ln q_e$  data with pressure particularly for the He-HT mixture where the mass difference between the components is practically nil, is almost right.

### 3. Theoretical formulations to calculate $\alpha_T$

Theoretical  $\alpha_T$  can, however, be estimated from

$$\alpha_T = \frac{1}{6[\lambda_{ij}]_1} \frac{S^{(i)}\chi_i - S^{(j)}\chi_j}{[X_\lambda + Y_\lambda]} (6C_{ij}^* - 5) \quad (7)$$

where  $(6C_{ij}^* - 5)$  depends mainly on the temperature while the other factors involved in (7) are the complicated functions of composition, masses and thermal conductivities of gases and gas mixtures. The  $\alpha_T$ , calculated from (7), is presented in the 12th column of table 1, and shown graphically in figures 3-4 for He-DT and He-HT respectively.

Table 1. Experimental and Theoretical  $\alpha_T$  values of binary gas mixtures with temperature.

System	Hot wall temp $T_h$ in K	Cold wall $T_c$ in K	Mean Temp $\bar{T}$ in K	$a'$ in $(\text{atm})^2$	$b'$ in $(\text{atm})^4$	In $q_{\max}$ computed from Eq (5)	Expt $F_s$ Ref (6)	Expt $\alpha_T$ with			Theor. $\alpha_T$ from Eq (6) elastic theor. method	Theoretical $\alpha_T$ from Eq (7) with $Z_{\text{rot}}$		
								Our calibration factor method Eq. (1)	Maxwell shape factor	Sliker shape factor		300	Barua et al	Parker
He-HT	393	283	338	0.0674	0.6116	0.0431	4.001	0.0107	0.0014	0.0017	0.030	0.121	0.055	0.002
	473	283	378	0.0155	0.2104	0.0169	6.026	0.0020	0.0028	0.0007	0.030	0.124	0.037	0.009
	563	283	423	0.0024	0.3559	0.0064	6.691	0.0009	0.0010	0.0006	0.030	0.129	0.005	0.005
He-DT	393	283	338	1.289	1.0519	0.6284	4.001	0.1567	0.060	0.186	0.105	0.100	0.158	0.158
	473	283	378	1.371	0.6670	0.8331	6.026	0.1382	0.054	0.187	0.104	0.105	0.188	0.154
	563	283	423	1.660	0.6580	1.0232	6.691	0.1529	0.050	0.194	0.103	0.109	0.226	0.159

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The inelastic thermal diffusion factor  $\alpha_{ij}$  is given by according to Monchick *et al* [11]

$$\alpha_T = \frac{(6C_{ij}^* - 5)\mu_{ij} \left( \frac{\lambda_{j\text{trans}}^\alpha}{\chi_j m_j} - \frac{\lambda_{i\text{trans}}^\alpha}{\chi_i m_i} \right) + \frac{1}{5nk[D_{ij}]_1}}{\left[ \frac{(6\tilde{C}_{ji} - 5)\lambda_{j\text{int}}^\alpha}{\chi_j} - \frac{(6\tilde{C}_{ij} - 5)\lambda_{i\text{int}}^\alpha}{\chi_i} \right]} \quad (8)$$

where the symbols have their usual meanings only the collision integral ratio  $\tilde{C}_{ij}$  differs from  $C_{ij}^*$ . In fact  $\tilde{C}_{ij}$  is not symmetric with respect to the interchange of the indices  $i$  and  $j$  and is very sensitive to inelastic collision.

For a pure gas the exact values of  $\lambda_{j\text{trans}}^\alpha$  and  $\lambda_{i\text{trans}}^\alpha$  is given by

$$\lambda_{i\text{trans}}^\alpha = \frac{\eta}{M} \left[ \left( \frac{5}{2} C_{v\text{trans}} + \frac{\rho D_{\text{int}}}{\eta} C_{\text{int}} \right) - \left( \frac{2 C_{i\text{int}}}{\pi Z_{\text{rot}}} \right) \left( \frac{5}{2} - \frac{\rho D_{\text{int}}}{\eta} \right)^2 \right. \\ \left. \left\{ 1 + \frac{2}{\pi Z_{\text{rot}}} \left( \frac{5 C_{\text{int}}}{3 R} + \frac{\rho D_{\text{int}}}{\eta} \right) \right\}^{-1} \right] \quad (9)$$

Here  $C_{v\text{trans}} = 3R/2$ , the constant value of translational heat capacity,  $Z_{\text{rot}}$  is the rotational translational collision number for inelastic collision.

The nonspherical terms of (8) we used Hirschfelder–Euken expression [10] to calculate the thermal conductivity  $\lambda_{i\text{int}}^\alpha$  from

$$\lambda_{i\text{int}}^\alpha = \frac{n[D_{ii}]_1 C_{\text{int}}}{1 + (\chi_j/\chi_i)(D_{ii}/D_{ij})_1} \quad (10)$$

Theoretical inelastic  $\alpha_T$ 's for He–DT and He–HT thus calculated from (8) with the help of (9) and (10) are shown in table 1 and also in figures 3–4 respectively for comparison with other experimental  $\alpha_T$  values.

### 4. Results and discussion

The inherent asymmetry in the column geometry is however, taken into account by Maxwell, Sliker and Lennard–Jones dimensionless shape factors [7]. We calculated the experimental  $\alpha_T$ 's of He–HT and He–DT trace mixtures at  $T = 338, 378$  and  $423$  K respectively from (5) using those shape factors. Sliker's case does not involve any molecular model and it gives rather a rough estimation of the experimental  $\alpha_T$  while the former includes inverse fifth power potential. As the cold wall temperature  $T_c$  was held fixed experimental  $\alpha_T$  due to L–J case cannot be applicable here. The  $\alpha_T$  thus obtained due to Maxwell and Sliker cases is presented in table 1 and shown graphically by the curves 2 and 3 respectively of figures 3 and 4.

The experimental  $\alpha_T$  from (1) as obtained in terms of  $\ln q_{\text{max}}$  of (6) and  $F_s$  is shown by curve 1 in figures 3 and 4. When they are compared with those due to Maxwell (curve 2) and Sliker (curve 3) it is found that so far as the trend is concerned the data due to Sliker agree better than those due to Maxwell's shape factors. This is perhaps due to the fact that both Sliker and our method are free from any binary molecular model. As the mass difference between the components of a binary mixture decreases as in the case of He–HT the agreement is more close.

The theoretical  $\alpha_T$  based on elastic collision theory, (7), as shown by curve 4 in

figures 3-4 appears to be temperature independent. Unlike He-HT, He-DT however show slightly lower value at higher temperature. The inelastic  $\alpha_T$  as calculated from (8) with  $Z_{rot} = 300$ , show its positive temperature dependence as represented by curve 5 in figures 3-4.

When  $\alpha_{ij}$  were calculated with the available rotational translational collision number of Barua et al [12] an interesting feature is that the curve 6 of figures 3-4 coincide with  $\alpha_T$ 's of our CCF method. This fact prompted us to adjust  $Z_{rot}$  from Parker's formula [13]. Using  $Z_{rot} = 2.78, 2.91$  and  $3.05$  for HT and  $Z_{rot} = 4.78, 5.01$  and  $5.23$  for DT at 338, 378 and 423 K respectively inelastic  $\alpha_{ij}$ 's are then estimated for both He-DT and He-HT trace mixtures and were shown by curve 7 in figures 3-4 respectively for comparison with other  $\alpha_T$ 's.

With  $Z_{rot}$  determined by us inelastic theoretical  $\alpha_T$ 's curve 7 (15th column of table 1) so far as the magnitude and trend are concerned in the case of He-DT, support our  $\alpha_T$ 's curve 1 (9th column of table 1) and only in trend with  $\alpha_T$ 's due to Slieker (11th column of table 1). In the case of He-HT these theoretical  $\alpha_T$ 's almost coincide with our  $\alpha_T$ 's, but in trend with the experimental  $\alpha_T$ 's due to Maxwell.

All these comparison of  $\alpha_T$ 's so far obtained thus reveal that inelastic collisions play an important role in such trace mixtures. Again the variation of  $\ln q_{max}$  against  $\bar{T}$  for He-HT is given by

$$\ln q_{max} = 0.89879 - 4.2097 \times 10^{-3} \bar{T} + 4.9647 \times 10^{-6} \bar{T}^2$$

showing that at  $\bar{T} \approx 429$  K,  $\ln q_{max}$  may be zero as shown in figure 5. The isobaric He-HT mixture may yield an interesting phenomenon of inversion of both  $\ln q_{max}$  and  $\alpha_T$  with respect to temperature like isobaric system  $N_2$ -CO as studied in our recent publication of Saha et al [14]. The system He-HT deserves a detailed study of measurements of  $\ln q_e$  against pressure for its different composition and temperatures.

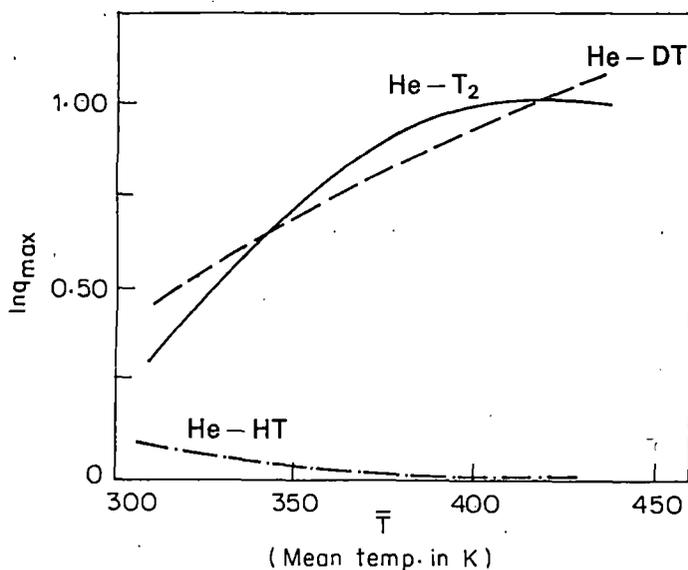


Figure 5. Variation of  $\ln q_{max}$  with temperature  $\bar{T}$  in K for He-DT He-T<sub>2</sub> and He-HT mixtures.

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We are, therefore, now in a position to conclude that CCF is an accurate  $\alpha_T$  determining factor of isotopic, nonisotopic and isobaric  $\alpha_T$ 's of binary gas mixtures. The functional relationship of  $F_s$  with  $r_c$ ,  $r_h$ ,  $L$  and  $\bar{T}$  should be studied both from the theoretical and experimental viewpoints.

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## Estimation of Column Calibration Factor and Force Parameters to Predict Temperature Dependence of Thermal Diffusion Factor of Some Simple Molecules

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The column calibration factor (CCF)  $F_s$  of a column (Roos and Rutherford 1969) has been accurately estimated to yield the thermal diffusion factor  $\alpha_T$ 's of  $\text{Kr}^{80}\text{-Kr}^{86}$ ,  $\text{Xe}^{129}\text{-Xe}^{136}$ ,  $\text{CO}^{28}\text{-CO}^{29}$ ,  $\text{CH}_4^{16}\text{-CH}_4^{17}$  and  $\text{N}_2^{28}\text{-N}_2^{29}$  respectively at two different experimental temperatures. The probable temperature dependence of  $\alpha_T$ 's are used to obtain the force parameters  $\varepsilon_{ij}/k$  and  $\sigma_{ij}$  of the respective molecules. Again, the  $\alpha_T$ 's as obtained from  $\ln q_{\max}$  and  $F_s$  are compared with the experimental  $\alpha_T$ 's by the existing method involved with column shape factors as well as theoretical  $\alpha_T$ 's based on elastic and inelastic collisions among the molecules. The comparison of the estimated force parameters with the reported ones finally suggests the technique of predicting  $\alpha_T$ 's as a function of temperature is extremely useful.

KEYWORDS: thermal diffusion factor, elastic and inelastic collisions, column calibration factor

### §1. Introduction

The theoretical thermal diffusion factor as derived from Chapman-Enskog gas kinetic theory,<sup>1)</sup> based on spherical molecule with spherically symmetric potential field is generally not in good agreement with the experimental  $\alpha_T$ 's of a binary nonisotopic or even isotopic gas mixture. It is still of special interest, from the technical point of view to enrich rare as well as ordinary isotopes. The close correlation between the theoretical  $\alpha_T$ 's with the intermolecular forces may conveniently be used as an effective tool to investigate the molecular force parameters  $\varepsilon_{ij}/k$  and  $\sigma_{ij}$  where  $\varepsilon_{ij}$  is the depth of the potential well,  $k$  is the Boltzmann constant and  $\sigma_{ij}$  is the molecular diameter as the process of thermal diffusion unlike viscosity is a second order effect.

Although, TD column was supposed not to yield the actual  $\alpha_T$  values both in trend and in magnitude with respect to temperature and composition of the mixture, still it is far superior to any other  $\alpha_T$  measuring instruments like two bulbs and trennschaukel as the equilibrium separation factor  $q_e$  defined by;  $q_e = (x_i/x_j)_{\text{top}}/(x_i/x_j)_{\text{bottom}}$  is very large even in the case of isotopic gas mixture where the mass difference between the components  $i$  and  $j$  is practically very small.  $x_i$  and  $x_j$  are the mass or mole fractions of the lighter ( $i$ ) and the heavier ( $j$ ) molecules respectively. The equilibrium separation factor  $q_e$  of any binary gas mixture is usually determined for different compositions of a gas mixture at a fixed temperature  $\bar{T}$  or for mixture of fixed composition at different experimental temperatures. With the help of  $q_e$  thus measured at different pressures well below and around one atmosphere,  $\alpha_T$  of a gas mixture could be ascertained. The existing method to evaluate the experimental  $\alpha_T$  from  $\ln q_e$  measured in a column at

different pressures is usually involved with Maxwell and Lennard-Jones model dependent as well as model independent Sliker column shape factors.

In order to obtain the actual  $\alpha_T$  of a binary gas mixture, a large number of workers<sup>2-5)</sup> has, however, introduced a scaling factor  $F_s$  called the column calibration factor (CCF) for a TD column in the relation:

$$\ln q_{\max} = \alpha_T F_s (r_{\text{cold}}, r_{\text{hot}}, L, \bar{T}) \quad (1)$$

where  $r_{\text{cold}}$  and  $r_{\text{hot}}$  are the cold and hot wall radii of a column of geometrical length  $L$ .  $\bar{T}$  is the mean temperature of the gas mixture defined by  $\bar{T} = \frac{T_{\text{hot}} + T_{\text{cold}}}{2}$  where  $T_{\text{hot}}$  and  $T_{\text{cold}}$  are the hot and cold wall temperatures in K respectively.  $F_s$  is supposed to be a molecular model independent parameter and entirely depends on the geometry of a TD column.

Roos and Rutherford<sup>6)</sup> had measured the pressure dependence of  $\ln q_e$  of  $\text{Kr}^{80}\text{-Kr}^{86}$ ,  $\text{Xe}^{129}\text{-Xe}^{136}$ ,  $\text{CO}^{28}\text{-CO}^{29}$ ,  $\text{CH}_4^{16}\text{-CH}_4^{17}$  and  $\text{N}_2^{28}\text{-N}_2^{29}$  with their natural isotopic abundances at two experimental temperatures in K in a hot wire TD column of  $L = 487.7$  cm,  $r_{\text{cold}} = 0.9525$  cm and  $r_{\text{hot}} = 0.0795$  cm respectively. The measured  $\ln q_e$  at different pressures in atmosphere by Roos and Rutherford<sup>6)</sup> were plotted in Figs. 2 and 3 respectively by least square fitted curves with the estimated  $a'$  and  $b'$  values at two available temperatures. The  $a'$  &  $b'$  for the third temperature were also obtained and the variation of  $\ln q_e$  at that temperature is, however, selected for each of them and shown in Figs. 2 and 3 by dotted curves.

From the known and reliable  $\alpha_T$  values<sup>7)</sup> as well as experimentally determined  $\ln q_{\max}$  of  $\text{Ar}^{36}\text{-Ar}^{40}$ ,  $F_s$  for a column as was derived by Datta and Acharyya<sup>4)</sup> was first carried out to yield the temperature dependence of  $\alpha_T$  of  $\text{Kr}^{80}\text{-Kr}^{86}$  as

$$\alpha_T = 0.0453 - 11.0479 \frac{1}{\bar{T}} \quad (2)$$

The corresponding  $\alpha_T$ 's at the required experimental temperatures  $\bar{T} = 455.5, 530.5$  and  $680.5$  K in the column of Roos and Rutherford<sup>6)</sup> were then obtained. They are shown in Table I. These values together with the experimentally estimated  $\ln q_{\max}$  of  $Kr^{80}-Kr^{86}$  from the curves of  $\ln q_e$  vs  $p$  as shown elsewhere<sup>8)</sup> at those temperatures were then utilised to arrive at the probable temperature dependence of  $F_s$  for a column.<sup>6)</sup>

$$F_s = 67.1066 - 0.15809\bar{T} + 3.29153 \times 10^{-4}\bar{T}^2 \quad (3)$$

which is shown graphically in Fig. 1. The values of  $F_s$  together with the corresponding experimental  $\ln q_{\max}$  at any temperature give us  $\alpha_T$ 's of the different systems from eq. (1). The force parameters  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  were estimated from the comparative study of the probable temperature dependence of  $\alpha_T$  and  $C_{ij}^*$  (12-6 Lennard-Jones potential) with respect to  $\frac{1}{\bar{T}}$  and  $\frac{1}{\bar{T}^*}$  respectively where  $\bar{T}^* = \bar{T}/(\epsilon_{ij}/k)$ . The temperature dependence of  $\alpha_T$  could not be predicted with  $\alpha_T$ 's measured at only two experimental temperatures. Nevertheless, an approximate middle temperature is, however, essential to be selected to reveal the actual variation of  $\alpha_T$ 's of those systems under consideration with respect to temperature in consistent with the estimation of the actual force parameters among the molecules.

