

C H A P T E R - III

THEORETICAL FORMULATION TO ESTIMATE
EXPERIMENTAL α_T BY USING COLUMN THEORY
DISCUSSED IN CHAPTER I AS WELL AS OUR
COLUMN CALIBRATION FACTOR METHOD.

Both ends being closed for an ideal column, having no asymmetries at all, eq. (1.34) yields that

$$\ln q_e = \frac{HL}{K_c + K_d} \quad (3.1)$$

for which the net transport \mathcal{Z}_1 up the column is zero, when an equilibrium is reached in a T.D. column.

Since H , K_c and K_d are proportional to the second, the fourth and the zeroth power of the operating pressure p in atmosphere of the binary gas mixture, Furry and Jones showed that

$$\ln q_e = \frac{ap^2}{b + p^4} \quad (3.2)$$

where a and b are constants given by $a = HL/K_c$ and $b = K_d/K_c$, respectively.

In most T.D. columns parasitic remixing always occurs. This inevitable fact is, however, be avoided by Furry and Jones by adding a term K_p proportional to the fourth power of the operating pressure in atmosphere, in the denominator of eq. (3.1) such that we get

$$\ln q_e = \frac{a'p^2}{b' + p^4} \quad (3.3)$$

where $a = a' (1 + K_p/K_c)$ and $b = b' (1 + K_p/K_c)$ respectively.

Eq. (3.3) can be written as $p^2/\ln q_e = b'/a' + \frac{1}{a' p^4}$ (3.4)

which is a straight line of $p^2/\ln q_e$ and p^4 , having the slope

$1/a'$ and the intercept b'/a' .

Again $1 + K_p/K_c = \frac{K_d}{K_c} \cdot \frac{1}{b'}$ we have

$$H = \frac{1}{L} \cdot \frac{a'K_d}{b'} = K_d/LC \quad (3.5)$$

where the constant term C represents the intercept of b'/a' of the plot of $p^2/\ln q_e$ against p^4 as demanded by the eq. (3.4). The existing column theory can be employed to obtain the experimental thermal diffusion factor α_T through the use of eq. (3.5) and the transport coefficients H , K_c and K_d as obtained by Maxwellian model, Lennard-Jones model and the last one called the model independent Sliker's method.

Now the important parameters a' and b' of eq. (3.3) govern the very nature of the variation of $\ln q_e$ against the pressure p in atmosphere at any mean experimental temperature \bar{T} where $\bar{T} = (T_h + T_c)/2$. It is found out that in most cases, as the pressure of a given gas mixture increase, $\ln q_e$ also increases and becomes maximum at $p = (b')^{1/4}$ where $\frac{\partial \ln q_e}{\partial p}$ is zero, and then decreases again. However at the point of maximum $\ln q_e$ of eq. (3.3) becomes $\ln q_{\max}$ where

$$\ln q_{\max} = a'/2\sqrt{b'} \quad (3.6)$$

where a' and b' are estimated by fitting the following equations with the experimental data of $\ln q_e$ measured at different pressures p in atmosphere:

$$\begin{aligned}\sum p^4 \ln q_e &= a' \sum p^2 - b' \sum \ln q_e \\ \sum p^6 \ln q_e &= a' \sum p^4 - b' \sum p^2 \ln q_e\end{aligned}\quad (3.7)$$

Thus the knowledge of a' and b' at different experimental temperatures helps us to calculate the value of $\ln q_{\max}$ which, with the help of reliable and accurate α_T values of a binary gas mixture makes it possible to fix the experimental F_s values for a given column at any experimental temperature by using the following equation:

$$\ln q_{\max} = \alpha_T F_s (r_c, r_h, L, \bar{T}) \quad (3.8)$$

The function F_s is supposed to be free from binary molecular interaction model, but solely depends on the geometry of a given column. Moreover the column calibration factor may be regarded as an apparatus constant having different natures for different columns of varying radii r_c and r_h and the geometrical lengths L with respect to temperature variation like

$$F_s = A + B \bar{T} + C \bar{T}^2 \quad (3.9)$$

The constants A , B and C involved in eq. (3.9) can also be estimated for a given T.D. column.

