Reprinted from
Journal of the Physical Society of Japan
Vol. 56, No. 1, January, 1987, pp. 105-114

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(Received September 26, 1985)

The variation of column calibration factor F_s with respect to temperature change has been attained for a given column (C.J.G. Slieker and A. E. de Vries: J. Chim. Phys. **60** (1963) 172) to estimate the temperature dependence of thermal diffusion factor α_T of trace mixtures of hydrogenic isotopes in helium only to detect the existence of inelastic collision effect in the mixtures as predicted by T. K. Chattopadhyay and S. Acharyya (J. Phys. B **7** (1974) 2277). Attempts have also been made to interpret the α_T's thus obtained in terms of the available elastic and inelastic collision theories of thermal diffusion to establish the importance of the column calibration factor in column measurements.

§1. Introduction

It is a well-known fact that, in the perspective of the existing column theory[1-3] the column geometry plays a vital role in determining the value of thermal diffusion factor α_T. As asymmetry in the column geometry is almost unavoidable, the column measurement as such can not yield an actual α_T value because the question of molecular binary interaction of the gas molecules is ultimately called into play. Inspite of that, the column has a great advantage. It is far superior to any other α_T measuring instruments like a swing separator or a two bulb apparatus with respect to showing very high equilibrium separation factor q_e defined by $q_e=(x_1/x_2)_T/(x_1/x_2)_B$, where x_1 and x_2 are the mole fractions of lighter and heavier components of the gas mixture, respectively. T and B represent the top and bottom of a column of a certain geometrical length L.

With this unique property of the column in view, it would be rather convenient to bring the column into lime-light as a reliable α_T measuring instrument after calibrating with a suitable gas mixture of accurately known α_T.[4,5] In fact, when the mass difference between the components of a binary gas mixture is very small, as in the case of isotopic or isobaric gas mixture, it is more desirable to use a calibrated T.D. column for the faithful measurement of small α_T. This is because of the fact that the enhanced separation factor q_e ensures α_T to be of high degree of accuracy.

Now in view of avoiding the use of column geometry through the rigorous column theory, it is better to introduce the column calibration factor F_s appearing in the relation:

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

Here $\bar{T}$ is the column mean temperature given by $\bar{T}=(T_h+T_c)/2$, where T_h is the temperature of the hot wall of radius r_h and T_c the temperature of the cold wall of radius r_c. The function F_s is supposed to be independent of a binary molecular interaction model. Fortunately, it contains everything that is related with the column geometry and can furnish us the reliable α_T directly from column measurements without assuming any molecular models. Moreover, the column calibration factor may be regarded as an apparatus constant having probably the common nature concerning temperature variation.[4,5] This is really an experimental problem to be resolved only by careful and extensive works. T. K. Chattopadhyay and S. Acharyya[6] showed that a theory on the inelastic collision effect in ther-