The experimental  $\alpha_T$ 's for these systems by the existing method, involved with column shape factors due to Maxwell model<sup>9)</sup> and Sliker,<sup>10)</sup> as presented in Table II, were obtained and shown graphically in Figs. 4-8. The theoretical  $\alpha_T$ 's based on elastic and inelastic collisions were also computed with the estimated force parameters  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  (Table II) and are shown in Figs. 4-8, for comparison with experimental  $\alpha_T$ 's. The data thus obtained are, however, shown in Table I together with the

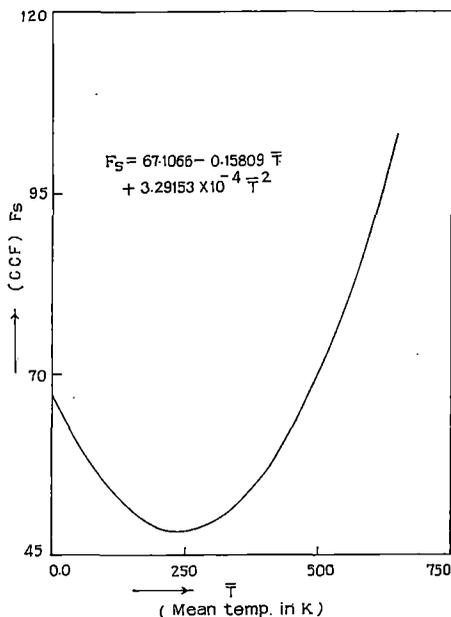


Fig. 1. Variation of column calibration factor  $F_s$  (CCF) against temperature in K.

other essential data. The CCF method together with the technique of simultaneous determination of force parameter is thus found to be successful in predicting the exact, reliable and correct temperature variation of  $\alpha_T$  of a binary isotopic mixture.

The curves of  $\alpha_T$ 's against  $\bar{T}$  in Figs. 4-8, however, support the possibility of estimation of binary interactions among the molecules as one obtains those from the viscosity of gases and gas mixtures. The estimation of  $\alpha_T$ 's by the present CCF method are found to be in close agreement so far trends are concerned, as observed

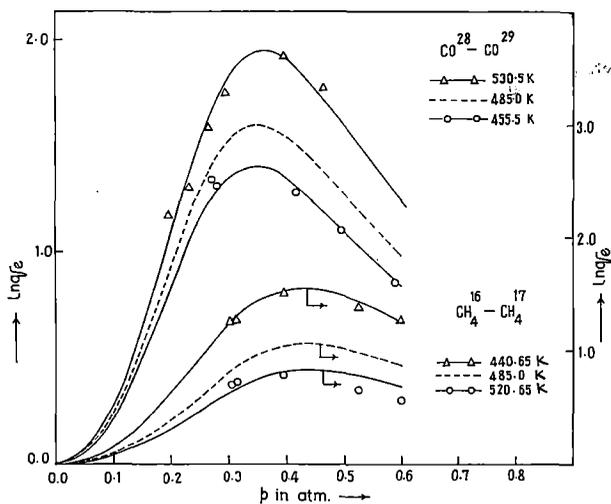


Fig. 2. Variation of  $\ln q_e$  against pressure  $p$  in atmosphere.  $-\Delta-\Delta-$  Experimental  $\ln q_e$  at  $\bar{T}=530.5$  K for  $CO^{28}-CO^{29}$ .  $-----$  Predicted  $\ln q_e$  at  $\bar{T}=485$  K for  $CO^{28}-CO^{29}$ .  $-o-o-$  Experimental  $\ln q_e$  at  $\bar{T}=455.5$  K for  $CO^{28}-CO^{29}$ .  $-\Delta-\Delta-$  Experimental  $\ln q_e$  at  $\bar{T}=520.65$  K for  $CH_4^{16}-CH_4^{17}$ .  $-----$  Predicted  $\ln q_e$  at  $\bar{T}=485$  K for  $CH_4^{16}-CH_4^{17}$ .  $-o-o-$  Experimental  $\ln q_e$  at  $\bar{T}=440.65$  K for  $CH_4^{16}-CH_4^{17}$ .

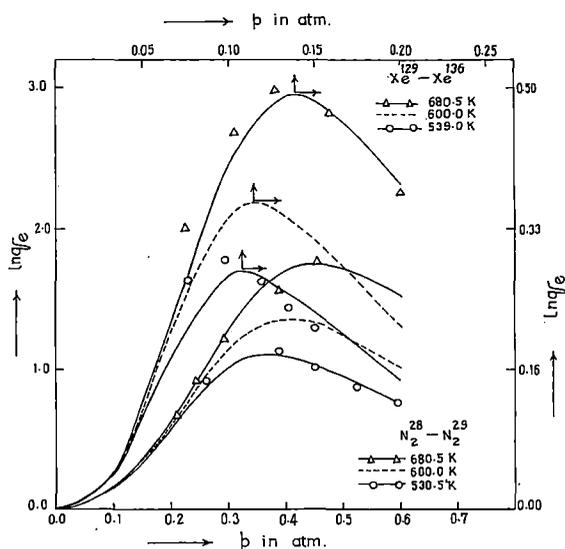


Fig. 3. Variation of  $\ln q_e$  against pressure  $p$  in atmosphere.  $-\Delta-\Delta-$  Experimental  $\ln q_e$  at  $\bar{T}=680.5$  K for  $Xe^{129}-Xe^{136}$ .  $-----$  Predicted  $\ln q_e$  at  $\bar{T}=600.0$  K for  $Xe^{129}-Xe^{136}$ .  $-o-o-$  Experimental  $\ln q_e$  at  $\bar{T}=539.0$  K for  $Xe^{129}-Xe^{136}$ .  $-\Delta-\Delta-$  Experimental  $\ln q_e$  at  $\bar{T}=680.5$  K for  $N_2^{28}-N_2^{29}$ .  $-----$  Predicted  $\ln q_e$  at  $\bar{T}=600.0$  K for  $N_2^{28}-N_2^{29}$ .  $-o-o-$  Experimental  $\ln q_e$  at  $\bar{T}=530.5$  K for  $N_2^{28}-N_2^{29}$ .

in Figs. 4–8, with the theoretical ones in terms of the estimated force parameters (Table II). Thus the methodology so far extended is really a simple, straightforward and unique one.

## §2. Mathematical Formulation to Estimate the Experimental $\alpha_T$

Both ends being closed for an ideal column of length  $L$  of a gas mixture at any temperature  $\bar{T}$  is given by<sup>11)</sup>

$$\ln q_e = \frac{HL}{K_c + K_d} \quad (4)$$

where  $H$ ,  $K_c$  and  $K_d$  are the functions of transport coefficients of a gas mixture. They are proportional to  $p^2$ ,  $p^4$  and  $p^0$  respectively,  $p$  being pressure in atmosphere. In order to remove parasitic remixing effect, Furry and

Jones<sup>11)</sup> simply added a term  $K_p$  called remixing coefficient, being proportional to  $p^4$  to the denominator of eq. (4). Hence eq. (4) finally becomes

$$\ln q_e = \frac{a'p^2}{b' + p^4} \quad (5)$$

or,

$$p^2 / \ln q_e = \frac{b'}{a'} + \frac{1}{a'} p^4 \quad (6)$$

$a'$  and  $b'$  are, however, related by

$$\frac{HL}{K_c} \cdot p^2 = a' \left( 1 + \frac{K_p}{K_c} \right)$$

and

$$\frac{K_d}{K_c} \cdot p^4 = b' \left( 1 + \frac{K_p}{K_c} \right)$$

Table I. Experimental and theoretical thermal diffusion factors  $\alpha_T$  of binary isotopic mixtures of simple gases with temperatures in K.

Column used	System	Hot wall Temp. ( $T_{hot}$ ) in K	Cold wall Temp. ( $T_{cold}$ ) in K	Mean Temp. in K $\bar{T} = \frac{T_{hot} + T_{cold}}{2}$	$a'$ (atm) <sup>2</sup>	$b'$ (atm) <sup>4</sup>	Computed $\ln q_{max}$ from eq. (15)	Column Calibration factor $F_s$ (CCF)
L=Length of the column =487.7 cm	Kr	623	288	455.5	0.0622	0.00055	1.333	63.586
		773	288	530.5	0.1007	0.00074	1.855	75.869
		1073	288	680.5	0.2464	0.00143	3.252	111.94
	Xe	790	288	539	0.0066	0.00014	0.280	77.562
		912	288	600	0.0099	0.00019	0.362	90.748
		1073	288	680.5	0.0187	0.00036	0.492	111.94
Hot wall radius $r_{hot} = 0.0795$ cm	CO	623	288	455.5	0.3336	0.0142	1.398	63.586
		682	288	485	0.3919	0.0149	1.603	67.858
		773	288	530.5	0.5028	0.0166	1.951	75.869
Cold wall radius $r_{cold} = 0.9525$ cm	CH <sub>4</sub>	593.15	288.15	440.65	0.3414	0.0376	0.886	61.357
		682.00	288.00	485.00	0.4768	0.0361	1.255	65.858
		753.15	288.15	520.65	0.6059	0.0340	1.643	74.023
	N <sub>2</sub>	773	288	530.5	0.3156	0.0201	1.115	75.869
		912	288	600	0.4423	0.0265	1.360	90.748
		1073	288	680.5	0.7311	0.0437	1.707	111.94

Column used	System	Estimated $\alpha_T$ using			Computed theoretical $\alpha_T$	
		Present method	Maxwell shape factor	Slieker shape factor	Elastic	Inelastic
L=Length of the column =487.7 cm	Kr	0.0210	0.0134	0.0146	0.0107	
		0.0245	0.0165	0.0184	0.0127	
		0.0291	0.0252	0.0290	0.0150	
	Xe	0.0036	0.0010	0.0018	0.0087	
		0.0040	0.0018	0.0021	0.0096	
		0.0044	0.0022	0.0025	0.0102	
Hot wall radius $r_{hot} = 0.0795$ cm	CO	0.0221	0.0100	0.0113	0.0052	0.2861
		0.0236	0.0107	0.0117	0.0057	0.3104
		0.0257	0.0114	0.0127	0.0061	0.3334
	CH <sub>4</sub>	0.0144	0.0070	0.0076	0.0036	0.0230
		0.0191	0.0086	0.0095	0.0046	0.0296
		0.0222	0.0099	0.0110	0.0054	0.0342
Cold wall radius $r_{cold} = 0.9525$ cm	N <sub>2</sub>	0.0147	0.0065	0.0073	0.0090	0.4010
		0.0150	0.0069	0.0078	0.0094	0.4081
		0.0153	0.0077	0.0088	0.0102	0.4148

The constants  $a'$  and  $b'$  were, however, estimated by fitting eq. (6) with the experimentally observed  $\ln q_e$  at different pressures in atmosphere. Both  $a'$  and  $b'$  are now the experimental parameters to govern the variation of  $\ln q_e$  against pressure as shown graphically in Figs. 2 and 3 for  $\text{CO}^{28}\text{-CO}^{29}$ ,  $\text{CH}_4^{16}\text{-CH}_4^{17}$ ,  $\text{Xe}^{129}\text{-Xe}^{136}$  and  $\text{N}_2^{28}\text{-N}_2^{29}$  respectively with the experimental data<sup>6,8)</sup> placed on them at two available temperatures. The third temperature would then be selected from the plot of  $\alpha_T = A + B/\bar{T}$  with the measured  $\alpha_T$ 's at two temperatures.

In each case as observed in Figs. 2 and 3,  $\ln q_e$  increases gradually with pressure and assumes maximum value  $\ln q_{\max}$  at a pressure  $p = (b')^{\frac{1}{2}}$  for which  $\frac{\partial}{\partial p}(\ln q_e) = 0$ . Hence from eq. (5) we have

$$\ln q_{\max} = \frac{a'}{2\sqrt{b'}} \quad (7)$$

Now  $a'$  and  $b'$ , in Table I, help us fix the values of  $\ln q_{\max}$  from eq. (7) and hence the experimental  $\alpha_T$ 's for the above mentioned systems could, however, be determined from eq. (1) with  $F_s$ . To use the existing method with Maxwell and Sliker column shape factors eq. (4) also becomes.

$$\ln q_{\max} = \frac{HL}{2\sqrt{k_c k_d}} \quad (8)$$

when  $\frac{\partial}{\partial p}(\ln q_e) = 0$ . The final expressions of the experimental  $\alpha_T$ 's in terms of the column shape factors are finally given by:

$$\alpha_T = 2.39 \times \frac{r_{\text{cold}} - r_{\text{hot}}}{L} \times \frac{\bar{T}}{\Delta T} \ln q_{\max} \cdot \frac{\sqrt{k_c k_d}}{h'} \quad (9)$$

and

$$\alpha_T = 2.00 \times \frac{r_{\text{cold}}}{L} \cdot \frac{\bar{T}}{\Delta T} \ln q_{\max} \frac{\{\pi(1-a^2)[S \cdot F]_3\}^{\frac{1}{2}}}{[S \cdot F]_1} \quad (10)$$

respectively, where the symbols used are of usual significance as mentioned elsewhere.<sup>9,10)</sup> The column shape factors which are supposed to take into account the inherent asymmetry of the column geometry are presented in Table II. The computed  $\alpha_T$ 's with Maxwell and Sliker column shape factors (Table II) are placed in Table I and shown graphically in Figs. 4-8 by curve No. 2 and 3 respectively in order to compare with those by the present CCF and theoretical ones.

### §3. Derivation of Force Parameters

The principal contribution<sup>12)</sup> to the temperature dependence of  $\alpha_{T \text{ theor}}$  comes from the factor  $(6C_{ij}^* - 5)$  of Chapman-Enskog expression<sup>1)</sup> where

$$\alpha_{T \text{ theor}} = g(6C_{ij}^* - 5). \quad (11)$$

The term  $(6C_{ij}^* - 5)$  contains only unlike interactions among the molecules. The other part i.e., ' $g$ ' depends on the composition of the gas mixture. Although, ' $g$ ' depends slowly on temperature it can be taken fairly constant for a short range of temperature and for a fixed composition of the gas mixture as in the case of the present investigation. It is also seen that<sup>13)</sup>

$$\alpha_{T \text{ expt}} = A + \frac{B}{\bar{T}} \quad (12)$$

where  $A$  and  $B$  are two arbitrary constants.  $C_{ij}^*$  of eq. (11) can also be written as a function of reduced temperature  $\bar{T}^*$

$$C_{ij}^* = C + \frac{D}{\bar{T}^*} \quad (13)$$

$C$  and  $D$  are two new constants. Now from eqs. (11) and (13) we have

$$\alpha_{T \text{ theor}} = \left[ (6C - 5) + \frac{6D}{\bar{T}^*} \right] g. \quad (14)$$

When  $\alpha_{T \text{ theor}} = \alpha_{T \text{ expt}}$  we may write from eqs. (12) and (14)

$$(6C - 5)g = A. \quad (15)$$

The experimental  $\alpha_T$ 's at two available temperatures by the CCF method are now used to get values of  $A$  and  $B$ . Similarly with the reported  $C_{ij}^*$  vs  $\bar{T}^*$  curve<sup>14)</sup> for 12-6 Lennard-Jones potential within a short range of temperature  $\bar{T}^*$ ,  $C$  and  $D$  of eq. (13) were easily evaluated.  $(6C-5)$  and  $A$  could yield ' $g$ ' which enables one to locate the value of  $C_{ij}^*$  and  $\bar{T}^*$ ; and hence  $\varepsilon_{ij}/k$ .

This sort of evaluation was further improved by taking into account the small variation of ' $g$ ' with temperature. This was done by repeating the entire procedure as mentioned earlier to get the exact value of ' $g$ ' with the initially estimated  $\varepsilon_{ij}/k$  and hence the exact value of  $\varepsilon_{ij}/k$  is finally located. The  $\varepsilon_{ij}/k$  thus estimated agrees well with the literature values as shown in Table II, for molecules Ar, Kr, Xe, CO,  $\text{CH}_4$  and  $\text{N}_2$  respectively. With these  $\varepsilon_{ij}/k$ , the respective  $\sigma_{ij}$ 's were also determined from available viscosity data and are placed in Table II, together with the literature values.

### §4. Theoretical Formula to Estimate $\alpha_{T \text{ theor}}$

(i) **Elastic:** The  $\alpha_{T \text{ theor}}$  due to Chapman-Enskog<sup>1)</sup> is already given by eq. (11) which consists of two factors:

$$g = \frac{1}{6[\lambda_{ij}]_1} \cdot \frac{s^{(i)}x_i - s^{(j)}x_j}{x_\lambda + y_\lambda} \quad \text{and} \quad (6C_{ij} - 5).$$

The first factor is the complicated functions of composition, thermal conductivities of gas and gas mixture while the second one is strongly a temperature dependent term. The symbols used are described in detail in MTGL.<sup>1)</sup> The  $\alpha_{T \text{ theor}}$  thus computed with  $\varepsilon_{ij}/k$  and  $\sigma_{ij}$  (Table II) are presented in the 13th column of Table I and shown graphically in Figs. 4-8 for comparison with  $\alpha_{T \text{ expt}}$  by existing and the present CCF method.