B.N. Srivastava et al¹ (1967) measured $\ln q_e$ of 1:1 isobaric gas mixture like $N_2O - CO_2$ in an all metal T.D. column installed in the department of general physics and X-rays, Indian Association for the Cultivation of Science (I.A.C.S.), Calcutta-32, for different pressures in atmosphere at three

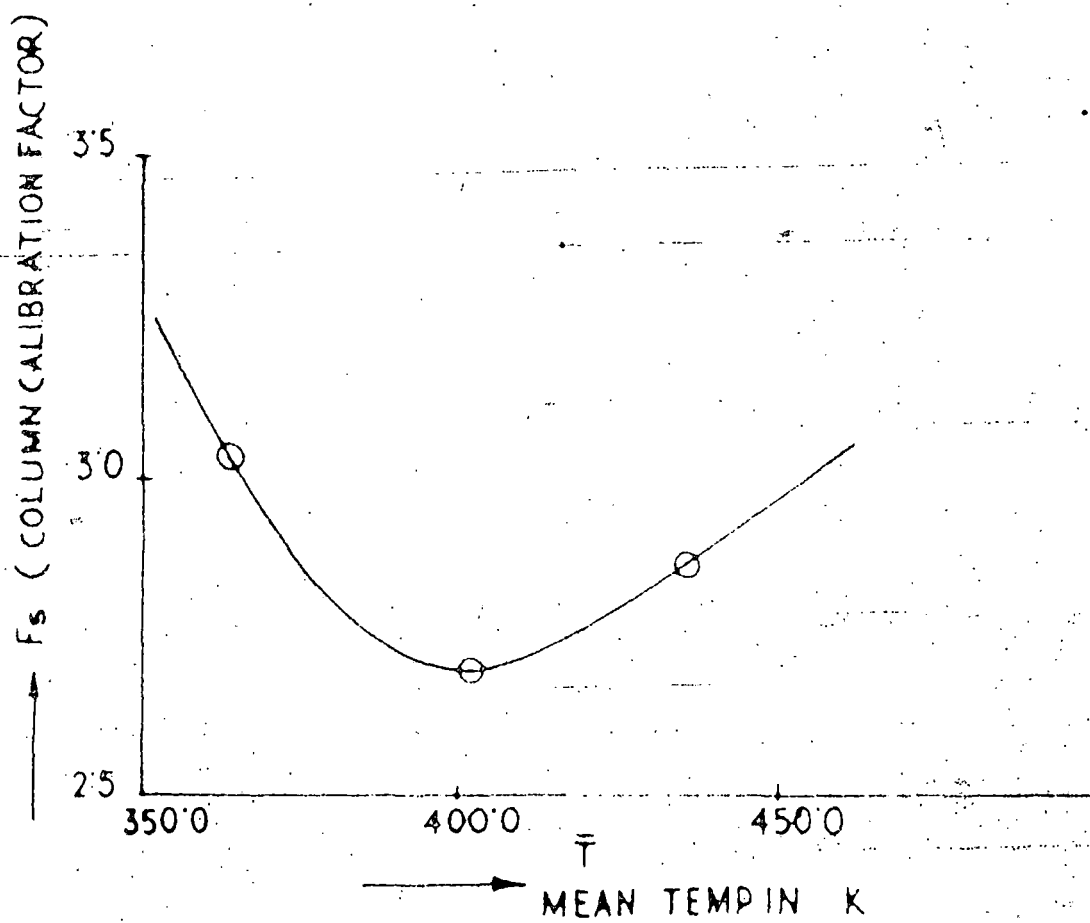


Fig. 3.1 Calibration factor F_s of the column as a function of the mean gas temperature \bar{T} .

experimental temperatures $\bar{T} = 363\text{K}$, 401.5K and 435.5K respectively. S. Acharyya et al² (1981) however measured the pressure dependence of $\ln q_e$ of another isobaric gas mixture 1:1 composition of $\text{N}_2 - \text{CO}$ in the same column at $\bar{T} = 350.1$, 378.5 and 413.5K respectively. This T.D. column is provided with the cold wall radius $r_c = 1.1113$ cm and the hot wall radius $r_h = 0.5556$ cm and of geometrical length $L = 305.2$ cm respectively.