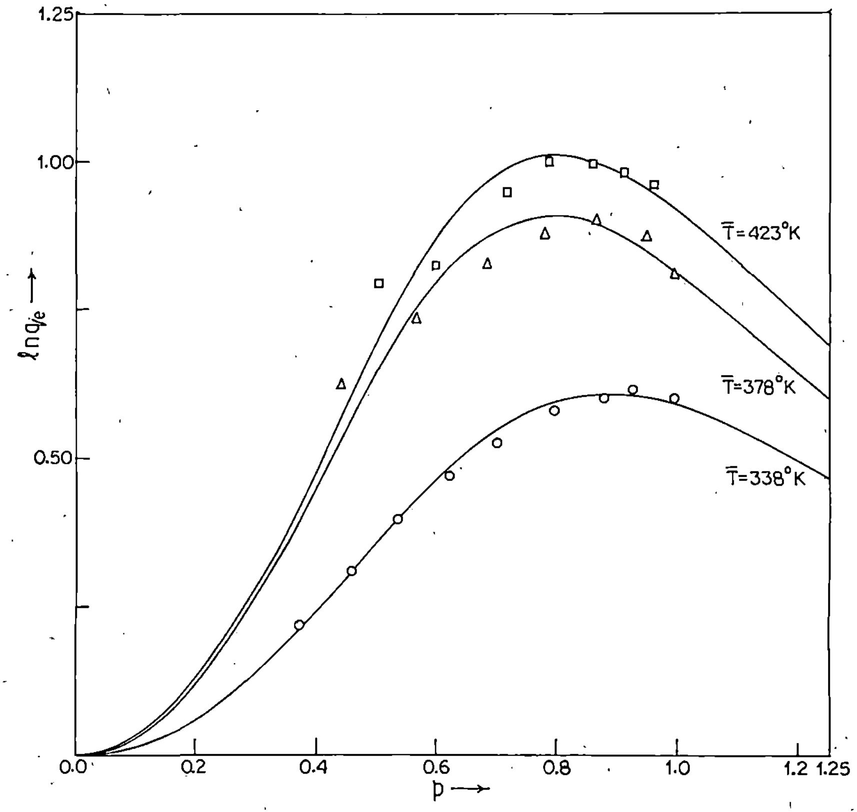

Fig. 1. The plot of ln q_e against pressure in atmosphere at different $\bar{T}$ ——— (Least square fitting) expt. points: ○ at $\bar{T}$=338 K; △ at $\bar{T}$=378 K & □ at $\bar{T}$=423 K respectively.

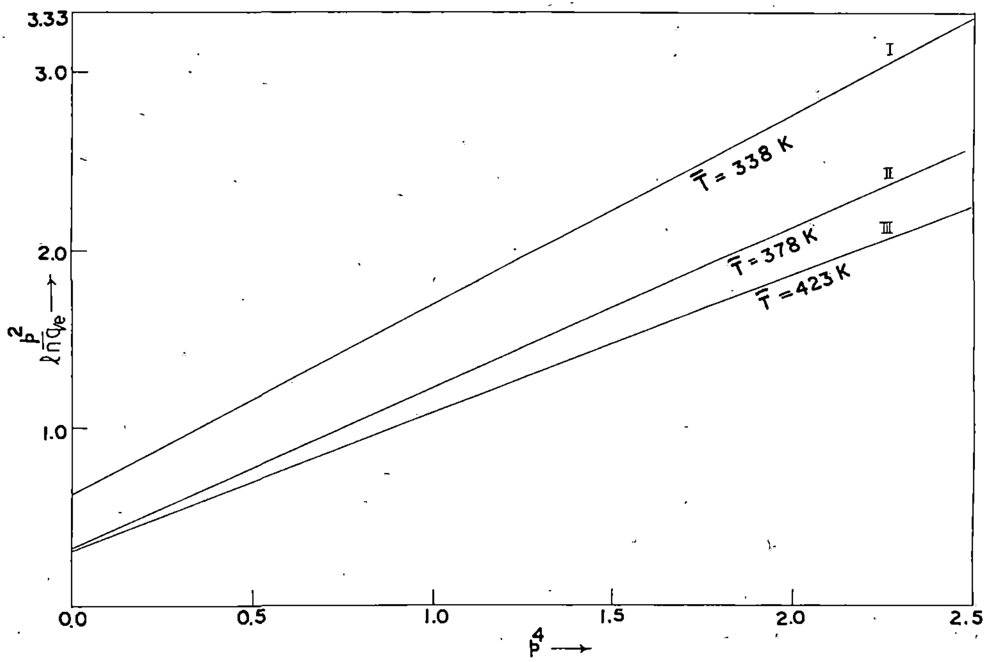

Fig. 2. The curves of $p^2/\ln q_e$ against p^4 at different expt. $\bar{T}$.

mal diffusion was applicable in the case of binary gas mixtures containing HT, DT etc. All these facts tempted us to analyse the works of C. J. G. Slieker and A. E. deVries who measured the pressure dependence of $\log_{10} q_e$ of He–T_2, He–HT and He–DT at three experimental temperatures using a TD column of length $L=120$ cm, $r_c=2.15$ cm and $r_h=0.5$ cm. Hydrogenic components in the mixtures were traces, never becoming higher than 5%. We converted $\log_{10} q_e$ data to the corresponding $\ln q_e$ values. These are shown in Fig. 1, along with their fitted curves obtained by the least square technique. The data thus obtained are found to obey the column theory because the plots of $p^2/\ln q_e$ against p^4, as shown in Fig. 2, result in straight lines having certain slopes and intercepts. For a He–T_2 mixture, we arrive at the following fitted equations:

$$p^2/\ln q_e = 0.6265 + 1.0741\, p^4 \text{ at } \bar{T} = 338.0\text{ K},$$

$$p^2/\ln q_e = 0.3296 + 0.9092\, p^4 \text{ at } \bar{T} = 378.0\text{ K},$$

and

$$p^2/\ln q_e = 0.31 + 0.78\, p^4 \text{ at } 423.0\text{ K}.$$

Unlike HT and DT molecules which are eccentrically loaded spheres, T_2 is symmetric and hence the inelastic collision effect is expected to be negligibly small because the presence of T_2 is a trace concentration in helium. That is why we have decided to use He–T_2 trace mixtures as the calibrating gas since their reliable[8] experimental α_T in the range of 100 C to 500 C and experimental[7] $\ln q_{max}$ are available, and therefore the experimental F_s values at different $\bar{T}$ are obtained from eq. (1), as shown in Table I. The following fitted equation gives the most probable temperature dependence of F_s,

$$F_s = -66.52202 + 0.3502286\, \bar{T} - 4.1879 \times 10^{-4}\, \bar{T}^2, \quad (2)$$

which is similar to the previous equations[4,5] except that the coefficients A, B and C in eq. (2) differ from the previous ones[4,5] regarding their signs; most probably due to a high value of r_c/r_h for this column and thus it is wise to show F_s by curve I in Fig. 3. With the knowledge of F_s and $\ln q_{max}$ (Table I), the experimental α_T

Table I. Experimental and theoretical α_T values of hydrogenic trace mixture with helium.

System	Expt. temp. in K: T_h of hot wall	Expt. temp. in K: T_c of cold wall	$\bar{T}$ mean temp	a' (atm)^2	b' (atm)^4	$\ln q_{max}$ (expt.): Computed from eq. (8)	F_s: expt.	F_s: theor	α_T(expt.) by existing column theory eq. (7) with shape factors: Max well	α_T(expt.) by existing column theory eq. (7) with shape factors: Slieker	α_T(expt.) by calibration method eq. (1)	α_T(theor) (elastic) from eq. (9)	α_{ij}(theor) (inelastic) eq. (10) with Z_{rot}: 300	α_{ij}(theor) (inelastic) eq. (10) with Z_{rot}: Barua *et al.*	α_{ij}(theor) (inelastic) eq. (10) with Z_{rot}: Parker
He–T_2	393	283	338	0.931	0.5833	0.6096	4.011	3.763	0.072	0.231	0.152	0.162	0.085	0.140	x
	473	283	378	1.106	0.3645	0.9160	6.026	5.654	0.075	0.267	0.152	0.162	0.088	0.166	x
	563	283	423	1.282	0.3974	1.0170	6.691	6.278	0.062	0.236	0.152	0.162	0.091	0.203	x
He–HT	393	283	338	—	—	0.0061	4.011	3.763	—	—	0.002	0.030	0.121	0.055	0.002
	473	283	378	—	—	0.0169	6.026	5.654	—	—	0.003	0.030	0.124	0.037	0.009
	563	283	423	—	—	0.0414	6.691	6.278	—	—	0.006	0.030	0.129	0.005	0.005
He–DT	393	283	338	—	—	0.6352	4.011	3.763	—	—	0.158	0.104	0.100	0.158	0.158
	473	283	378	—	—	0.8258	6.026	5.654	—	—	0.137	0.105	0.105	0.188	0.154
	563	283	423	—	—	1.032	6.691	6.278	—	—	0.154	0.103	0.109	0.226	0.159