(ii) **Inelastic:** According to Monchick *et al.*<sup>15)</sup> the  $\alpha_{T \text{ theor}}$  due to inelastic collisions is given by:

$$\alpha_{T \text{ theor}} = \frac{(6C_{ij}^* - 5)}{5nk[D_{ij}]_1} \left[ \frac{\lambda_j^\alpha \text{trans}}{x_j M_j} - \frac{\lambda_i^\alpha \text{trans}}{x_i M_i} \right] + \frac{1}{5nk[D_{ij}]_1} \times \left[ \frac{(6\bar{C}_{ji} - 5)\lambda_j^\alpha \text{int}}{x_j} - \frac{(6\bar{C}_{ij} - 5)\lambda_i^\alpha \text{int}}{x_i} \right] \quad (16)$$

where the symbols used have their usual meanings.<sup>15)</sup> The collision integral ratio  $\bar{C}_{ij}$  which differs from  $C_{ij}^*$ ,

is very sensitive to inelastic collision and not symmetric with respect to the interchange of the indices  $i$  and  $j$ . The exact value of  $\lambda_j^{\alpha \text{ trans}}$  or  $\lambda_i^{\alpha \text{ trans}}$  for a pure gas is given by<sup>15)</sup>

$$\lambda_j^{\alpha \text{ trans}} = \frac{\eta}{M} \left[ \left( \frac{5}{2} C_v \text{ trans} + \frac{\rho D_{\text{int}}}{\eta} C_{\text{int}} \right) - \left( \frac{2}{\pi} \cdot \frac{C_{\text{int}}}{Z_{\text{rot}}} \right) \left( \frac{5}{2} - \frac{\rho D_{\text{int}}}{\eta} \right)^2 \right] \times \left\{ 1 + \frac{2}{\pi Z_{\text{rot}}} \left( \frac{5}{3} \frac{C_{\text{int}}}{R} + \frac{\rho D_{\text{int}}}{\eta} \right) \right\}^{-1}. \quad (17)$$

Here,  $C_v = \frac{3}{2}R$  = the constant value of translational heat capacity,  $Z_{\text{rot}}$  = rotational translational collision number for inelastic collision. To evaluate the nonspherical part of eq. (16) we used Hirschfelder-Euken expression<sup>15)</sup> to calculate the internal thermal conductivity  $\lambda_i^{\alpha \text{ int}}$  from:

$$\lambda_i^{\alpha \text{ int}} = \frac{n[D_{ij}]_1 C_{\text{int}}}{1 + (x_j/x_i)(D_{ii}/D_{ij})}. \quad (18)$$

The inelastic  $\alpha_T$  theor for  $\text{CO}^{28}\text{-CO}^{29}$ ,  $\text{CH}_4^{16}\text{-CH}_4^{17}$  and  $\text{N}_2^{28}\text{-N}_2^{29}$  were calculated from eq. (16) with the help of eqs. (17) and (18). The mass density  $\rho_{ij}$ , the coefficient of viscosity  $\eta_{ij}$  and the diffusion coefficient  $D_{ij}$  of the gas mixtures were calculated from MTGL,<sup>1)</sup> in terms of the evaluated  $\varepsilon_{ij}/k$  and  $\sigma_{ij}$  (Table II). The  $\alpha_T$  theor (inelastic) thus calculated for CO,  $\text{CH}_4$  and  $\text{N}_2$  isotopic mixtures are placed in Table I and shown graphically in Figs. 6–8 for comparison.

## §5. Results and Discussions

The least square fitted equations of  $p^2/\ln q_e$  against  $p^4$  were worked out from the pressure dependence of experimental  $\ln q_e$ <sup>6)</sup> for  $\text{Kr}^{80}\text{-Kr}^{86}$ ,  $\text{Xe}^{129}\text{-Xe}^{136}$ ,  $\text{CO}^{28}\text{-CO}^{29}$ ,  $\text{CH}_4^{16}\text{-CH}_4^{17}$  and  $\text{N}_2^{28}\text{-N}_2^{29}$  with their natural isotopic abundances. In case of later four systems  $\ln q_{\text{max}}$  were estimated in terms of  $a'$  and  $b'$  at two available experimental temperatures. The pressure dependence of  $\ln q_e$  at any intermediate temperature could, however, be obtained from the temperature dependence of both  $\alpha_T$  and  $F_s$  of eqs. (12) and (3). The linearity of  $b'$  with a short range of temperature fixes  $b'$  and hence  $a'$  from eq. (7) at the intermediate temperature. The pressure

dependence of  $\ln q_e$  in the selected intermediate temperature for all the systems except  $\text{Kr}^{80}\text{-Kr}^{86}$  is shown in Figs. 2 and 3 by dotted lines. The least square fitted equations of  $p^2/\ln q_e$  against  $p^4$  at all the temperatures for the aforesaid binary mixtures are given by:

- i)  $\text{Kr}^{80}\text{-Kr}^{86}$ ;  $p^2/\ln q_e$   
 $= 0.0088 + 16.0771p^4$  at 455.5 K  
 $= 0.0074 + 9.9602p^4$  at 530.5 K  
 $= 0.0058 + 4.0584p^4$  at 680.5 K
- ii)  $\text{Xe}^{129}\text{-Xe}^{136}$ ;  $p^2/\ln q_e$   
 $= 0.0212 + 151.515p^4$  at 539.0 K  
 $= 0.0192 + 101.0101p^4$  at 600.0 K\*  
 $= 0.0192 + 53.4759p^4$  at 680.5 K
- iii)  $\text{CO}^{28}\text{-CO}^{29}$ ;  $p^2/\ln q_e$   
 $= 0.0426 + 2.9976p^4$  at 455.5 K  
 $= 0.0382 + 2.5517p^4$  at 485.0 K\*  
 $= 0.0330 + 1.9888p^4$  at 530.5 K
- iv)  $\text{CH}_4^{16}\text{-CH}_4^{17}$ ;  $p^2/\ln q_e$   
 $= 0.1101 + 2.9291p^4$  at 440.65 K  
 $= 0.0757 + 2.0973p^4$  at 485.0 K\*  
 $= 0.0561 + 1.6504p^4$  at 520.65 K

and

- v)  $\text{N}_2^{28}\text{-N}_2^{29}$ ;  $p^2/\ln q_e$   
 $= 0.0637 + 3.1686p^4$  at 520.5 K  
 $= 0.0599 + 2.2609p^4$  at 600.0 K\*  
 $= 0.0598 + 1.3678p^4$  at 680.5 K

\* Intermediate temperature.

The experimental  $\alpha_T$ 's due to Maxwell and Sliker column shape factors were placed in the 10th and 11th columns of Table I and are shown graphically by curve Nos. 2 and 3 respectively in Figs. 4–8 as a function of temperature. They are almost of the same trends with those of CCF method as evident in Table I and Figs. 4–8, although, the Sliker column shape factors are very crude in comparison with those of Maxwell inverse fifth power potential model.

The experimental  $\alpha_T$ 's as obtained in terms of  $\ln q_{\text{max}}$  and  $F_s$  from eqs. (1) and (3) are placed in the 9th column of Table I and shown graphically by the curve No. 1 in all the Figs. 4–8. These are slightly higher than those due

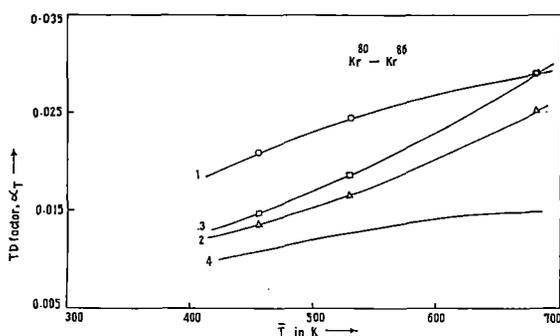


Fig. 4. Plot of  $\alpha_T$ 's against  $\bar{T}$  in K for  $\text{Kr}^{80}\text{-Kr}^{86}$ . —o—o— Curve 1: Experimental  $\alpha_T$  from  $F_s$  and  $\ln q_{\text{max}}$ . —Δ—Δ— Curve 2: Experimental  $\alpha_T$  using Maxwell shape factors. —□—□— Curve 3: Experimental  $\alpha_T$  using Sliker shape factors. Curve 4: Theoretical  $\alpha_T$  based on elastic collision.

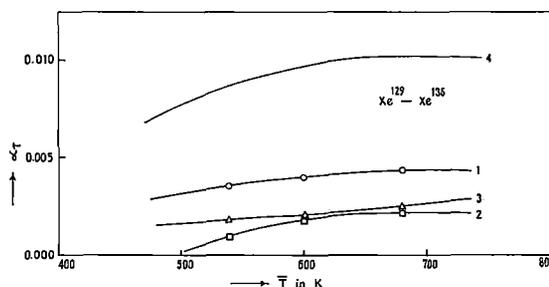


Fig. 5. Plot of  $\alpha_T$ 's against  $\bar{T}$  in K for  $\text{Xe}^{129}\text{-Xe}^{136}$ . —o—o— Curve 1: Experimental  $\alpha_T$  from  $F_s$  and  $\ln q_{\text{max}}$ . —Δ—Δ— Curve 2: Experimental  $\alpha_T$  using Maxwell shape factors. —□—□— Curve 3: Experimental  $\alpha_T$  using Sliker shape factors. Curve 4: Theoretical  $\alpha_T$  based on elastic collision.

Table II. Maxwell's model dependent and Sliker's model independent column shape factors, coefficient of viscosity  $\eta_{ij}$  and Diffusion coefficient  $D_{ij}$  together with estimated force parameters  $\epsilon_{ij}/k$  and molecular diameters  $\sigma_{ij}$  used in the calculation of  $\alpha_T$  of simple isotopic gas mixtures.

System	Model Potential	Estimated		Reported		Mean Temp. ( $\bar{T}$ ) in K
		$\epsilon_{ij}/k$ in K	$\sigma_{ij}$ in Å	$\epsilon_{ij}/k$ in K	$\sigma_{ij}$ in Å	
Ar <sup>36</sup> -Ar <sup>40</sup>	LJ 12-6	125.03	3.516	125.2*	3.405*	371.0
				119.5**		378.0
						387.5
Kr <sup>80</sup> -Kr <sup>86</sup>	LJ 12-6	199.55	3.712	199.2*	4.020*	455.5
				166.7**		530.5
						680.5
Xe <sup>129</sup> -Xe <sup>136</sup>	LJ 12-6	228.20	4.253	222.2*	4.362*	539
				229.0**		600
						680.5
CO <sup>28</sup> -CO <sup>29</sup>	LJ 12-6	200.56	3.620	110.0†	3.590†	455.5
						485.0
						530.5
CH <sub>4</sub> <sup>16</sup> -CH <sub>4</sub> <sup>17</sup>	LJ 12-6	323.28	3.360	148.9*	3.630*	440.65
				310.0*		485.00
						520.65
N <sub>2</sub> <sup>28</sup> -N <sub>2</sub> <sup>29</sup>	LJ 12-6	80.963	3.914	95.2*	3.341*	530.5
				91.5*		600.0
						680.5

System	Model Potential	Column shape factors						$\eta_{ij} \times 10^5$ gm cm <sup>-1</sup> sec <sup>-1</sup>	$D_{ij}$ cm <sup>-1</sup> sec <sup>-1</sup>
		Maxwell			Sliker				
		$h'$	$k'_c$	$k'_d$	$[S \cdot F]_1 \times 6.1$	$\pi(1 - a^2)$	$[S \cdot F]_3 \times 9.1$		
Ar <sup>36</sup> -Ar <sup>40</sup>	LJ 12-6								
Kr <sup>80</sup> -Kr <sup>86</sup>	LJ 12-6	1.015	2.05	0.8143			28.53		
		1.225	3.00	0.7829			32.25		
		1.580	4.81	0.7571			39.01		
Xe <sup>129</sup> -Xe <sup>136</sup>	LJ 12-6	1.251	3.105	0.7804			33.61		
		1.405	3.85	0.7679			36.62		
		1.579	4.81	0.7571			40.39		
					1.2165	3.121	0.7702		
CO <sup>28</sup> -CO <sup>29</sup>	LJ 12-6	1.015	2.05	0.8143			24.17	0.4157	
		1.095	2.40	0.8000			25.45	0.4629	
		1.225	3.00	0.7829			27.33	0.5499	
CH <sub>4</sub> <sup>16</sup> -CH <sub>4</sub> <sup>17</sup>	LJ 12-6	0.965	1.84	0.8229			12.58	0.3639	
		1.095	2.40	0.8000			13.77	0.4379	
		1.195	2.85	0.7857			14.68	0.5009	
N <sub>2</sub> <sup>28</sup> -N <sub>2</sub> <sup>29</sup>	LJ 12-6	1.225	3.00	0.7829			33.31	0.6742	
		1.405	3.85	0.7679			35.85	0.8293	
		1.580	0.81	0.7571			38.97	1.0141	

\* Maitland *et al.* (1981).

\*\* Hirschfelder *et al.* (1964).

† G. Vasaru (1975).

to Maxwell (curve 2) and Sliker (curve 3), but exhibit the similar trends as mentioned earlier.

The reliability of the temperature dependence of the experimental  $\alpha_T$ 's by the CCF method of the aforesaid binary mixtures is, however, ensured with the determination of the respective molecular force parameter  $\epsilon_{ij}/k$ 's and  $\sigma_{ij}$ 's for the molecules. The estimated force parameters seem to be very sensitive to intermolecular interac-

tions and agree excellently well for Ar, Kr and Xe while for CO, CH<sub>4</sub> and N<sub>2</sub> they deviate remarkably. Both  $\epsilon_{ij}/k$ 's and  $\sigma_{ij}$ 's are all presented in columns 3 and 4 to compare with the literature values placed in columns 5 and 6 respectively of Table II. This fact at once suggests the existence of inelastic collisions in the later three isotopic mixtures. It was, however, pointed out by some workers<sup>16,17</sup> that the theory of inelastic collision effect

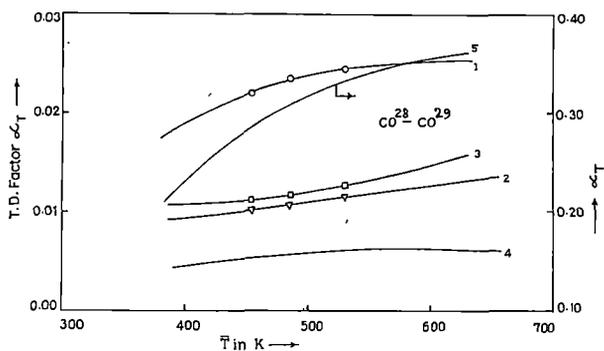


Fig. 6. Plot of  $\alpha_T$ 's against  $\bar{T}$  in K for  $\text{CO}^{28}\text{-CO}^{29}$ . -o-o- Curve 1: Experimental  $\alpha_T$  from  $F_s$  and  $\ln q_{\max}$ . - $\Delta$ - $\Delta$ - Curve 2: Experimental  $\alpha_T$  using Maxwell shape factors. - $\square$ - $\square$ - Curve 3: Experimental  $\alpha_T$  using Sliker shape factors. Curve 4: Theoretical  $\alpha_T$  based on elastic collision. Curve 5: Theoretical  $\alpha_T$  based on inelastic collision.

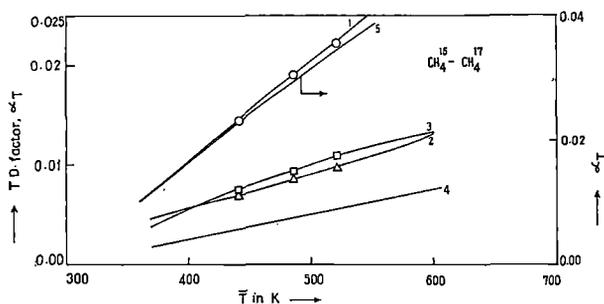


Fig. 7. Plot of  $\alpha_T$ 's against  $\bar{T}$  in K for  $\text{CH}_4^{16}\text{-CH}_4^{17}$ . -o-o- Curve 1: Experimental  $\alpha_T$  from  $F_s$  and  $\ln q_{\max}$ . - $\Delta$ - $\Delta$ - Curve 2: Experimental  $\alpha_T$  using Maxwell shape factors. - $\square$ - $\square$ - Curve 3: Experimental  $\alpha_T$  using Sliker shape factors. Curve 4: Theoretical  $\alpha_T$  based on elastic collision. Curve 5: Theoretical  $\alpha_T$  based on inelastic collision.

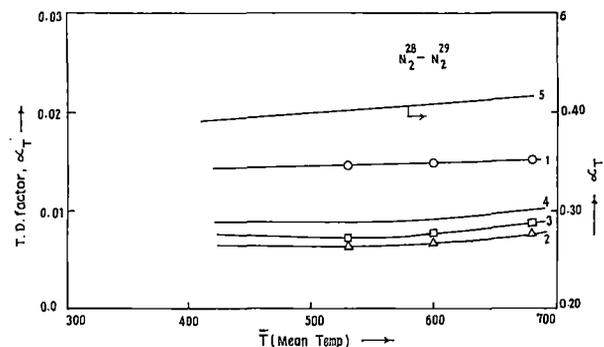


Fig. 8. Plot of  $\alpha_T$ 's against  $\bar{T}$  in K for  $\text{N}_2^{28}\text{-N}_2^{29}$ . -o-o- Curve 1: Experimental  $\alpha_T$  from  $F_s$  and  $\ln q_{\max}$ . - $\Delta$ - $\Delta$ - Curve 2: Experimental  $\alpha_T$  using Maxwell shape factors. - $\square$ - $\square$ - Curve 3: Experimental  $\alpha_T$  using Sliker shape factors. Curve 4: Theoretical  $\alpha_T$  based on elastic collision. Curve 5: Theoretical  $\alpha_T$  based on inelastic collision.

in thermal diffusion is not widely applicable except for eccentrically loaded sphere molecule as one of the component in binary mixtures. The simple theory so far adopted here to estimate the force parameters is based on the elastic collision amongst the molecules. The inelastic collision in molecules like  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{N}_2$  may be the reason of such deviations (Table II).