S.K. Bhattacharyya et al³ (1975) in the meantime measured in their all glass eight tubes trennschaukel apparatus $\ln q_e$ and hence the thermal diffusion factors α_T of both $\text{N}_2\text{O} - \text{CO}_2$ and $\text{N}_2 - \text{CO}$ systems at different temperatures and at different composition. The $\ln q_{\max}$ of $\text{N}_2\text{O} - \text{CO}_2$ as well as $\text{N}_2 - \text{CO}$ were then estimated in terms of a' and b' at different temperatures. The accurate α_T of $\text{N}_2\text{O} - \text{CO}_2$ was obtained from S.K. Bhattacharyya et al³ and the corresponding F_s of the column at different temperatures to yield the best fit equation :

$$F_s = 34.030495 - 0.15472984 \bar{T} + 1.9101183 \times 10^{-4} \bar{T}^2 \quad (3.10)$$

the graphical plot of F_s for this column against the mean temperature \bar{T} K is shown in figure (3.1). The values of F_s thus obtained at $\bar{T} = 350.1$, 378.5 and 413.5K were then used to estimate α_T of $\text{N}_2 - \text{CO}$ (1:1) gas mixture from its $\ln q_{\max}$ and F_s from eq. (3.8). The experimental α_T 's of the system $\text{N}_2 - \text{CO}$ were also estimated from eq. (3.5) by the existing methods based on the column theory of Furry-Jones and Onsager⁴ in terms of H , K_c , K_d and K_p using Maxwell and Lennard-Jones model and the model independent Sliker's⁵ method. The comparisons

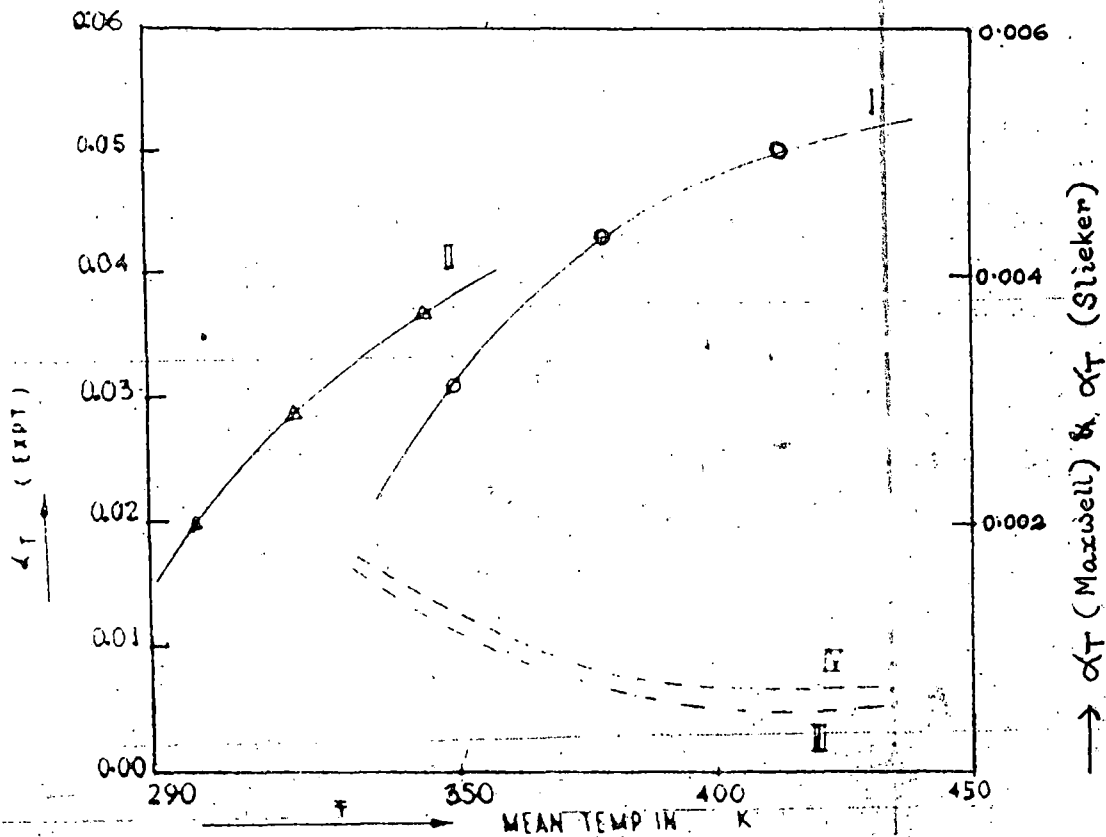


Fig. 3.2 Experimental α_T against \bar{T} . Curve-II $-\Delta-$ Reported α_T for 29.5% of N_2 . Curve-I $-\circ-$, α_T obtained from the $\ln q_{max}$ and F_s for 50% of N_2 . Curve-III $-\cdot-$, α_T (Maxwell). Curve-IV $-\dots-$, α_T (Sliker).