The  $\alpha_T$ 's due to elastic collision theory from eq. (11) in terms of  $\varepsilon_{ij}/k$  and  $\sigma_{ij}$  are also shown graphically by the curve no 4 of Figs. 4-8 for comparison with  $\alpha_T$ 's by CCF method. They are placed in the 12th column of Table I. The graphs in Figs. 4-8 and Table I, clearly show that in case of Kr and Xe elastic  $\alpha_T$ 's almost coincide with  $\alpha_T$ 's by CCF method so far the magnitudes and trends are concerned. But in case of  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{N}_2$  elastic  $\alpha_T$ 's are of one-order smaller in magnitudes and not with the same trends with  $\alpha_T$ 's from CCF method.

The fact as mentioned above indicates that Chapman-Enskog gas kinetic theory<sup>1)</sup> could not interpret the variation of  $\alpha_T$ 's of  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{N}_2$  isotopic mixtures with temperature probably due to the presence of inelastic collision among such molecules as shown in Tables I and II. But the theory appears to be successful to explain the temperature dependence of  $\alpha_T$  of spherically symmetric molecules like Ar, Kr and Xe as evident from Tables I and II and Figs. 4 and 5.

The  $\alpha_T$  based on inelastic collisions as derived by Monchick *et al.*<sup>15)</sup> from eq. (16) for  $\text{CO}^{28}\text{-CO}^{29}$ ,  $\text{CH}_4^{16}\text{-CH}_4^{17}$  and  $\text{N}_2^{28}\text{-N}_2^{29}$  are presented in column 13 of Table I. They are plotted graphically by the curve No. 5 in all the Figs. of 6-8 for comparison.

From all the discussions we may conclude that  $\alpha_T$ 's as obtained by CCF method is a simple, straightforward and unique one. This study further indicates that the nature of variation of  $F_s$  is the same as observed earlier,<sup>2-4, 17)</sup> but differing in the magnitudes of coefficients A, B and C in  $F_s = A + B\bar{T} + C\bar{T}^2$ . Thus the nature of variation of  $F_s$  with temperature  $\bar{T}$  (Fig. 1) confirms that the CCF method to locate the magnitude and trend of  $\alpha_T$  in Figs. 4-8 is correct.

## §6. Conclusions

Although,  $F_s$  is supposed to be an essential tool in determining the experimental  $\alpha_T$  in a column measurement, still the functional relationship of  $F_s$  with  $r_{\text{cold}}$ ,  $r_{\text{hot}}$ , L and  $\bar{T}$  remains unexplored. Simultaneous determination of  $F_s$  and the force parameters seems to be an important step forward to observe  $\alpha_T$  of both isotopic and nonisotopic binary mixtures of simple molecules as a function of temperature. A rigorous study of experimental  $F_s$  through experimentally determined  $\ln q_{\max}$  of binary mixture having accurate  $\alpha_T$  is needed with different column geometries to serve this purpose.

The very existence of inelastic collision effects in thermal diffusion of suitable molecules forming binary mixture have to be studied in detail through  $\ln q_{\max}$  and  $F_s$  to improve the theory of inelastic collision effects in thermal diffusion.

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## Molecular Force Parameters through Thermal Diffusion to Ensure the Model Independency of Column Calibration Factor

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Using Ar<sup>36</sup>-Ar<sup>40</sup> as calibrating gas, the simultaneous determination of thermal diffusion factors  $\alpha_T$ 's at two available experimental temperatures as well as the prediction of pressure dependence of  $\ln q_e$  at an intermediate temperature is possible for some isotopic inert gas mixtures in terms of column calibration factor  $F_s$  (CCF) of a given column. The variation of  $\alpha_T$  with  $\bar{T}$  is then used to estimate the force parameters of the molecules only to ensure the reliability of the proposed temperature dependence of  $\alpha_T$ . The experimental  $\alpha_T$ 's due to Maxwell and Sliker shape factors are also calculated for comparison with those by the CCF method as well as by theoretical ones based on elastic collisions among the molecules. It seems that  $\alpha_T$ 's by CCF method play an important role in determining the force parameters of molecules indicating thereby the model independency of  $F_s$  as a sensitive  $\alpha_T$  measuring parameter.

KEYWORDS: thermal diffusion factor, column calibration factor, elastic and inelastic collisions

### §1. Introduction

The theoretical formulation of thermal diffusion factor  $\alpha_T$  as derived from Chapman-Enskog gas kinetic theory<sup>1)</sup> is based on the assumption that the molecules are elastic spheres with spherically symmetric potential field. The theory can, however, hardly explain the experimental  $\alpha_T$  of binary nonisotopic or even isotopic gas mixtures. Thermal diffusion is still interesting for its close correlation with the intermolecular forces. Moreover, unlike viscosity, thermal diffusion is a second order effect. Thus it is generally used to investigate the elastic or inelastic collisions among the molecules. The phenomenon is also responsible to enrich rare as well as ordinary isotopes in thermal diffusion column.

The temperature dependence of experimental  $\alpha_T$ 's of a binary gas mixture may offer a convenient method to estimate the molecular force parameters like  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  where  $\epsilon_{ij}$  is the depth of potential well,  $k$  is the Boltzmann constant and  $\sigma_{ij}$  is the molecular diameter.  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  become  $\epsilon_{ii}/k$  or  $\epsilon_{jj}/k$  and  $\sigma_{ii}$  or  $\sigma_{jj}$  for isotopic components in a binary mixture of gases. They are, therefore, expected to play an important role to yield the exact theoretical  $\alpha_T$ 's based on elastic or inelastic collisions.

To estimate experimental  $\alpha_T$  the theory of TD column which was already developed by a large number of workers,<sup>2-4)</sup> is still insufficient. TD column, on the other hand, is a very sensitive instrument to investigate the temperature and composition dependence of  $\alpha_T$ , particularly for a binary isotopic gas mixture of molecules having practically no mass difference.

The equilibrium separation factor ' $q_e$ ' of a gas mixture in a TD column is defined by:

$$q_e = (x_i/x_j)_{top}/(x_i/x_j)_{bottom}$$

where  $x_i$  and  $x_j$  are the mass or mole fractions of the lighter ( $i$ ) and heavier ( $j$ ) components respectively. In a TD column  $q_e$  is usually measured at different pressures in atmospheres, for a fixed composition of a binary gas mixture at different temperatures or at a fixed temperature for different compositions. The existing method of evaluating the experimental  $\alpha_T$  is involved with Maxwell, Lennard-Jones model dependent as well as Sliker model independent column shape factors (CSF). The method is, however, complicated and the resulting  $\alpha_T$ 's are usually not in agreement with the theoretical  $\alpha_T$  so far its temperature and composition dependences are concerned.

We,<sup>5-7)</sup> therefore, introduced a scaling factor  $F_s$  called CCF for a TD column to get the actual  $\alpha_T$  of a binary gas mixture from column measurements by the following relation:

$$\ln q_{max} = \alpha_T F_s(r_c, r_h, L, \bar{T}). \quad (1)$$

Here  $\ln q_{max}$  is the logarithmic maximum equilibrium separation factor,  $r_c$  and  $r_h$  are the cold and hot wall radii maintained at temperatures  $T_c$  and  $T_h$  respectively in a TD column of geometrical length  $L$  and the mean temperature  $\bar{T}$  of the gas mixture is given by  $\bar{T} = \frac{T_c + T_h}{2}$ .

The molecular model independent parameter,<sup>7,8)</sup>  $F_s$  can now be used to evaluate the actual  $\alpha_T$ 's of binary isotopic or nonisotopic gas mixtures from their  $\ln q_{max}$  measurements. Moran and Watson<sup>9)</sup> had already measured the pressure dependence of  $\ln q_e$  of Ne<sup>20</sup>-Ne<sup>22</sup>, Ar<sup>36</sup>-Ar<sup>40</sup>, and Kr<sup>80</sup>-Kr<sup>86</sup> mixtures at two experimental temperatures in a TD column of  $L = 182.0$  cm,  $r_c = 0.635$  cm and  $r_h = 0.0754$  cm respectively. The measurements,<sup>9)</sup> however, inspired us to observe the probable temperature dependence of  $\alpha_T$  of those isotopic mixtures in terms of CCF together with the estimation of  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  of the respective molecules. The purpose of such study is to establish the molecular model independency

of  $F_s$ , too.

The experimental<sup>9)</sup>  $\ln q_{\max}$  of Ar<sup>36</sup>-Ar<sup>40</sup> at 432 K and 537 K and the reliable<sup>10)</sup>  $\alpha_T$ 's of Ar were, however, used to give two values of  $F_s$ . As  $F_s$  is a molecular mobility independent parameter, the experimental<sup>9)</sup>  $\ln q_{\max}$  and reliable<sup>10)</sup>  $\alpha_T$  of Ne<sup>20</sup>-Ne<sup>22</sup> were used again to get  $F_s$  at the intermediate temperature 447 K. The probable temperature dependence of  $F_s$  for the column<sup>9)</sup> is then obtained:

$$F_s = 54.3777 - 0.1152\bar{T} + 1.4350 \times 10^{-4}\bar{T}^2 \quad (2)$$

which is shown graphically in Fig. 1. This  $F_s$  and the experimental  $\ln q_{\max}$  for any gas mixture yield  $\alpha_T$  at the experimental temperature  $\bar{T}$  from eq. (1).

A large number of workers<sup>11,12)</sup> had expressed  $\alpha_T$  in the form:

$$\alpha_T = A + B/\bar{T} \quad (3)$$

where  $A$  and  $B$  are two arbitrary constants. The experimental  $\alpha_T$ 's for Ne<sup>20</sup>-Ne<sup>22</sup>, Ar<sup>36</sup>-Ar<sup>40</sup> and Kr<sup>80</sup>-Kr<sup>86</sup> as a function of  $\bar{T}$  are, however given by

$$\begin{aligned} \alpha_T &= 0.03019 - 0.80013 \cdot \frac{1}{\bar{T}}, \\ \alpha_T &= 0.03476 - 5.08155 \cdot \frac{1}{\bar{T}} \quad \text{and} \\ \alpha_T &= 0.27993 - 69.3446 \cdot \frac{1}{\bar{T}} \end{aligned} \quad (4)$$

which are shown in Figs. 3-5 respectively. The plot of experimental  $\alpha_T$ 's against  $\bar{T}$  thus enables us to evaluate  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  of the respective molecules.<sup>13,14)</sup> The results are shown in Table II for comparison with the literature values. The comparison finally indicates that curves as shown in Figs. 3-5 in terms of  $F_s$  and  $\ln q_{\max}$  from eq. (1) for Ne, Ar and Kr gas mixtures are claimed to be perfect. The theoretical as well as the experimental  $\alpha_T$ 's by the CCF method as a function of  $\bar{T}$  were, however, used to estimate  $a'$  and  $b'$  and hence  $\ln q_c$  at any intermediate temperature between 432 K to 537 K for each system. They are also shown in Fig. 2 by the dotted lines together with actual  $\ln q_c$  at two available  $\bar{T}$  K.

The experimental  $\alpha_T$ 's by the existing method involved with CSF due to Maxwell and Sliker were also evaluated and shown in Figs. 3-5. The CSF due to L-J model can not be applied here as the cold wall temperature of the column was held fixed. The theoretical  $\alpha_T$ 's based on elastic collisions were also found out with the estimated  $\epsilon_{ij}/k$  and  $\sigma_{ij}$ , placed in Table II, and shown in Figs. 3-5 only to see how far the elastic theory is now successful to explain the experimental  $\alpha_T$ 's (Table I) by the CCF and the existing method. The theoretical  $\alpha_T$ 's are placed in the last column of Table I. Both the Tables I and II however, indicate the adequacy or otherwise of the CCF method to predict the actual and reliable  $\alpha_T$  of such isotopic mixtures together with their correct force parameters from thermal diffusion.

## §2. Mathematical Formulations to Estimate Experimental $\alpha_T$

In case of an ideal column of length  $L$ , both ends being

closed,  $\ln q_c$  of a gas mixture at any mean temperature  $\bar{T}$  is given by:<sup>7,8)</sup>

$$\ln q_c = \frac{III}{K_c + K_d} \quad (5)$$

$III$ ,  $K_c$  and  $K_d$  are the functions of the transport coefficients of a gas mixture and are proportional to  $p^2$ ,  $p^4$  and  $p^0$  respectively,  $p$  being the pressure in atmosphere. The above eq. (5) thus becomes

$$\ln q_c = \frac{ap^2}{b+p^4} \quad (6)$$

But in case of actual column, parasitic remixing generally occurs. This can be taken into consideration by adding a term  $K_p$ , proportional to  $p^4$ , in the denominator of eq. (5),  $\ln q_c$  then becomes

$$\ln q_c = \frac{a'p^2}{b'+p^4} \quad (7)$$

where  $a'$  and  $b'$  are related to  $a$  and  $b$  by:

$$a = a' \left(1 + \frac{K_p}{K_c}\right) \quad \text{and} \quad b = b' \left(1 + \frac{K_p}{K_c}\right)$$

The above eq. (7) can then be written as

$$p^2 / \ln q_c = \frac{b'}{a'} + \frac{1}{a'} p^4 \quad (8)$$

where  $a'$  and  $b'$  are two arbitrary constants which can be obtained from experimental  $\ln q_c$  at different pressures  $p$  in atm. at a given temperature  $\bar{T}$  K.

Again, it has been found in Fig. 2 that the experimental  $\ln q_c$  increases with  $p$  and eventually becomes maximum at  $p = (b')^{1/4}$  for which  $\frac{\partial}{\partial p}(\ln q_c) = 0$ . The eq. (7) then becomes

$$\ln q_{\max} = \frac{a'}{2\sqrt{b'}} \quad (9)$$

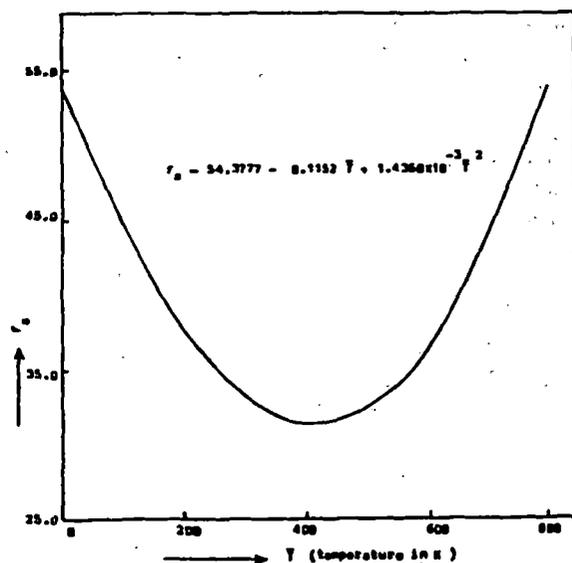


Fig. 1. Variation of column calibration factor  $F_s$  (CCF) against temperature in K.

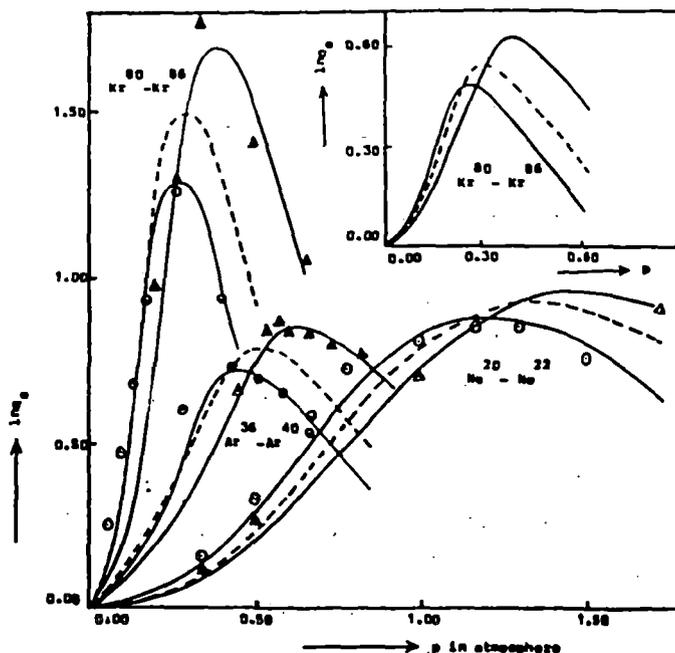


Fig. 2: i) Variation of  $\ln q_0$  against  $p$  in atmosphere for  $\text{Ne}^{20}\text{-Ne}^{22}$ . -O-O- Experimental  $\ln q_0$  at 447 K. ----- Predicted  $\ln q_0$  at 492 K. - $\Delta$ - $\Delta$ - Experimental  $\ln q_0$  at 537 K. ii) Variation of  $\ln q_0$  against  $p$  in atmosphere for  $\text{Ar}^{36}\text{-Ar}^{40}$ . -O-O- Experimental  $\ln q_0$  at 432 K. ----- Predicted  $\ln q_0$  at 484.5 K. - $\Delta$ - $\Delta$ - Experimental  $\ln q_0$  at 537 K. iii) Variation of  $\ln q_0$  against  $p$  in atmosphere for  $\text{Kr}^{80}\text{-Kr}^{86}$ . -O-O- Experimental  $\ln q_0$  at 447 K. ----- Predicted  $\ln q_0$  at 492 K. - $\Delta$ - $\Delta$ - Experimental  $\ln q_0$  at 537 K. iv)  $\text{Kr}^{80}\text{-Kr}^{86}$  (Adjacent graph). ----- Adjusted  $\ln q_0$  against  $p$  in atmosphere at 447 K. ----- Predicted  $\ln q_0$  against  $p$  in atmosphere at 492 K. ----- Adjusted  $\ln q_0$  against  $p$  in atmosphere at 537 K.