of all these α_T 's of $N_2 - CO$ system thus obtained, showed really an interesting features as illustrated graphically in figure (3.2). The values α_T 's as obtained in terms of the column calibration factor method are shown by the curve I along with the curve II with the reported α_T 's of a $N_2 - CO$ mixture having 29.5% N_2 in the lower temperature region between $296^\circ K$ to $350^\circ K$ by Bhattacharyya et al³ (1975). Both the curves are found to be convex in nature with respect to temperature showing the very existence of the inelastic collisions in the mixtures. But the existing theory of inelastic collision effect in thermal diffusion⁶ as it has been developed can not interpret the trend and magnitude of α_T with respect to temperature and composition of the mixture as pointed out by T.K. Chattopadhyay and S. Acharyya⁷ (1974). Moreover both the elastic as well as inelastic theoretical α_T 's for $N_2 - CO$ gas mixture having 29.5% of N_2 calculated by Bhattacharyya et al³ are found to be almost constant with respect to \bar{T} .

The quantitative agreement between the two sets of data as evidenced by curve I and II in figure (3.2), although can not be made due to their different composition and temperature ranges, it is interesting to note that they (curve I and II) are of the same order of magnitudes maintaining the same tendency with respect to temperature \bar{T} . But the experimental α_T 's using Maxwell model (curve III) and Sliker's method (curve IV) were computed from eq. (3.5). The α_T 's are of one order of magnitude less, showing the opposite \bar{T} dependence. Alternative molecular models

for binary molecular interactions have little chance to improve the magnitude and the trends of Maxwell or Slikek data using the existing column theory.

Thus the importance of the column calibration factor was soon first realised in this case and then subsequently applied by S. Acharyya et al⁸ (1982) in some inert gas mixtures like $\text{Ne}^{20} - \text{Ne}^{22}$, $\text{Ar}^{36} - \text{Ar}^{40}$, $\text{Kr}^{80} - \text{Kr}^{86}$ and $\text{Xe}^{128} - \text{Xe}^{136}$ respectively with their natural isotopic abundances.

D.G. Alvarez et al⁹ (1969) worked with a T.D. Column of geometrical length $L = 149$ cm, $r_c = 1.37$ cm and $r_h = 0.6$ cm to get the pressure dependence of the reduced logarithmic separation factors $\ln \tilde{Q}_{\text{exp}}$. The $\ln q_e$ values from $q_e = (\tilde{Q}_{\text{exp}})^{1/100}$ at different pressure were then calculated at three experimental temperatures : 371.0K, 378.0K and 387.5^oK. The experimental data of $p^2/\ln q_e$ in all the systems mentioned above against p^4 were found out to be :



$$p^2/\ln q_e = 3.63065 + 13.97988 p^4,$$

$$p^2/\ln q_e = 4.38884 + 12.92903 p^4,$$

$$p^2/\ln q_e = 7.04444 + 11.89776 p^4,$$



$$p^2/\ln q_e = 0.78377 + 125.68478 p^4,$$

$$p^2/\ln q_e = 1.07431 + 118.28424 p^4,$$

$$p^2/\ln q_e = 1.55437 + 114.90161 p^4,$$

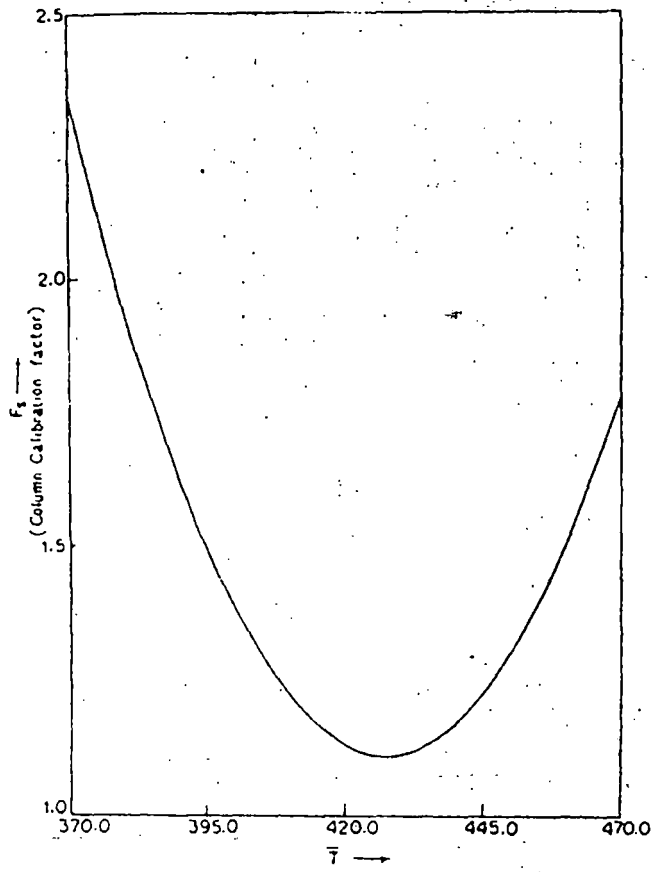


Fig. 3.3 Column calibration factor against \bar{T} the mean temperature.

$$\frac{\text{Kr}^{80} - \text{Kr}^{86}}{p^2 / \ln q_e} = 0.31374 + 645.3989 p^4,$$

$$p^2 / \ln q_e = 0.39338 + 595.5562 p^4,$$

$$p^2 / \ln q_e = 0.59322 + 524.7607 p^4,$$

$$p^2 / \ln q_e = 0.59322 + 524.7607 p^4,$$

and $\frac{\text{Xe}^{128} - \text{Xe}^{136}}{p^2 / \ln q_e} = 0.16980 + 2970.613 p^4,$

$$p^2 / \ln q_e = 0.19487 + 2782.950 p^4,$$

$$p^2 / \ln q_e = 0.19487 + 2782.950 p^4,$$

$$p^2 / \ln q_e = 0.32794 + 2523.025 p^4,$$

at three experimental temperatures 371.0K, 378.0K and 387.5K respectively, in excellent agreement of column theory. The corresponding $\ln q_{\max}$ of Ar³⁶ - Ar⁴⁰ and the accurate and reliable α_T of that system being available from F. Vander Volk¹⁰ (1963), the values of the column calibration factors of this column were then estimated to yield the temperature dependence of F_s given by

$$F_s = 68.94796 - 0.3174514 T + 3.71383 \times 10^{-4} T^2 \quad (3.11)$$

The fitted curve of the temperature variation of the column calibration factor is shown in figure (3.3). The nature of this curve is quite similar to F_s v.s. T curve of I.A.C.S. column (Fig. 3.1) in which it is also seen that F_s attains a minimum value at a certain T and then increases again. With the known and fixed values of F_s and experimental $\ln q_{\max}$ of Ne²⁰ - Ne²², Ar³⁶ - Ar⁴⁰, Kr⁸⁰ - Kr⁸⁶ and Xe¹²⁸ - Xe¹³⁶ the thermal diffusion factors α_T 's were computed and presented graphically in the