With the known  $\ln q_{\max}$  in terms of  $a'$  and  $b'$  (Table I) and  $F_0$  (Fig. 1) of a given column,<sup>9)</sup>  $\alpha_T$  of binary isotopic gas mixtures of Ne, Ar, Kr were found out from eq. (1). They are placed in Table I and shown graphically in Figs. 3-5.

One may obtain the experimental  $\ln q_{\max}$  from eq. (5) which is also given by:

$$\ln q_{\max} = \frac{HL}{2\sqrt{K_c K_d}} \quad (10)$$

The exact expressions for  $H$ ,  $K_c$  and  $K_d$  are given by:

$$\begin{aligned} \text{(i)} \quad H &= \frac{2\pi}{6!} \left( \frac{\alpha_T \rho_{ij}^2 g}{\eta_{ij}} \right)_1 \cdot \frac{1}{2} (r_c + r_h) (r_c - r_h)^3 (2u)^2 h' \\ K_c &= \frac{2\pi}{9!} (\rho_{ij}^3 g^2 / \eta_{ij}^2 D_{ij})_1 \frac{1}{2} (r_c + r_h) (r_c - r_h)^7 (2u)^2 k'_c \\ K_d &= 2\pi (\rho_{ij} D_{ij})_1 \frac{1}{2} (r_c + r_h) (r_c - r_h) k'_d \end{aligned} \quad (11)$$

and

$$\begin{aligned} \text{(ii)} \quad H &= C_1 = [S \cdot F]_1 r_c^4 \left( \frac{\alpha_T \rho_{ij}^2 g}{\eta_{ij}} \right)_1 \left( \frac{\Delta T}{T} \right)^2 \\ K_c &= C_3 = [S \cdot F]_3 r_c^6 (\rho_{ij}^3 g^2 / \eta_{ij}^2 D_{ij})_1 \left( \frac{\Delta T}{T} \right)^2 \\ K_d &= C_2 = \pi (1 - a^2) r_c^2 (\rho_{ij} D_{ij})_1 \end{aligned} \quad (12)$$

in Maxwell model and Slicker's model independent methods. The  $\alpha_T$  in Maxwell model dependent and Slicker's model independent methods<sup>15, 16)</sup> could, however, be ob-

tained by using eqs. (10) & (11), and (10) & (12) respectively in the following forms:

$$\alpha_T \left( \begin{array}{c} \text{Maxwell} \\ \text{model} \end{array} \right) = 2.39 \frac{r_c - r_h}{L} \cdot \frac{T}{\Delta T} \frac{\sqrt{K_c K_d}}{h'} \ln q_{\max} \quad (13)$$

and

$$\alpha_T (\text{Slicker}) = 2.00 \frac{r_c}{L} \frac{T}{\Delta T} \frac{\sqrt{\pi(1-a^2)[S \cdot F]_3}}{[S \cdot F]_1} \ln q_{\max} \quad (14)$$

The symbols  $h'$ ,  $k'_c$  &  $k'_d$ ;  $[S \cdot F]_1$ ,  $\pi(1-a^2)$  &  $[S \cdot F]_3$  are dimensionless CSF due to Maxwell and Slicker respectively.  $\rho_{ij}$  is the mass density of the gas mixture of coefficient of viscosity  $\eta_{ij}$  and diffusion coefficient  $D_{ij}$ ,  $u = \frac{T_h - T_c}{T_h + T_c}$ ,  $\Delta T = T_h - T_c$  and  $g$  is the acceleration due to gravity.

The  $\alpha_T$ 's thus evaluated from eqs. (13) and (14) due to Maxwell model and Slicker's CSF respectively are placed in Table I. They are also shown in Figs. 3-5 for  $\text{Ne}^{20}\text{-Ne}^{22}$ ,  $\text{Ar}^{36}\text{-Ar}^{40}$  and  $\text{Kr}^{80}\text{-Kr}^{86}$  mixtures in order to compare them with the theoretical  $\alpha_T$  computed with their respective  $\epsilon_{ij}/k$  and  $\sigma_{ij}$ .

### §3. Theoretical Elastic $\alpha_T$ together with Force Parameters $\epsilon_{ij}/k$ and $\sigma_{ij}$

According to gas kinetic theory the theoretical  $\alpha_T$  based on elastic collisions<sup>1)</sup> is

$$\alpha_T = g(6C_{ij}^2 - 5) \quad (15)$$

where

Table I. Experimental and theoretical thermal diffusion factor  $\alpha_T$  of binary isotopic mixtures of Neon, Argon and Krypton with temperatures in K.

Column used	System	Hot Wall Temp. ( $T_h$ ) in K.	Cold Wall Temp. ( $T_c$ ) in K.	Mean Temp in K $T = \frac{T_h + T_c}{2}$	$a'$ (atm) <sup>2</sup>	$b'$ (atm) <sup>4</sup>	Computed $\ln_2$ max from eq. (9)	Column calibration factor ( $F_c$ )
L=Length of the column =182.0 cm.	Ne <sup>20</sup> -Ne <sup>22</sup>	596	298	447	2.5470	2.0188	0.8963	31.5599
		656	328	492	3.3670	3.3025	0.9264	32.4355
		716	358	537	4.3365	4.9660	0.9730	33.9012
Hot Wall radius $r_h = 0.0254$ cm.	Ar <sup>36</sup> -Ar <sup>40</sup>	576	288	432	0.2942	0.0415	0.7221	31.3957
		646	323	484.5	0.4149	0.0701	0.7836	32.2485
		716	358	537	0.7037	0.1683	0.8577	33.9012
Cold Wall radius $r_c = 0.635$ cm.	Kr <sup>80</sup> -Kr <sup>86</sup>	596	298	447	0.5342	0.0046	3.9382	31.5599
					0.0653	0.0046	0.4814	
		656	328	492	0.7963	0.0078	4.5082	32.4355
				0.0973	0.0078	0.5511		
		716	358	537	1.5540	0.0231	5.1123	33.9012
					0.1900	0.0231	0.6250	

Column used	System	Estimated $\alpha_T$ using			Computed theoretical $\alpha_T$
		Present method	Maxwell's shape factor	Slicker's shape factor	
L=Length of the column =182.0 cm.	Ne <sup>20</sup> -Ne <sup>22</sup>	0.0284	0.0156	0.0179	0.0294
		0.0286	0.0161	0.0185	0.0298
		0.0287	0.0169	0.0195	0.0297
Hot Wall radius $r_h = 0.0254$ cm.	Ar <sup>36</sup> -Ar <sup>40</sup>	0.0230	0.0126	0.0144	0.0259
		0.0243	0.0136	0.0156	0.0266
		0.0253	0.0149	0.0171	0.0277
		0.1248			
		0.0153	0.0684	0.0785	0.0135
Cold Wall radius $r_c = 0.635$ cm.	Kr <sup>80</sup> -Kr <sup>86</sup>	0.1390			
		0.0170	0.0783	0.0899	0.0157
		0.1508			
		0.0184	0.0888	0.1019	0.0170

$$g = \frac{1}{6[\lambda_{ij}]_1} \frac{S^{(i)}x_i - S^{(j)}x_j}{X_\lambda + Y_\lambda}$$

is a complicated function of composition and thermal conductivities of a gas mixture. The temperature dependence of  $\alpha_T$  is mainly governed by  $(6C_{ij}^* - 5)$  which involves with like or unlike interactions. The experimental  $\alpha_T$  as a function of  $\bar{T}$  is:<sup>17)</sup>

$$(\alpha_T)_{\text{expt.}} = A + B/\bar{T}. \quad (16)$$

Although  $g$  is a slowly varying function of  $\bar{T}$ , we may assume it to be a temperature independent one.  $C_{ij}^*$  may be expressed as a function of reduced temperature  $T^*$  like

$$C_{ij}^* = C + D/\bar{T}^* \quad (17)$$

where

$$\bar{T}^* = \bar{T}/(\epsilon_{ij}/k).$$

The above eq. (15) thus becomes

$$(\alpha_T)_{\text{theor.}} = (6C - 5)g + \frac{6gD}{\bar{T}^*} \quad (18)$$

where  $C$  and  $D$  are new constants. Comparing eqs. (16) and (18) one may get

$$g = \frac{A}{(6C - 5)}$$

From the fitted equations of  $(\alpha_T)_{\text{expt.}}$  against  $1/\bar{T}$ ,  $A$  and  $B$  were first evaluated. Similarly  $C_{ij}^*$  reported elsewhere<sup>18)</sup> for (12-6) L-J potential was plotted against  $1/\bar{T}^*$  to get  $C$  and  $D$  of eq. (17).

Thus 'g' along with  $(\alpha_T)_{\text{expt.}} = (6C_{ij}^* - 5)g$  fixes

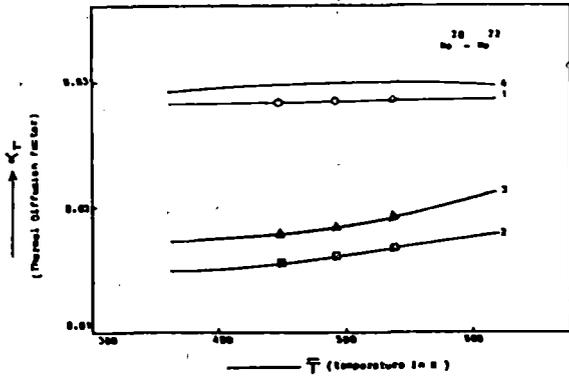


Fig. 3. Plot of  $\alpha_T$ 's against  $T$  in K for  $\text{Ne}^{20}\text{-Ne}^{22}$ . —○—○— Curve 1: Experimental  $\alpha_T$  from  $F_0$  and  $\ln q_{\max}$ . —□—□— Curve 2: Experimental  $\alpha_T$  from Maxwell's shape factors. —△—△— Curve 3: Experimental  $\alpha_T$  using Sliker's shape factors. ——— Curve 4: Theoretical  $\alpha_T$  based on elastic collision.

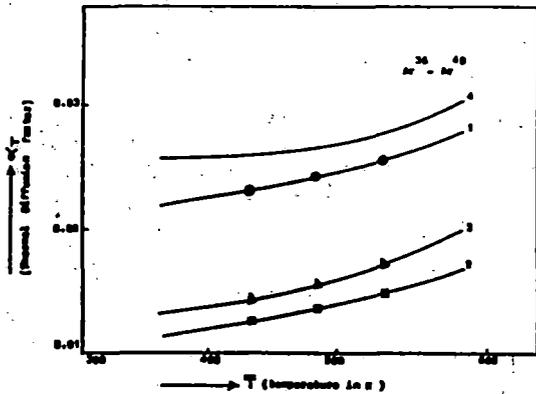


Fig. 4. Plot of  $\alpha_T$  against  $T$  for  $\text{Ar}^{36}\text{-Ar}^{40}$ . —○—○— Curve 1: Experimental  $\alpha_T$  from  $F_0$  and  $\ln q_{\max}$ . —□—□— Curve 2: Experimental  $\alpha_T$  using Maxwell's shape factors. —△—△— Curve 3: Experimental  $\alpha_T$  using Sliker's shape factors. ——— Curve 4: Theoretical  $\alpha_T$  based on elastic collision.

$C_{ij}^*$  and hence  $\bar{T}^*$  to estimate  $\epsilon_{ij}/k$  of the respective molecule.

With the value of  $\epsilon_{ij}/k$  first estimated, one may repeat the total procedure as mentioned above, to get more correct  $\epsilon_{ij}/k$  in order to present them in Table II. They are found in good agreement with the available literature values. Reported viscosity data are then used with the estimated  $\epsilon_{ij}/k$  to get the molecular diameter  $\sigma_{ij}$  as shown in Table II. The theoretical  $\alpha_T$ 's for  $\text{Ne}^{20}\text{-Ne}^{22}$ ,  $\text{Ar}^{36}\text{-Ar}^{40}$  and  $\text{Kr}^{80}\text{-Kr}^{86}$  were then evaluated with those  $\epsilon_{ii}/k$ ,  $\epsilon_{jj}/k$  and  $\epsilon_{ij}/k$  (Table II) and shown in Figs. 3–5 respectively.

#### §4. Results and Discussions

The least square fitted equations of  $p^2/\ln q_e$  against  $p^4$  from the available  $\ln q_e$  vs  $p$  in atmosphere<sup>9)</sup> as illustrated graphically in Fig. 2, were worked out for 9.7% of  $\text{Ar}^{36}$  in  $\text{Ar}^{40}$ ,  $\text{Ne}^{20}\text{-Ne}^{22}$  and  $\text{Kr}^{80}\text{-Kr}^{86}$ , the latter two with their natural isotopic abundances, at two experimental temperatures. The pressure dependence of  $\ln q_e$  at any

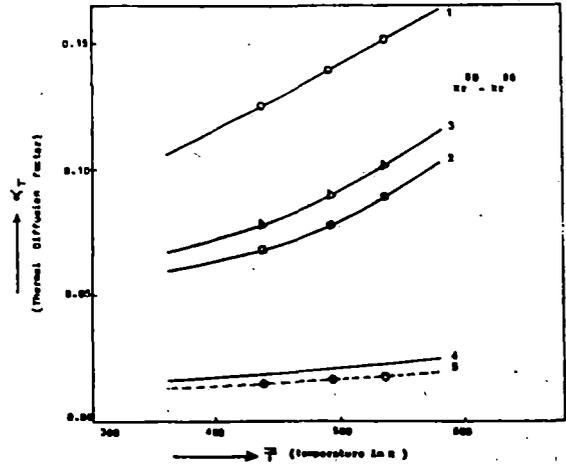


Fig. 5. Plot of  $\alpha_T$  against  $T$  for  $\text{Kr}^{80}\text{-Kr}^{86}$ . —○—○— Curve 1: Experimental  $\alpha_T$  from  $F_0$  and  $\ln q_{\max}$ . —□—□— Curve 2: Experimental  $\alpha_T$  using Maxwell's shape factor. —△—△— Curve 3: Experimental  $\alpha_T$  using Sliker's shape factor. ——— Curve 4: Theoretical  $\alpha_T$  based on elastic collision. —○—○— Curve 5: Experimental  $\alpha_T$  from  $F_0$  and adjusted  $\ln q_{\max}$ .

intermediate temperature for them, as shown by dotted lines in Fig. 2, were also inferred from  $\ln q_{\max}$  in terms of known  $F_0$  and  $\alpha_T$  assuming the linear relationship of  $(b'/a')$  with  $T$  for the three aforesaid mixtures.  $p^2/\ln q_e$  as a linear function of  $p^4$  are, however, expressed by the following equations for

i)  $\text{Ar}^{36}\text{-Ar}^{40}$  (with 9.7% of  $\text{Ar}^{36}$  in  $\text{Ar}^{40}$ )

$$p^2/\ln q_e = 0.1411 + 3.3990p^4 \quad \text{at } 432 \text{ K}$$

$$p^2/\ln q_e = 0.1590 + 2.4102p^4 \quad \text{at } 484 \text{ K}$$

$$p^2/\ln q_e = 0.2392 + 1.4210p^4 \quad \text{at } 537 \text{ K}$$

ii)  $\text{Ne}^{20}\text{-Ne}^{22}$  (with natural isotopic abundances)

$$p^2/\ln q_e = 0.7926 + 0.3926p^4 \quad \text{at } 447 \text{ K}$$

$$p^2/\ln q_e = 0.9808 + 0.2970p^4 \quad \text{at } 492 \text{ K}$$

$$p^2/\ln q_e = 1.1452 + 0.2306p^4 \quad \text{at } 537 \text{ K}$$

and for  $\text{Kr}^{80}\text{-Kr}^{86}$  (with natural isotopic abundances)

$$p^2/\ln q_e = 0.0086 + 1.8720p^4 \quad \text{at } 447 \text{ K}$$

$$p^2/\ln q_e = 0.0098 + 1.2558p^4 \quad \text{at } 492 \text{ K}$$

$$p^2/\ln q_e = 0.0149 + 0.6435p^4 \quad \text{at } 537 \text{ K}$$

respectively. But  $\ln q_{\max}$  of Krypton, estimated from the measured values of  $\ln q_e$  as a function of pressure (Fig. 2) in terms of  $a'$  and  $b'$  (Table I) is found to be 8.18 times larger than the widely reported data elsewhere.<sup>7)</sup> Adjustment of  $\ln q_e$  is, therefore, necessary to get actual  $\alpha_T$ 's of  $\text{Kr}^{80}\text{-Kr}^{86}$ , as shown by curve 5 in Fig. 5, from the following  $p^2/\ln q_e$  against  $p^4$  relations:

$$p^2/\ln q_e = 0.0704 + 15.3139p^4 \quad \text{at } 447 \text{ K}$$

$$p^2/\ln q_e = 0.0802 + 10.2775p^4 \quad \text{at } 492 \text{ K}$$

$$p^2/\ln q_e = 0.1216 + 5.2632p^4 \quad \text{at } 537 \text{ K.}$$

Table II. Maxwell's model dependent and Slicker's model independent column shape factors, (CSF coefficient of viscosity together with estimated force parameters  $\epsilon_{ij}/k$  and molecular diameter  $\sigma_{ij}$  used in the calculation of  $\alpha_T$  of simple isotopic gas mixtures.