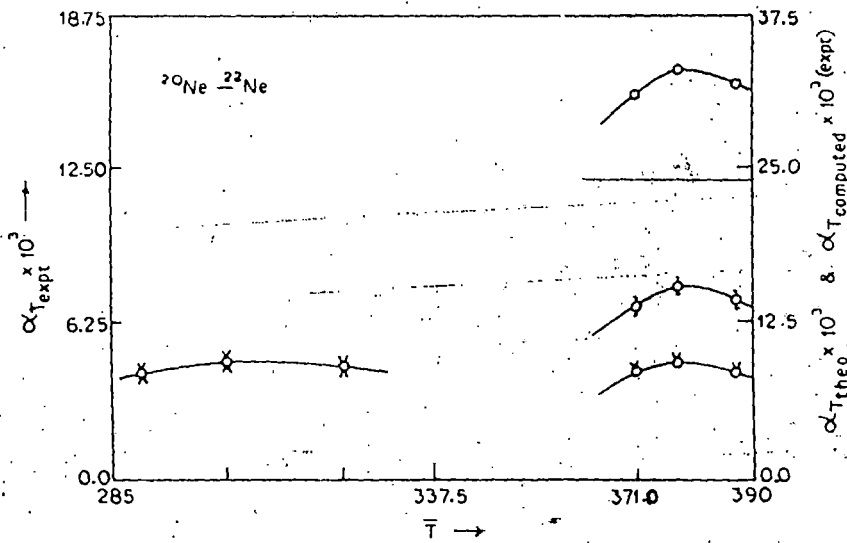
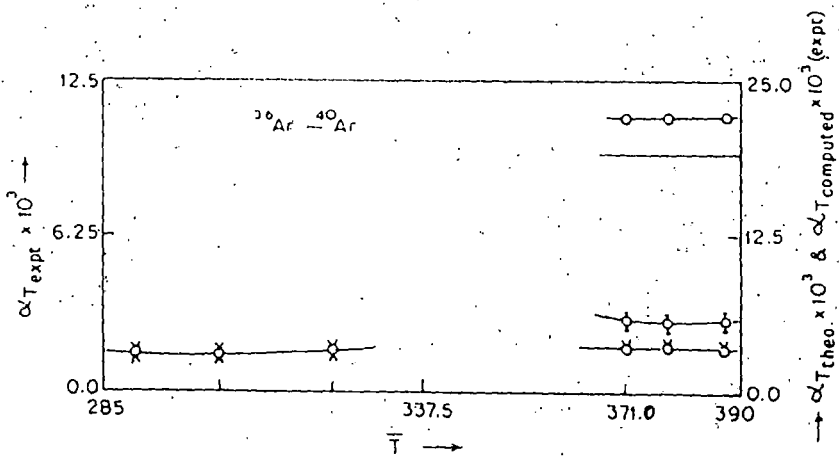


Fig. 3.4 α_T vs \bar{T} curves: $\text{---} \circ \text{---}$, α_T , computed from $\ln q_{\max}$ & F_s , $\text{---} \circ \text{---}$, α_T , theor. (eq. 4.1) (L-J), $\text{---} \times \text{---}$, α_T (Sliker), $\text{---} \times \text{---}$, α_T (Maxwell), $\text{---} \times \text{---}$, α_T



3.5 α_T vs \bar{T} curves: $\text{---} \circ \text{---}$, α_T , computed from $\ln q_{\max}$ & F_s , $\text{---} \circ \text{---}$, α_T , theor. (eq. 4.1) (L-J), $\text{---} \times \text{---}$, α_T (Sliker), $\text{---} \times \text{---}$, α_T (Maxwell), $\text{---} \times \text{---}$, α_T

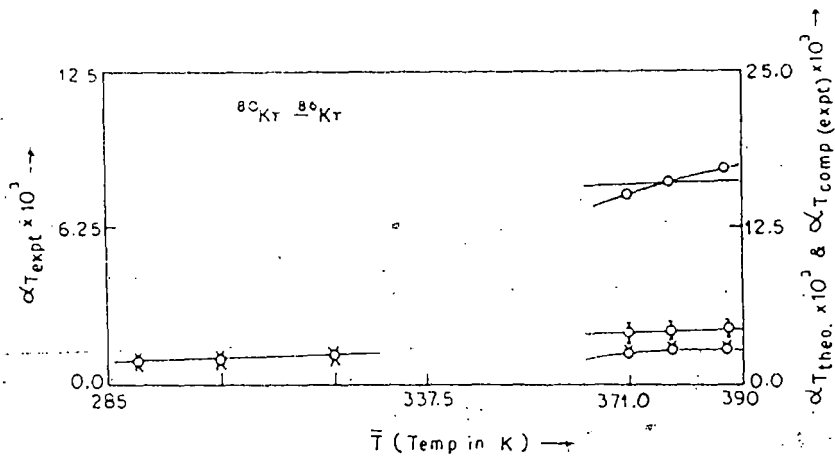


Fig. 3.6 α_T vs \bar{T} curves: $\text{---}\circ\text{---}$, $\alpha_{T,\text{computed}}$ from $\ln q_{\text{max}}$ & F_s , $\text{---}\times\text{---}$, $\alpha_{T,\text{theor.}}$ (eq. 4.1) (L-J), $\text{---}\circ\text{---}$, α_T (Slieker), $\text{---}\times\text{---}$, α_T (Maxwell), $\text{---}\times\text{---}$, α_T

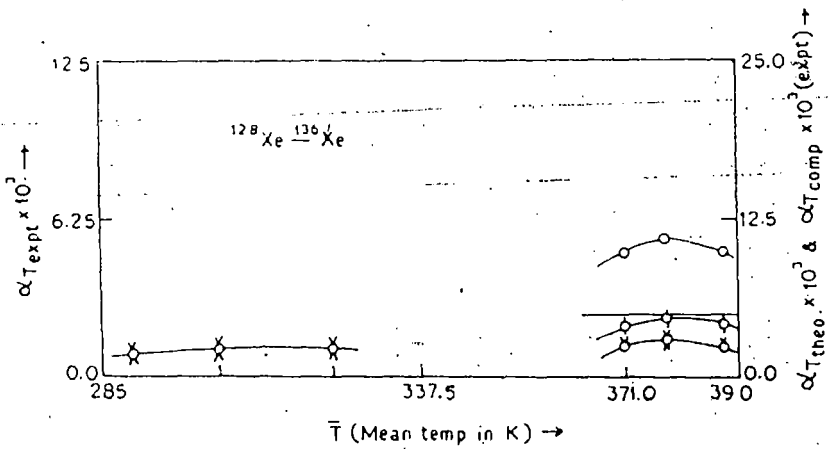


Fig. 3.7 α_T vs \bar{T} curves: $\text{---}\circ\text{---}$, $\alpha_{T,\text{computed}}$ from $\ln q_{\text{max}}$ & F_s , $\text{---}\times\text{---}$, $\alpha_{T,\text{theor.}}$ (eq. 4.1) (L-J), $\text{---}\circ\text{---}$, α_T (Slieker), $\text{---}\times\text{---}$, α_T (Maxwell), $\text{---}\times\text{---}$, α_T

Figures (3.4) to (3.7), along with those obtained by the existing method. The existing theoretical formulation which usually takes into account the inherent asymmetry of the column geometry are developed using Maxwell, Sliker and Lennard-Jones shape factors of which the last one, in addition to the present one includes the models of binary interactions of the gaseous mixtures, isotopic or nonisotopic. The shape factors and the necessary force parameters (table 3.1) to calculate α_T at $\bar{T} = 371.0, 378.0$ and 387.5 K for cases using model of Maxwell and Sliker's method while for L-J case they are evaluated at the cold wall temperatures, $290.0\text{K}, 304.0\text{K}$ and 323.0K respectively. The experimental α_T 's thus calculated from the existing methods for Ne, Ar, Kr and Xe isotopic mixtures were again found to be one order less in magnitudes than those of theoretical ones obtained from eq. (4.1) discussed in Chapter IV under the head of "theoretical formulation of thermal diffusion factors", used in this thesis. Other alternative molecular models for binary molecular interactions than those which are given in table 3.1, have little possibility to improve the magnitudes of α_T data which are graphically shown in Figs. 3.4 to 3.7 respectively using the existing column theory.

Now using F_s from the calibration curve Fig. (3.3) and the corresponding $\ln q_{\max}$, the thermal diffusion factors of Ne and Xe systems, although slightly higher than those of theoretical α_T , they are of the same order of magnitudes. But for Ar and Kr the α_T are in excellent agreement with theoretical ones.

Table 3.1 Molecular parameters and shape factors utilised to evaluate α_T

System	ϵ/k K (a)	$\sigma \times 10^8$ cm (a)	Shape factors			Temp. K	Interaction model
			h	k_c	k_d		
Ne ²⁰ -Ne ²²	27.5	2.858	1.05113	1.024	0.96950	371.0	Maxwell (n= 1)
Ar ³⁶ -Ar ⁴⁰	119.5	3.826	1.06388	1.009	0.96775	378.0	
Kr ⁸⁰ -Kr ⁸⁶	166.7	4.130	1.08188	0.991	0.96538	387.5	
Xe ¹²⁸ -Xe ¹³⁶	229.0	4.055	0.5433	0.0334	$\pi(1-a^2)$	371.0	Slikeer
			6!	9!		378.0	
						387.5	
Ne ²⁰ -Ne ²²	27.5	2.858	0.1356E-01	0.6547E-03	0.45811	290.0	Lennard-Jones (b)
			0.1163E-01	0.6201E-03	0.45124	304.0	
			0.0901E-01	0.5783E-03	0.44289	323.0	
Ar ³⁶ -Ar ⁴⁰	119.5	3.826	0.1562E-01	0.5873E-03	0.47204	290.0	
			0.1305E-01	0.5638E-03	0.46254	304.0	
			0.1005E-01	0.5371E-03	0.45141	323.0	
Kr ⁸⁰ -Kr ⁸⁶	166.7	4.130	0.1739E-01	0.5645E-03	0.47845	290.0	
			0.1427E-01	0.5483E-03	0.46796	304.0	
			0.1072E-01	0.5269E-03	0.45573	323.0	
Xe ¹²⁸ -Xe ¹³⁶	229.0	4.055	0.2389E-01	0.5353E-03	0.48569	290.0	
			0.1816E-01	0.5238E-03	0.47412	304.0	
			0.1224E-01	0.5082E-03	0.46035	323.0	