System	Model potential	Estimated		Reported		Mean Temp. (T) in K			
		$\epsilon_{ij}/k$ in K	$\sigma_{ij}$ in Å	$\epsilon_{ij}/k$ in K	$\sigma_{ij}$ in Å				
Ne <sup>20</sup> -Ne <sup>22</sup>	LJ 12-6	40.77	3.1840	41.19*	3.074*	447			
				27.50**	2.858**	492			
Ar <sup>36</sup> -Ar <sup>40</sup>	LJ 12-6	118.41	3.9543	125.20*	3.405*	432			
				119.50**	3.826**	484.5			
Kr <sup>80</sup> -Kr <sup>86</sup>	LJ 12-6	202.41	4.1689	199.20*	4.020*	447			
				166.70**	4.130**	492			
Column shape factors (CSF)									
System	Model potential	Maxwell					Slicker		$\eta_{ij} \times 10^5$ gm x cm <sup>-1</sup> x sec <sup>-1</sup>
		$k'$	$k'_c$	$k'_d$	$[S \cdot F]_1 \times 6!$	$\pi(1 - a^2)$	$[S \cdot F]_3 \times 9!$		
Ne <sup>20</sup> -Ne <sup>22</sup>	LJ 12-6	0.815	1.760	0.790	0.937	3.137	0.711	31.40	
								33.35	
								35.17	
Ar <sup>36</sup> -Ar <sup>40</sup>	LJ 12-6	0.815	1.760	0.790	0.937	3.137	0.711	21.80	
								23.95	
								26.10	
Kr <sup>80</sup> -Kr <sup>86</sup>	LJ 12-6	0.815	1.760	0.790	0.937	3.137	0.711	25.50	
								28.15	
								30.80	

\*Maitland et al. (1981)

\*\*Hirschfelder et al. (1964)

The new  $\ln q_e$  against  $p$  in atmosphere is shown by the adjacent curves in Fig. 2. The corresponding  $\ln q_{max}$ 's are placed in Table I, together with those obtained from  $\ln q_e$  vs  $p$  measured by Moran and Watson.<sup>9)</sup> The  $\ln q_{max}$ 's for all the isotopic molecular mixtures were, however, determined from eq. (9) with  $a'$  and  $b'$  governing their pressure variation of  $\ln q_e$  as shown in Fig. 2. They are placed in the 8th column of Table I.

Since  $F_s$  is supposed not to depend on molecular model we therefore, estimated three values of  $F_s$  from eq. (1) for this column<sup>9)</sup> through the measured  $\ln q_{max}$  and reliable  $\alpha_T$ 's from the other sources:<sup>10)</sup> for Ar<sup>36</sup>-Ar<sup>40</sup> at 432 K, 537 K and Ne<sup>20</sup>-Ne<sup>22</sup> at 447 K respectively. It is interesting to note in Fig. 1, that the temperature variation of  $F_s$  is the same as observed earlier<sup>5-8)</sup> only the coefficients of  $\bar{T}$  and  $\bar{T}^2$  are slightly different. Although  $r_c/r_h$  (=25) for the present column is too large, the temperature variation of  $F_s$  is found to be concave in nature.

The magnitudes and trends of  $\alpha_T$  with respect to temperature  $\bar{T}$  could, now be obtained for Ne<sup>20</sup>-Ne<sup>22</sup>, Ar<sup>36</sup>-Ar<sup>40</sup> and Kr<sup>80</sup>-Kr<sup>86</sup> from eq. (1) in terms of  $\ln q_{max}$  and  $F_s$ . The expected close agreement of  $\alpha_T$ 's from the CCF method with theoretical ones might express the reliability of  $F_s$  and the model independency of CCF method may once again be confirmed. The  $\alpha_T$ 's by the CCF method are placed in the 10th column of Table I. The variation of these  $\alpha_T$ 's with  $\bar{T}$  are shown graphically in Figs. 3-5 for Ne<sup>20</sup>-Ne<sup>22</sup>, Ar<sup>36</sup>-Ar<sup>40</sup> and Kr<sup>80</sup>-Kr<sup>86</sup> respectively by the curve No. 1.

In order to ensure the reliability of the temperature

dependence of  $\alpha_T$  the molecular force parameters  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  were also determined by using eq. (18) and the available coefficients of viscosity respectively. The estimated  $\epsilon_{ij}/k$  or  $\epsilon_{jj}/k$  and  $\sigma_{ij}$  or  $\sigma_{jj}$  of the isotopic gases are placed in the 3rd and the 4th columns of Table II. The close agreement of them with the literature values at once suggests the technique to estimate  $\alpha_T$  is really accurate and reliable. The experimental  $\alpha_T$ 's were also computed from eqs. (13) and (14) by using Maxwell's inverse fifth power potential and Slicker's model independent column shape factors (CSF) which are placed in Table II. These  $\alpha_T$ 's are placed in the 11th and the 12th columns of Table I respectively. The variation of these  $\alpha_T$ 's with  $\bar{T}$  are also shown graphically by curves 2 and 3 respectively in Figs. 3-5. The  $\alpha_T$ 's as shown in Figs. 3-5, due to Maxwell and Slicker's methods agree excellently with  $\alpha_T$ 's by the CCF method, so far their trends with  $\bar{T}$  are concerned, although the magnitude of  $\alpha_T$  by the present method is higher.

The existing frame work of derivations of eqs. (13) and (14) are really very interesting. The formulations so derived show that the molecular model appears in them through CSF which seems to be an important step forward in the existing method based on Furry<sup>2)</sup> and Jones<sup>4)</sup> column theory.

With the estimated force parameters of  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  presented in Table II theoretical  $\alpha_T$ 's based on the elastic collisions were also evaluated and placed in the 13th column of Table I. The variation of theoretical  $\alpha_T$ 's with  $\bar{T}$  are shown graphically by curve 4 in each of the Figs. 3

5 for Ne<sup>20</sup>-Ne<sup>22</sup>, Ar<sup>36</sup>-Ar<sup>40</sup> and Kr<sup>80</sup>-Kr<sup>86</sup> respectively. The  $\alpha_T$ 's due to elastic collision theory are found to be almost of the same magnitude with those by the CCF method. Besides all these, it is seen that the trends of  $\alpha_T$ 's with respect to temperature by the present CCF method agree excellently well with the theoretical ones in all the systems.

From the discussions made above, it is confirmed that  $F_s$  is a molecular model independent parameter.  $F_s$  is further, claimed to be a perfect, simple and straightforward one to locate the magnitude and trend of  $\alpha_T$  with respect to  $\bar{T}$ . Moreover,  $\alpha_T$  against  $1/\bar{T}$  may be considered as a simple and useful technique in determining the exact force parameter of molecules too, to observe the temperature dependence of  $\alpha_T$  of any binary isotopic and nonisotopic gas mixture.

### §5. Conclusion

Model independency of CCF  $F_s$ , is now once again established in determining the reliable  $\alpha_T$ 's of any binary gas mixture in column measurements. It is, therefore, desirable to study more TD columns of different column geometries to arrive at the functional relationship of  $F_s$  with  $r_c$ ,  $r_h$ ,  $L$  and  $\bar{T}$  with the experimentally determined  $\ln q_{max}$  and  $\alpha_T$  of interesting pair of molecules. The simultaneous estimation of  $\alpha_T$ 's and  $F_s$  with the corresponding force parameters from  $\alpha_T$  vs  $1/\bar{T}$  seems to be an important stepforward to test the applicability of  $F_s$ . Furthermore, the very existence of inelastic collisions among the molecules in the process of thermal diffusion might be detected and improved with certainty through such rigorous study.

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# The functional relationship of the column calibration factor in thermal diffusion column measurement

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**Abstract.** An approximate formulation of the column calibration factor (CCF),  $F_s$ , at any given temperature  $\bar{T}$  is derived for thermal diffusion columns (TDC) from the Navier–Stokes equation in cylindrical coordinates. The values of  $F_s$  are then used to estimate the experimental thermal diffusion factor  $\alpha_T$  of a neon gas mixture with its natural isotopic abundances from  $\ln q_{max}$  measured in four columns of different column geometries. The molecular force parameters of the molecule are estimated from the intercepts and slopes of the linear variations of  $\alpha_T$  and the collision integral  $C_{ij}^*$  against  $1/\bar{T}$  and  $1/\bar{T}^*$  respectively. The excellent agreement of the estimated force parameters with the available literature values and the comparison of the temperature variation of  $\alpha_T$  by the CCF method with the existing experimental and theoretical ones establish the fact that the derived relationship of  $F_s$  with the column geometries is more than adequate.

## Mathematical symbols used in the text and tables

$F_s$	column calibration factor (CCF)
$\alpha_T$	thermal diffusion factor (TDF)
$\bar{T}$	mean temperature $\bar{T} = (T_h + T_c)/2$
$T_h$	temperature of hot wall of radius $r_h$
$T_c$	temperature of cold wall of radius $r_c$
$C_{ij}^*$	collision integral
$q_e$	equilibrium separation factor defined by $q_e = (x_i/x_j)_{top}/(x_i/x_j)_{bottom}$
$x_i$	mass or mole fraction of the $i$ th component
$\epsilon_{ij}$	depth of the potential well
$\sigma_{ij}$	molecular diameter
$L$	length of the column
$q_{max}$	maximum value of separation factor at optimum pressure $p_{opt}$
$\lambda_{ij}$	coefficient of thermal conductivity of a binary gas mixture
$\eta_{ij}$	coefficient of viscosity of a binary gas mixture
$H$	column transport coefficient
$K_c$	column remixing coefficient
$K_d$	back diffusion coefficient
$D_{ij}$	diffusion coefficient
$h', k'_c$ and $k'_d$	Maxwell-model-dependent column shape factors (CSF) and
$(SF)_1, (SF)_3$ and $\pi(1 - a^2)$	Sliker-model-independent CSFs.

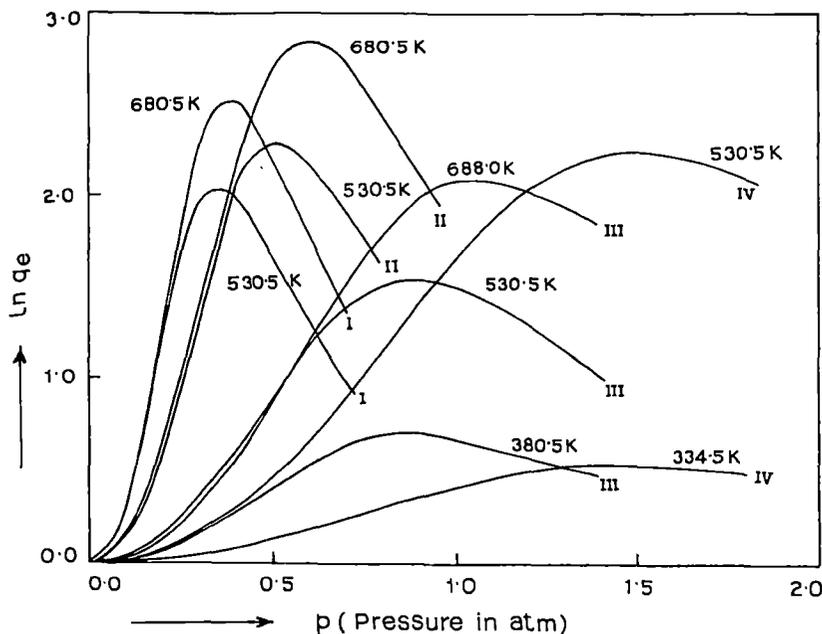
## 1. Introduction

The thermal diffusion column (TDC) is a very useful device for concentrating impurities of a gas. The enrichment of impurities becomes squared when the length of the column is doubled. The TDC is also used to determine the thermal diffusion factor  $\alpha_T$  of any isotopic or non-isotopic gas mixture. The column theory, on the other hand, may be improved by the accurate experimental determination of  $\alpha_T$  of the binary gas mixture in a column. Again, the close correlation of  $\alpha_T$  with the molecular force parameters allows one to locate the exact force parameters of the interacting molecules. Thus, both from experimental and from theoretical points of view, an accurate estimation of  $\alpha_T$  is necessary.

In the absence of a theoretical possibility of estimating the actual experimental  $\alpha_T$  from the existing column theory, Acharyya *et al* [1] and Datta *et al* [2], however, introduced a scaling factor  $F_s$  called the column calibration factor (CCF) into the relation:

$$\ln q_{max} = \alpha_T F_s(r_c, r_h, L, \bar{T}). \quad (1)$$

$r_c$  and  $r_h$  are the cold and hot wall radii of a given column of geometrical length  $L$  and  $\bar{T} = (T_h + T_c)/2$ ,  $T_h$  and  $T_c$  being the hot and cold wall temperatures in kelvins respectively. Here  $\ln q_{max}$  is the maximum value of  $\ln q_e$  at the optimum pressure and  $q_e$  is the equilibrium separation factor. Although, the model independency of  $F_s$  is well established [3] for its important role in the estimation of reliable  $\alpha_T$  [1–4], the functional relationship of  $F_s$  with  $r_c, r_h, L$  and  $\bar{T}$  remains unknown.



**Figure 1.** A plot of  $\ln q_e$  against the pressure  $p$  in atmospheres of  $\text{Ne}^{20}\text{-Ne}^{22}$  mixtures: curve I, for column I at 530.5 K and 680.5 K; curve II, for column II at 530.5 K and 680.5 K; curve III, for column III at 380.5 K, 530.5 K and 688.0 K; and curve IV, for column IV at 334.5 K and 530.5 K.

Rutherford and Kaminsky [5] had measured the column coefficients  $H'$ ,  $K'_c$  and  $K'_d$  using  $\text{Ne}^{20}\text{-Ne}^{22}$  gas mixtures with their natural isotopic abundances at various experimental temperatures in four different columns; see table 1. The hot Nichrome V wire of their [5] I, II and III TD columns had radius  $r_h = 8 \times 10^{-4}$  m. Their column IV was a thin-walled Nichrome V tube of radius  $r_h = 3.2 \times 10^{-3}$  m. The radii of water-cooled metal tubes of all these columns were  $r_c = 1.6 \times 10^{-2}$  m,  $1.27 \times 10^{-2}$  m,  $9.43 \times 10^{-3}$  m and  $9.43 \times 10^{-3}$  m respectively. The geometrical length of columns I and II was  $L = 3.05$  m whereas columns III and IV had  $L = 1.524$  m. This inspired us to observe  $\alpha_T$  values from the pressure dependences of  $\ln q_e$  values of  $\text{Ne}^{20}\text{-Ne}^{22}$  mixtures at the experimental temperatures. The  $\ln q_e$  of  $\text{Ne}^{20}\text{-Ne}^{22}$  gas mixtures as a function of the atmospheric pressure are shown in figure 1 by the least square fitted curves for these columns. The  $H'$ ,  $K'_c$  and  $K'_d$  [5] are used to study the temperature dependence of  $\alpha_T$  and hence the molecular force parameters of neon. The experimental  $\alpha_T$  values due to Maxwell's model-dependent and Sliker's model-independent column shape factors (CSF) together with the theoretical  $\alpha_T$  values based on Chapman-Enskog gas kinetic theory [6] were also estimated. They are plotted against  $\bar{T}$  in figure 2 for comparison. The experimental and theoretical  $F_s$  as well as the estimated experimental and theoretical  $\alpha_T$  values are presented in tables 1 and 2 respectively. The theoretical formulation of  $F_s$  is, however, derived in section 3 and is compared with the experimental  $F_s$  as seen in figure 3.

The plots of  $\alpha_T$  against  $\bar{T}$  obtained by the CCF method and of the collision integral  $C_{ij}^*$  against the reduced temperature  $\bar{T}^*$  were simultaneously used to calculate the force parameters  $\epsilon_{ii}/k$  or  $\epsilon_{jj}/k$  of the isotopic components of neon.  $\epsilon_{ii}/k$  or  $\epsilon_{jj}/k$  are the depths of the potential

well (see section 4). The molecular diameters  $\sigma_{ii}$  or  $\sigma_{jj}$  were then obtained from the coefficients of viscosity with the estimated force parameters (see table 3). The excellent agreement of the force parameters with the literature values (table 2) and the close agreement of  $\alpha_T$  obtained by the CCF method with the theoretical ones as seen in table 2 and figure 2 establish the fact that the derived relationship of  $F_s$  is reliable.

## 2. Formulations of the experimental thermal diffusion factor

Both ends being closed in an ideal TD column of length  $L$ ,  $\ln q_e$  is given by

$$\ln q_e = HL/(K_c + K_d) \quad (2)$$

where  $q_e$  is defined by

$$q_e = (x_i/x_j)_{top}/(x_i/x_j)_{bottom}.$$

$(x_i/x_j)_{top}$  and  $(x_i/x_j)_{bottom}$  represent the ratio of mole or mass fractions of lighter ( $i$ ) and heavier ( $j$ ) components of a binary gas mixture at the top and at the bottom of a TD column of geometrical length  $L$ . The column coefficients  $H$ ,  $K_c$  and  $K_d$  are proportional to the second, fourth and zeroth powers of the pressure  $p$  in atmospheres respectively. On writing  $H = H'p^2$ ,  $K_c = K'_c p^4$  and  $K_d = K'_d$ , equation (2) can be put into the form

$$\ln q_e = \frac{(H'L/K'_c)p^2}{(K'_d/K'_c) + p^4}$$

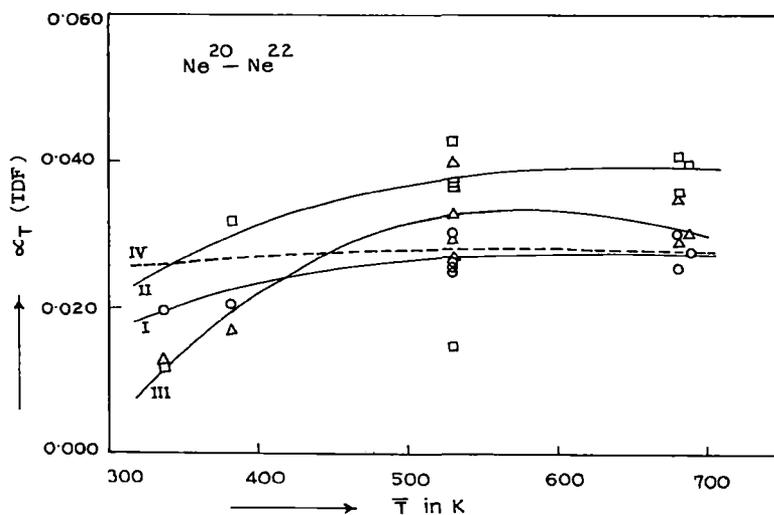
or

$$p^2/\ln q_e = b'/a' + (1/a')p^4 \quad (3)$$

where  $a' = (H'L/K'_c)$  and  $b' = (K'_d/K'_c)$ . The experimental parameters  $a'$  and  $b'$  of table 1 govern

**Table 1.** The geometry of the columns with length  $L$ , cold wall radius  $r_c$  and hot wall radius  $r_h$  together with column constants  $G_1$  and  $G_2$ , column calibration factor  $F_s$ ,  $a'$ ,  $b'$  and  $\ln q_{max}$ .