(a) Hirschfelder, Bird and Curtiss M.T.G.L. (John Willey & Sons., N.Y. 1964)

(b) Report no. K-1679 (1966) - Thermal diffusion column shape factors based on L-J (12:6) model by E. Von Halle and R.K. Hoglund.

The temperature range of only 17° was involved in the present column measurement of the four isotopic mixtures. Actually the variation of α_T with respect to temperature is such that this range essentially constitute the single temperature. Nevertheless, we tried to estimate α_T because of the availability of data⁹ and tried to observe the temperature dependency of the column calibration factor F_s while r_c , r_h and L of the column are held fixed. It is again interesting to note that this study ultimately establishes the fact that α_T of the same order of magnitude as those of theoretical ones can be obtained with the use of F_s and $\ln q_{\max}$ at any experimental temperature. It is also encouraging to note that the nature of variation of the column calibration factor with respect to temperature for any T.D. column is probably the same and interaction model independent too. This indicates that there exists a functional relationship of F_s with r_c , r_h , L and T . Thus, in absence of any reliable theoretical possibility to estimate the actual α_T using the existing column theory⁴ through the use of molecular model, this F_s really allows us to obtain the relative α_T data of any gas mixture from its $\ln q_{\max}$ measurements using the same column.

All these reasons tempted us to study further the importance of the column calibration factors of several selected hot wall or hot wire columns available in the literature and the subject matter of the works studied are then presented in "the role of column calibration factor in thermal diffusion column", chapter-wise. It is observed that the column calibration factor

of any column can however be written as

$$F_s = A + B\bar{T} + C\bar{T}^2 \quad (3.12)$$

in terms of temperature. A, B, and C are constants, the values of which depends strongly on the geometry of the column constructed. That is why it is desirable to study different types of hot wall and hot wire columns in order to arrive at the conclusions regarding the coefficients A, B and C involved in eq. (3.12) experimentally. It is hoped with the help of dimensional analysis on a large number of data of F_s in different columns, the functional relationship of A, B and C with r_c , r_h , L and \bar{T} could however be made. With this aim in view we chose different T.D. columns available in the literature to explore the relationship of F_s with the geometry of the column empirically; and applied these F_s values to obtain the expt. α_T of different binary systems. Finally these α_T 's are then compared with those of the existing methods using column theory and of theoretical formulation based on elastic and the inelastic collision. The comparisons however indicate that column calibration factor has an important role in column measurement.

R E F E R E N C E S

1. B.N. Srivastava, A.K. Batabyal, A.N. Roy and A.K. Ghosh,
J Chem Phys 47 (1967) 3470.
2. S. Acharyya, A.K. Das, P. Acharyya, S.K. Datta and
I.L. Saha, J phys Soc (Japan) 50 (1981) 1603-1607.
3. S.K. Bhattacharyya, A.K. Pal and A.K. Barua, Ind J Phys
49 (1975) 9.
4. W.H. Furry, R.C. Jones and L. Onsager, Phys Rev 55 (1939)
1083.
5. C.J.G. Slieker, Z-Naturforsch 20 (1965) 521.
6. L. Monchick, S.I. Sandler and E.A. Mason, J Chem Phys
49 (1968) 1178.
7. T.K. Chattopadhyay and S. Acharyya, J Phys B (London)
(Atomic and Molec Phys) 7 (1974) 2277.
8. S. Acharyya, I.L. Saha, P. Acharyya, A.K. Das and S.K.
Datta, J Phys Soc (Japan) 51 (1982) 1469.
9. D. Gonzalez Alvarez, J.M. Saviron and J.C. Yarza, J Chem
Phys 50 (1969) 3936.
10. F. Vander Valk, Ph.D. dissertation (1963).