Geometry of the column in m	Hot wall temp. $T_h$ (K)	Cold wall temp. $T_c$ (K)	Mean temp. $\bar{T}$ (K)	$a'$ (atm <sup>2</sup> )	$b'$ (atm <sup>4</sup> )	$\ln q_{max}$	Column constant $G_1(10^3)$	Column constant $G_2(10^4)$	Theoretical $F_s$ from equation (14)	Experimental $F_s$
Column I $L = 3.05$ $r_c = 1.6 \times 10^{-2}$ $r_h = 8.0 \times 10^{-4}$	773	288	530.5	0.5184	0.0158	2.0621	9.4145	3.4997	67.8322	76.3741
	1073	288	680.5	0.7367	0.0211	2.5358	11.6400		83.9669	91.8768
Column II $L = 3.05$ $r_c = 1.27 \times 10^{-2}$ $r_h = 8.0 \times 10^{-4}$	773	288	530.5	1.1982	0.0684	2.2907	9.6822	3.4138	88.7777	84.8407
	1073	288	680.5	2.0376	0.1282	2.8460	11.9803		110.3101	103.1159
Column III $L = 1.524$ $r_c = 9.43 \times 10^{-3}$ $r_h = 8.0 \times 10^{-4}$	473	288	380.5	1.0358	0.5498	0.6985	5.6300	3.6486	33.8041	27.0736
	773	288	530.5	2.3547	0.5902	1.5327	10.0152		60.1340	56.7667
	1088	288	688.0	4.7567	1.2955	2.0896	12.4915		75.0028	75.7101
Column IV $L = 1.524$ $r_c = 9.43 \times 10^{-3}$ $r_h = 3.2 \times 10^{-3}$	381	288	334.5	2.3265	4.6460	0.5397	3.3865	2.2993	27.1315	21.5880
	773	288	530.5	10.2385	5.2510	2.2340	10.4788		83.9535	82.7407

**Figure 2.** A plot of TD factor  $\alpha_T$  of  $\text{Ne}^{20}\text{-Ne}^{22}$  against  $\bar{T}$  in kelvins: curve I, (O), by the CCF method; curve II, ( $\square$ ), due to the Sliker CSF; curve III, ( $\Delta$ ), due to the Maxwell CSF; and curve IV, (---), due to the elastic collision theory.

the variation of the experimental  $\ln q_e$  as a function of the pressure  $p$  in atmospheres at a given temperature. They were obtained from the measured values of  $H'$ ,  $K'_c$  and  $K'_d$  by Rutherford and Kaminsky [5]. The pressure dependences of  $\ln q_e$  thus estimated are illustrated graphically in figure 1 by the fitted curves for four columns I, II, III and IV at various experimental temperatures. It is evident from equation (3) that, in each case seen in figure 1, as  $p$  increases  $\ln q_e$  of the gas mixture increases and eventually reaches a maximum value of  $\ln q_{max}$  given by

$$\ln q_{max} = \frac{a'}{2\sqrt{b'}} \quad (4)$$

at the optimum pressure  $p_{opt}$  given by  $p_{opt} = (b')^{1/4}$  for which  $(\partial/\partial p) \ln q_e = 0$ . The experimental  $\alpha_T$  or often the

experimental  $F_s$  is obtained by using equations (1) and (4) in terms of  $F_s$  and  $\ln q_{max}$  or  $\alpha_T$  and  $\ln q_{max}$ .

Again, equation (2) on maximization becomes

$$\ln q_{max} = \frac{HL}{2(K_c K_d)^{1/2}} \quad (5)$$

The column coefficients  $H$ ,  $K_c$  and  $K_d$  based on Maxwell-model-dependent CSF  $h'$ ,  $k'_c$  and  $k'_d$  [7] are

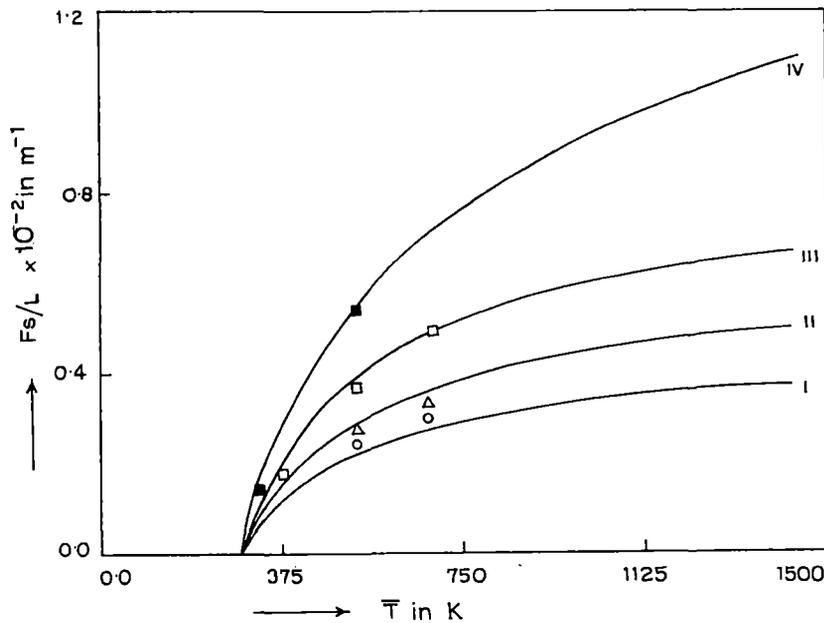
$$H = \frac{2\pi}{6!} \left( \frac{\alpha_T \rho_{ij}^2 g}{\eta_{ij}} \right) \frac{1}{2} (r_c + r_h)(r_c - r_h)^3 \left( \frac{\Delta T}{\bar{T}} \right)^2 h'$$

$$K_c = \frac{2\pi}{9!} \left( \frac{\rho_{ij}^3 g^2}{\eta_{ij}^2 D_{ij}} \right) \frac{1}{2} (r_c + r_h)(r_c - r_h)^7 \left( \frac{\Delta T}{\bar{T}} \right)^2 k'_c$$

$$K_d = 2\pi(\rho_{ij} D_{ij}) \frac{1}{2} (r_c + r_h)(r_c - r_h) k'_d.$$

**Table 2.** Experimental and theoretical  $\alpha_T$  at various experimental temperatures together with estimated force parameters  $\epsilon_{ij}/k$  and molecular diameters  $\sigma_{ij}$ .

Column	Mean temp. $\bar{T}$ (K)	Experimental $\alpha_T$ using			Theoretical $\alpha_T$ using equation (15)	Estimated		Reported	
		$F_s$ of equation (14)	Sliker's shape factor	Maxwell's shape factor		$\epsilon_{ij}/k$ (K)	$\sigma_{ij}$ ( $10^{10}$ m)	$\epsilon_{ij}/k$ (K)	$\sigma_{ij}$ ( $10^{10}$ m)
Column I	530.5	0.030	0.043	0.040	0.028				
	680.5	0.030	0.042	0.035	0.028				
Column II	530.5	0.026	0.037	0.033	0.028				
	680.5	0.026	0.036	0.029	0.028			47.0 <sup>a</sup>	2.72 <sup>a</sup>
						48.58	2.69		
								41.186 <sup>b</sup>	3.07 <sup>b</sup>
Column III	380.5	0.021	0.032	0.017	0.027				
	530.5	0.026	0.037	0.030	0.028				
	688.0	0.028	0.040	0.030	0.028				
Column IV	334.5	0.020	0.012	0.013	0.026				
	530.5	0.027	0.015	0.027	0.028				

<sup>a</sup> Clifford *et al* (1977) [13].<sup>b</sup> Aziz (1976) [13].**Figure 3.** A plot of the theoretical  $F_s$  (equation (14)) with the experimental  $F_s$  on it against  $\bar{T}$  in kelvins: curve I, for column I, (O), experimental points; curve II, for column II, ( $\Delta$ ), experimental points; curve III, for column III, ( $\square$ ), experimental points; and curve IV, for column IV, ( $\blacksquare$ ), experimental points.

The experimental  $\alpha_T$  due to the Maxwell-model-dependent CSF is thus

$$\alpha_T(\text{Maxwell model}) = 2.39 \frac{r_c - r_h}{L} \frac{\bar{T}}{\Delta T} \frac{(k'_c k'_d)^{1/2}}{h'} \ln q_{max} \quad (6)$$

where  $\Delta T = T_h - T_c$ . Similarly the column coefficients due to the model-independent Sliker's [8] CSF  $(SF)_1$ ,  $\pi(1-a^2)$  and  $(SF)_3$  are

$$H = (SF)_1 r_c^4 \frac{\alpha_T \rho_{ij}^2 g}{\eta_{ij}} \left( \frac{\Delta T}{\bar{T}} \right)^2$$

$$K_d = \pi(1-a^2) r_c^2 \rho_{ij} D_{ij}$$

$$K_c = (SF)_3 r_c^8 \left( \frac{\rho_{ij}^3 g^2}{\eta_{ij}^2 D_{ij}} \right)_1 \left( \frac{\Delta T}{\bar{T}} \right)^2$$

where  $a = r_h/r_c$ . Using Sliker's CSF,  $\alpha_T$  is given by

$$\alpha_T(\text{Sliker}) = 2.0 \frac{r_c}{L} \frac{\bar{T}}{\Delta T} \frac{[\pi(1-a^2)(SF)_3]^{1/2}}{(SF)_1} \ln q_{max}. \quad (7)$$

The experimental  $\alpha_T$  values using the CSF were obtained from equations (6) and (7) together with those by the CCF method from equations (1) and (4) in terms of measured  $\ln q_{max}$  and  $F_s$ . All these  $\alpha_T$  values are placed in table 2 for comparison with the theoretical ones. They are also shown graphically in figure 2 with respect to  $\bar{T}$  for  $\text{Ne}^{20}\text{-Ne}^{22}$

**Table 3.** Maxwell-model-dependent and Slieker-model-independent column shape factors, coefficient of viscosity  $\eta_{ij}$  and thermal conductivity  $\lambda_{ij}$  of Ne<sup>20</sup>-Ne<sup>22</sup> gas mixture.

Column	Mean temp $\bar{T}$ (K)	Column shape factor						$\eta_{ij}$ (10 <sup>5</sup> kg m <sup>-1</sup> s <sup>-1</sup> )	$\eta_{ij}$ (10 <sup>2</sup> cal m <sup>-1</sup> s <sup>-1</sup> K <sup>-1</sup> )	
		Maxwell			Slieker					
		$h'$	$k'_c$	$k'_d$	(SF) <sub>1</sub> (10 <sup>3</sup> )	(SF) <sub>3</sub> (10 <sup>6</sup> )				
Column I	530.5	1.035	3.300	0.700	1.3639	1.9717	5.0333	1.7900		
	680.5	1.585	6.075	0.725					6.2543	2.2236
Column II	530.5	1.060	3.100	0.715	1.3914	1.9140	5.0333	1.7900		
	680.5	1.600	5.525	0.740					6.2543	2.2236
Column III	380.5	0.800	1.050	0.745	1.2838	1.6646	5.0333	1.3558		
	530.5	1.120	2.975	0.750					6.3153	2.2459
	688.0	1.590	4.975	0.770					3.4378	1.2226
Column IV	334.5	0.970	0.500	0.912	239.23	4662.2	5.0333	1.7900		
	530.5	1.185	1.775	0.925						

gas mixtures. The corresponding CSFs based on Maxwell-model-dependent and Slieker-model-independent methods are entered in table 3.

**3. The theoretical formulation of the column calibration factor**

The column parameters in cylindrical coordinates derived from the most elementary theory of the thermal diffusion column by Cohen [9] are

$$H = -2\pi \int_{r_h}^{r_c} \alpha_T \frac{\partial}{\partial r} (\ln T) dr \left( \int_{r_h}^r \rho_{ij} v r dr \right),$$

$$K_c = 2\pi \int_{r_h}^{r_c} \frac{dr}{\rho_{ij} D_{ij} r} \left( \int_{r_h}^r \rho_{ij} v r dr \right)^2$$

and  $K_d = 2\pi \int_{r_h}^{r_c} \rho_{ij} D_{ij} r dr$

which can, however, be approximated almost in the same manner as was done earlier by Slieker [8]. Here  $\rho_{ij}$  and  $D_{ij}$  are the density and diffusion coefficients of the gas mixture,  $r$  is the radial coordinate and  $T$  is the absolute temperature in kelvins.

Under the influence of the temperature gradient along the horizontal plane of the column, the convective velocity  $v$  of the molecule in the vertical direction is obtained from the Navier-Stokes equation in cylindrical coordinates:

$$\frac{\partial^3 v}{\partial r^3} + \frac{1}{r} \frac{\partial^2 v}{\partial r^2} - \frac{1}{r^2} \frac{\partial v}{\partial r} = \frac{\rho_{ij} g}{\eta_{ij} \bar{T}} \frac{dT}{dr}.$$

If we consider the rectilinear flow of heat from the hot wire or wall of temperature  $T_h$  to the cold wall of temperature  $T_c$  of a TDC, the temperature  $T$  is given by

$$T = T_h - \frac{\Delta T}{r_c - r_h} (r - r_h)$$

or

$$\frac{dT}{dr} = -\frac{\Delta T}{r_c - r_h}.$$

Putting  $r = e^x$  and solving the above equation, we get

$$v = C_1 + C_2 \ln r + C_3 r^2 - \frac{\rho_{ij} g}{\eta_{ij} \bar{T}} \frac{\Delta T}{(r_c - r_h)} \frac{r^3}{9}$$

$$= Gr_c^2 (K_1 + K_2 \ln \phi + K_3 \phi^2 + \phi^3) \tag{8}$$

where

$$K_1 = \frac{C_1}{Gr_c^2} + \frac{C_2}{Gr_c^2} \ln r_c,$$

$$K_2 = \frac{C_2}{Gr_c^2}, \quad K_3 = C_3/G$$

and  $G = \frac{\rho_{ij} g}{\eta_{ij} \bar{T}} \frac{\Delta T}{(a - 1)} \frac{1}{9}.$

$C_1, C_2$  and  $C_3$  being the integration constants,  $\phi = r/r_c$  is the new variable and  $a = r_h/r_c$ . The boundary conditions are

- (i)  $v = 0$  at  $r = r_c$  for which  $\phi = 1$ ,
- (ii)  $v = 0$  at  $r = r_h$  for which  $\phi = a$  and since there is no transport of components of the gas mixture at equilibrium in the vertical direction up and down the column, we have
- (iii)  $r_c^2 \int_a^1 \rho v \phi d\phi = 0.$

Here,  $K_1, K_2$  and  $K_3$  are dimensionless constants which are, however, given explicitly in terms of  $a (= r_h/r_c)$  of a TDC by applying the boundary conditions mentioned above:

$$K_1 = \frac{5a^2(1-a)(1+2a^2 \ln a - a^2) + \ln a}{5(a^2 - 1)^2 + 5(1 - 2a^4) \ln a},$$

$$K_2 = \frac{5a^2(1-a)(1-2a^2) - (1-a^2)}{5(a^2 - 1)^2 + 5(1 - 2a^4) \ln a}$$

and  $K_3 = -(K_1 + 1).$

The column coefficients  $H, K_c$  and  $K_d$  are now derived as follows:

$$H = -2\pi r_c^2 \int_a^1 \alpha_T \frac{\partial}{\partial \phi} (\ln T) d\phi \int_a^\phi \rho_{ij} v \phi d\phi$$

$$= 2\pi\alpha_T \frac{\Delta T}{1-a} \rho_{ij} G r_c^4 \times \int_a^1 \frac{1}{T} \left( \frac{K_1 \phi^2}{2} + \frac{K_2 \phi^2}{2} \left( \ln \phi - \frac{1}{2} \right) + \frac{K_3 \phi^4}{4} + \frac{\phi^5}{5} + K_4 \right) d\phi$$

where

$$K_4 = -\frac{a^2}{2} \left[ K_1 + K_2 \left( \ln a - \frac{1}{2} \right) + \frac{K_3 a^2}{2} + \frac{2a^3}{5} \right].$$

Here, the temperature and composition dependences of  $\eta_{ij}$ ,  $\rho_{ij}$ ,  $D_{ij}$  and  $\alpha_T$  are not taken into account [7–9] and the above equation for  $H$  becomes

$$H = 2\pi\alpha_T r_c^4 \frac{\rho_{ij}^2 g}{\eta_{ij} T} \frac{\Delta T}{(a-1)} \frac{1}{9} G_1 \quad (9)$$

where

$$G_1 = \frac{\Delta T}{T(1-a)} \left( \frac{2K_1 - K_2}{12} (1-a^3) - \frac{K_2}{18} (1-a^3) - \frac{K_2 a^3}{6} \ln a + \frac{K_3}{20} + K_4 (1-a) + \frac{1}{30} \right) - \left( \frac{\Delta T}{T(1-a)} \right)^2 \left[ \frac{2K_1 - K_2}{48} - \frac{K_2}{24} \left( \frac{7}{12} + a^4 \ln a \right) + \frac{K_3}{120} + \frac{K_4}{2} (1-a^2) + \frac{1}{210} \right] + \left( \frac{\Delta T}{T(1-a)} \right)^3 \left( \frac{2K_1 - K_2}{240} - \frac{47K_2}{7200} + \frac{K_3}{840} + \frac{K_4}{6} (1-a^3) + \frac{1}{1680} \right) \quad (10)$$

retaining the term containing up to the third power of  $\Delta T/[T(1-a)]$  because the contributions of higher terms are negligibly small. Again,  $a^n$  is very small compared with unity for  $n \geq 4$ .

The coefficient  $K_c$  of a TDC is given by

$$K_c = 2\pi \int_a^1 \frac{d\phi}{\rho_{ij} D_{ij} \phi} \left( \int_a^\phi \rho_{ij} v \phi d\phi \right)^2 = \frac{2\pi \rho_{ij} G^2 r_c^8}{D_{ij}} \int_a^1 \frac{1}{\phi} \left( \frac{K_1 \phi^2}{2} + \frac{K_2 \phi^2}{2} \left( \ln \phi - \frac{1}{2} \right) + \frac{K_3 \phi^4}{4} + \frac{\phi^5}{5} + K_4 \right)^2 d\phi = \frac{2\pi \rho_{ij}^3 g^2}{\eta_{ij} D_{ij}} \left( \frac{\Delta T}{T} \right)^2 \frac{r_c^8}{81(1-a)^2} G_2 \quad (11)$$

where

$$G_2 = \frac{K_1^2}{16} + \frac{5K_2^2}{128} - K_4^2 \ln a + \frac{K_3^2}{128} - \frac{3K_1 K_2}{32} + \frac{K_1 K_3}{24} + \frac{K_1 K_4}{2} (1-a^2) - \frac{K_2 K_3}{36} + \frac{K_3 K_4}{8} - \frac{K_2 K_4}{4} (2 + 2a^2 \ln a - a^2) + \frac{K_1}{35} - \frac{9K_2}{490} + \frac{K_3}{90} + \frac{2K_4}{25} + \frac{1}{250} \quad (12)$$

and the coefficient  $K_d$  of a TDC is obtained from

$$K_d = 2\pi r_c^2 \int_a^1 \rho_{ij} D_{ij} \phi d\phi = \pi r_c^2 \rho_{ij} D_{ij} (1-a^2). \quad (13)$$

Thus the CCF per unit length,  $F_s/L$ , is finally obtained from equation (5) with the help of equations (9)–(13). It is given by

$$F_s/L = \frac{G_1}{r_c [2(1-a^2)G_2]^{1/2}}. \quad (14)$$

The theoretical CCF per unit length of any TD column can thus be approximated in terms of  $G_1$ ,  $G_2$ ,  $a$  and  $r_c$  of the column. The values of formulated  $F_s$  are placed in table 1 for columns I, II, III and IV. They are shown in figure 3 together with the experimental  $F_s/L$  obtained from  $\ln q_{max}$  and known  $\alpha_T$  values of Ne<sup>20</sup>–Ne<sup>22</sup> gas mixtures.  $F_s/L$  of equation (14) plays an important role in determining  $\alpha_T$  of any binary gas mixture [1–4]. Because its model independence is well established [3],  $F_s/L$  can safely be used to concentrate impurities of any gas to any desired level in TDC experiments.

#### 4. Force parameters from the TD factor

The theoretical  $\alpha_T$  based on Chapman–Enskog gas kinetic theory [6] is given by

$$\alpha_T = g(6C_{ij}^* - 5) \quad (15)$$

where

$$g = \frac{1}{6\lambda_{ij}} \frac{S^{(i)}x_i - S^{(j)}x_j}{X_\lambda + Y_\lambda}$$

is a complicated function of the composition of the gas mixture and of the thermal conductivity  $\lambda_{ij}$  whereas  $(6C_{ij}^* - 5)$  strongly depends on the temperature. The  $\lambda_{ij}$  terms are, however, obtained from the  $\eta_{ij}$  terms by using the relation

$$\lambda_{ij} = \frac{15}{4} \frac{R}{M} \eta_{ij}.$$

The experimental values of  $\eta_{ij}$  of the Ne<sup>20</sup>–Ne<sup>22</sup> gas mixture are taken from Yamamoto *et al* [10]. The estimated theoretical  $\alpha_T$  values for Ne<sup>20</sup>–Ne<sup>22</sup> are shown by curve IV of figure 2, in which they are compared with  $\alpha_T$  values obtained by the existing method, curve II and curve III, due to the Maxwell and Sliker CSFs as well as with  $\alpha_T$  values of curve I obtained by the CCF method.

Now, the slowly varying function of temperature  $g$  is given by [3, 11]

$$g = \frac{A}{6C - 5}.$$

$A$  and  $C$  are two arbitrary constants.  $A$  is determined from  $\alpha_T$  of the CCF method at two available temperatures  $\bar{T}$  in kelvins and  $C$  from the reported data of  $C_{ij}^*$  versus  $\bar{T}^*$  [12]. Using the relation

$$(6C_{ij}^* - 5) = \frac{(\alpha_T)_{\text{expt}}}{g} \quad (16)$$

the collision integral  $C_{ij}^*$  at the experimental temperature is determined. Now  $C_{ij}^*$  fixes  $\bar{T}^*$  [12] where  $\bar{T}^* = \bar{T}/(\epsilon/k)$

and hence,  $\epsilon_{ij}/k$  of the molecule is located. Because the variation of  $g$  with the temperature is very slow, the entire procedure with the initially estimated  $\epsilon_{ij}/k$  is repeated to get the exact value of  $\epsilon_{ij}/k$ . The molecular diameter  $\sigma_{ij}$  is then determined from the viscosity data [10] with the estimated  $\epsilon_{ij}/k$ . It is worthy of mention that, in the case of isotopic components, the force parameters due to binary interactions  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  become  $\epsilon_{ii}/k$  or  $\epsilon_{jj}/k$  and  $\sigma_{ii}$  or  $\sigma_{jj}$  respectively.

## 5. Results and discussion

The equations of  $p^2/\ln q_e$  against  $p^4$  of Ne<sup>20</sup>-Ne<sup>22</sup> gas mixtures were, however, worked out in terms of the measured values of  $H'$ ,  $K'_c$  and  $K'_d$  [5] from the pressure dependences of  $\ln q_e$  in four columns of different column geometries and at various experimental temperatures. They are for column I:

$$\frac{p^2}{\ln q_e} = \begin{cases} 0.0305 + 1.9290p^4 & \text{at } \bar{T} = 530.5 \text{ K} \\ 0.0286 + 1.3574p^4 & \text{at } \bar{T} = 680.5 \text{ K} \end{cases}$$

for column II:

$$\frac{p^2}{\ln q_e} = \begin{cases} 0.0571 + 0.8346p^4 & \text{at } \bar{T} = 530.5 \text{ K} \\ 0.0629 + 0.4908p^4 & \text{at } \bar{T} = 680.5 \text{ K} \end{cases}$$

for column III:

$$\frac{p^2}{\ln q_e} = \begin{cases} 0.5309 + 0.9654p^4 & \text{at } \bar{T} = 380.5 \text{ K} \\ 0.2506 + 0.4247p^4 & \text{at } \bar{T} = 530.5 \text{ K} \\ 0.2703 + 0.2102p^4 & \text{at } \bar{T} = 688.0 \text{ K} \end{cases}$$

for column IV:

$$\frac{p^2}{\ln q_e} = \begin{cases} 1.9970 + 0.4298p^4 & \text{at } \bar{T} = 334.5 \text{ K} \\ 0.5129 + 0.0977p^4 & \text{at } \bar{T} = 530.5 \text{ K} \end{cases}$$

The variation of  $\ln q_e$  with  $p$  in atmospheres is found to increase with increasing length  $L$  and  $r_h/r_c$  of the TD columns as shown in figure 1.  $p_{opt}$ , the optimum pressure at which  $\ln q_e$  becomes maximum as observed in figure 1, also increases on going from column I to column IV for increasing  $r_h/r_c$ . The variation of  $p^2/\ln q_e$  against  $p^4$  is governed by  $a'$  and  $b'$  of equation (3).  $a'$  and  $b'$  were, however, obtained by applying a least square fitting technique to equation (3) with the experimental data of  $H'$ ,  $K'_c$  and  $K'_d$  [5]. They are placed in the fifth and sixth columns of table 1.  $\ln q_{max}$  in terms of  $a'$  and  $b'$  of equation (4) are also placed in the seventh column of table 1.

An approximate formulation of theoretical  $F_s$  with the column geometry has been derived by considering the convective velocity of the molecules in a TD column from the Navier-Stokes equation in cylindrical coordinates. Rectilinear flow of heat from a hot wire or wall to a cold wall seems to be a better choice, unlike Sliker's derivation. Although the temperature and composition dependences of the transport parameters like  $\rho_{ij}$ ,  $\eta_{ij}$ ,  $D_{ij}$ ,  $\lambda_{ij}$  and  $\alpha_T$  were not taken into account, the derived relationship of  $F_s$  with

the column geometry and the temperature is nonetheless reliable, simple and straightforward. This is strictly valid in the case of a hot wire or cryogenic wall or even for a hot wall column.

The column constants  $G_1$  and  $G_2$  depending on the column geometry and wall temperatures were worked out for four columns and are placed in the eighth and ninth columns of table 1.  $F_s/L$  of each column at experimental temperatures were then determined using equation (14) and are placed in the tenth column of table 1.  $G_1$  and  $G_2$  of equations (10) and (12) are dimensionless column constants, suggesting the fact that these parameters are independent of the molecular model.  $G_1$  depends on  $\Delta T/\bar{T}$  and  $r_h/r_c$  of a TDC whereas  $G_2$  is expressed in terms of  $r_h/r_c$  alone. The physical meanings of  $G_1$  and  $G_2$  can be realized from equations (9) and (11).  $G_1$  is related to the column transport coefficient  $H$  which is involved in the process of thermal diffusion, whereas  $G_2$  is related to  $K_c$ , called the convective remixing coefficient, for convection occurring in a TD process. However,  $K_p$  and  $K_d$  are the longitudinal and back diffusion coefficients in a TDC. Nevertheless,  $G_1$  and  $G_2$  are of much importance for locating the exact values of  $F_s$ ,  $\alpha_T$  and  $p_{opt}$  at which  $\ln q_e$  becomes maximum. The available  $\alpha_T$  values of Ne<sup>20</sup>-Ne<sup>22</sup> gas mixtures, which are 0.0250, 0.0258, 0.0270, 0.0276 and 0.0276 at 334.5 K, 380.5 K, 530.5 K, 680.5 K and 688 K respectively [5], help one to get experimental  $F_s$  at various values of  $\bar{T}$  from estimated  $\ln q_{max}$  of equation (4) of the TD columns. The experimental  $F_s$  when plotted against  $\bar{T}$  in figure 3 are in close agreement with theoretical  $F_s$  derived from equation (14) at various  $\bar{T}$ .

Using equation (1) the  $\alpha_T$  values of Ne<sup>20</sup>-Ne<sup>22</sup> gas mixtures are estimated through theoretical  $F_s$  by the CCF method. These  $\alpha_T$  values are presented in the third columns of table 2 and plotted against  $\bar{T}$  in figure 2. The experimental  $\alpha_T$  values obtained by the CCF method from  $\ln q_{max}$  and  $F_s$  are found to fall almost on the same curve I and increase slowly with  $\bar{T}$ .

The slight disagreement between the experimental and theoretical  $F_s$  seen in figure 3 and table 1 results in a slight difference between the theoretical  $\alpha_T$  values and the experimental ones obtained by the CCF method. This may, perhaps, arise due to the effect of parasitic remixing in the thermal diffusion process.

The molecular force parameters of Ne<sup>20</sup>-Ne<sup>22</sup> were estimated from the slope and the intercept of the  $\alpha_T$  against  $1/\bar{T}$  equation. The  $\alpha_T$  at 500.0 and 600.0 K from curve 1 of figure 2 were found to obey an equation of the form  $\alpha_T = 0.02913 - 1.12501(1/\bar{T})$ . The molecular force parameters  $\epsilon_{ii}/k$  or  $\epsilon_{jj}/k$  of Ne<sup>20</sup>-Ne<sup>22</sup> were thus determined as explained elsewhere [3, 11]. The  $\eta_{ij}$  [10] of Ne<sup>20</sup>-Ne<sup>22</sup> were then used to obtain the molecular diameter  $\sigma_{ii}$  or  $\sigma_{jj}$ . The close agreement of the estimated force parameters, placed in table 2 with the reported ones [13], establishes the reliability of  $\alpha_T$  as obtained by CCF method.

The  $\alpha_T$  due to Sliker's CSF, as seen in table 3, are calculated from equation (7) and are placed in the fourth column of table 2. These  $\alpha_T$  values, although slightly higher in magnitude than the  $\alpha_T$  values obtained by the CCF method, are plotted with  $\bar{T}$  in figure 2 on curve II. The  $\alpha_T$

values from  $\ln q_{max}$  of column IV are scattered (figure 2), but still maintain the same trend as that of the CCF method. The magnitudes of the Maxwell-model-dependent CSF are really very difficult to locate exactly. They were, however, obtained by interpolation and extrapolation from the data of Väsaru [7] and placed in table 3. The probable temperature dependence of  $\alpha_T$  using the Maxwell-model-dependent CSF was then obtained from equation (6) and shown in the fifth column of table 2. They are plotted with  $\bar{T}$  in figure 2 on curve III, showing both the trend and the magnitude of  $\alpha_T$  against  $\bar{T}$ . It fails to accord with  $\alpha_T$  obtained by the other methods. The theoretical  $\alpha_T$  values based on elastic collisions among molecules were also calculated from equation (15) at 334.5 K, 380.5 K, 530.5 K, 680.5 K and 688.0 K for  $\text{Ne}^{20}\text{-Ne}^{22}$  and placed in the sixth column of table 2. These are plotted against  $\bar{T}$  on curve IV of figure 2. Both the magnitudes and the trends of these  $\alpha_T$  values are more or less the same as those of the  $\alpha_T$  values obtained from the CCF. It is also interesting to note that the theoretical  $\alpha_T$  values of curve IV exhibit the same trend of increasing with temperature as do the  $\alpha_T$  values obtained by the CCF method.

In fact, asymmetry in column geometry is an inherent property and as such it invited remixing. Thus in the TD column theory Furry and Jones [14] added a term  $K_p$  called the remixing coefficient, proportional to  $p^4$  in the denominator of equation (2). Obviously in an ideal column  $K_p$  is supposed to be zero. Leyarovski *et al* [15] had shown that  $K_p$  never exceeds 20% of  $K_c$ . Thus, owing to remixing effects, the maximum error that creeps into  $F_s$  and hence into  $\alpha_T$  is 9.54%. In spite of that the excellent agreement of the experimental  $\alpha_T$  (curve I) and the theoretical  $\alpha_T$  (curve IV) in figure 2 right from  $T = 2T_c$  and onwards (figure 2) is evidence that equation (14) is reliable for  $F_s/L$ . Moreover, it indicates that  $K_p$  decreases with  $\bar{T}$  and vanishes at and after  $\bar{T} = 2T_c$ ; that is, remixing stops from  $\bar{T} = 2T_c$  in a TD column.

The discussion above makes it clear that the theoretical formulation of the CCF, which is the central point of study in this paper, is a model-independent parameter, as observed earlier [1-4, 8, 16]. Furthermore, the  $\alpha_T$  values obtained from the CCF with  $\bar{T}$  of a binary gas mixture are convenient means of estimating the molecular force parameters like  $\epsilon_{ij}/k$  and  $\sigma_{ij}$  of the molecules. The subject in this paper is thus related to the efficiency of the gas separation using thermal diffusion column to throw some light on the basic physical properties of a gas mixture through the CCF and  $\alpha_T$ .

## 6. Conclusions

In fact, the theoretical background of the process of thermal diffusion simultaneously involved with longitudinal and back diffusion in a TDC is much too complicated. The presented mathematical formulation of equation (14), achieved so far, seems to be a significant improvement over the existing theories. Determination of  $F_s/L$  appears to be an important means of estimating the experimental  $\alpha_T$  through  $\ln q_{max}$ , particularly when  $\Delta T/\bar{T}$  is close to unity or  $\bar{T} = 2T_c$  and afterwards. When  $\Delta T/\bar{T}$  is well below

unity the experimental  $\alpha_T$  obtained by the CCF method differs from the theoretical  $\alpha_T$ . Again, experimental  $\alpha_T$  values obtained by using Sliker-model-independent and Maxwell-model-dependent CSFs are low compared with theoretical  $\alpha_T$  values in the lower temperature region. Asymmetry in column geometry through  $K_p$  may be a reason for such a deviation. The theoretical  $\alpha_T$  derived from the elastic collision theory is not in good agreement with experimental  $\alpha_T$  for the non-spherical molecules. Even in the cases of spherical molecules, the agreement is no better. The model-independent parameter  $F_s/L$  of equation (14) thus ought to be used to estimate  $\alpha_T$  for the pair of molecules concerned through experimental  $\ln q_{max}$  in the TDC. The procedure of determining  $\alpha_T$  by the CCF method is, therefore, necessary in order to improve the theory for obtaining  $\alpha_T$  for elastic or inelastic collisions among the molecules [17]. The simultaneous use of reliable  $\alpha_T$  by the CCF method and  $C_{ij}^*$  against  $1/\bar{T}$  and  $1/\bar{T}^*$  respectively appears to be a unique method of locating the exact force parameters of the molecules too.

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