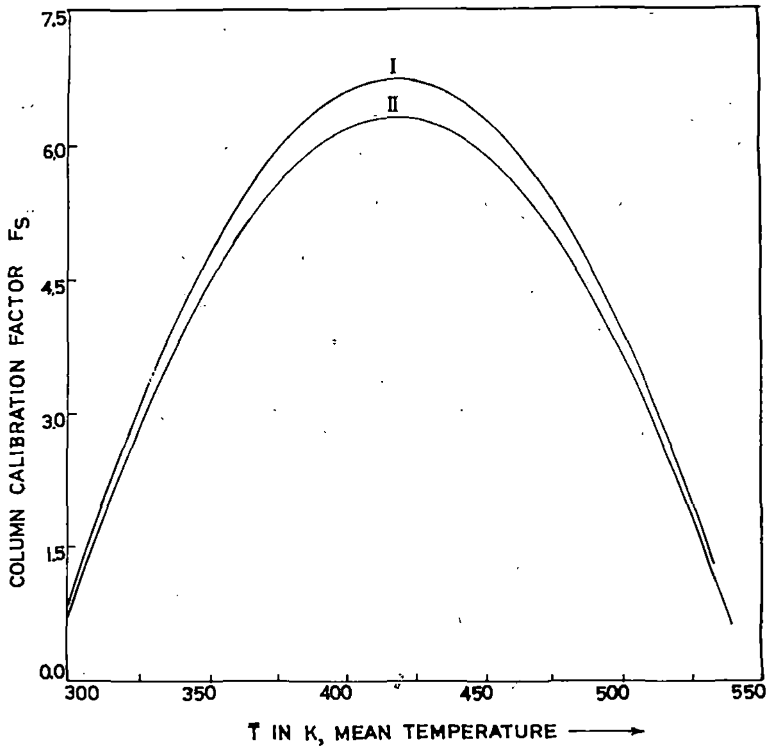

Fig. 3. The theoretical plot(curve II) and the experimental plot(curve I) of F_s against mean temperature $\bar{T}$.

values of He–T_2, He–HT and He-DT mixtures at different temperatures are then estimated. The temperature variation of α_T's thus obtained, are shown in Figs. 4–6.

Finally, we try to interpret the experimental α_T data in terms of elastic collision theory.[9] So far a co-related inelastic collision theory on loaded sphere molecules[10] in thermal diffusion is able only to establish the fact that the column calibration factor is an important parameter to yield the actual magnitude and trend of experimental α_T with respect to $\bar{T}$ for the trace mixtures mentioned earlier.

§2. Mathematical Formulations

For a closed column of length L, the $\ln q_e$ of a gas mixture at a mean gas temperature $\bar{T}[\bar{T}=(T_h+T_c)/2]$ is given by

$$\ln q_e=\frac{HL}{K_c+K_d}, \tag{3}$$

where T_h and T_c are the hot and cold wall temperatures in K respectively, while H, K_c and K_d are the functions of the transport coefficients of a gas mixture and proportional to p^2, p^4 and p^0 respectively, p being the pressure in atmosphere. Thus, eq. (2) becomes

$$\ln q_e=\frac{ap^2}{b+p^4}, \tag{4}$$

where

$$a=\left(\frac{HL}{K_c}\right)p^2 \text{ and } b=\left(\frac{K_d}{K_c}\right)p^4.$$

Now due to the existence of asymmetry in column geometry where usually parasitic remixing occurs, Furry and Jones[2] added a term K_p proportional to p^4, to the denominator of eq. (2). In consequence, eq. (2) becomes

$$\ln q_e=\frac{a'p^2}{b'+p^4}, \tag{5}$$

or

$$p^2/\ln q_e=\frac{b'}{a'}+\frac{1}{a'}p^4, \tag{6}$$

which is a straight line with the slope $1/a'$ and the intercept b'/a'. Obviously, a' and b' are related to a and b of eq. (4) by $a=a'(1+K_p/K_c)$ and $b=b'(1+K_p/K_c)$ respectively. Further, since $(1+K_p/K_c)=K_d/K_c\cdot 1/b'$,

$$H=\frac{1}{L}\frac{a'}{b'}K_d=\frac{K_d}{LC}. \tag{7}$$

Here the constant term C represents the intercept b'/a' of the plot $p^2/\ln q_e$ against p^4 shown in Fig. 2, as demanded by eq. (6).

So far as the exact expressions for H, K_c and K_d are concerned, we have the followings:

(i) Maxwellian case ($n=1$, α_T assumed to be temperature independent):

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

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

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

(ii) Slieker case(Interaction model independent):

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

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

$$C_3=K_c=[SF]_3 r_c^8(\rho^3 g^2/\eta^2 D)_1\left(\frac{\Delta T}{\bar{T}}\right)^2,$$

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

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

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

$$K_d=2\pi(\rho D)_1 r_c^4 k_d.$$

Here $\{h', k_c', k_d'\}$; $\{[SF]_1, \pi(1-a^2), [SF]_3\}$ and $\{h, k_c, k_d\}$ are the dimensionless Maxwell, Slieker and Lennard-Jones shape factor respectively and $u=(T_h-T_c)/(T_h+T_c)$, $a=r_h/r_c$ and $\Delta T=T_h-T_c$. Thus, evaluation of experimental α_T through the existing formulations involves the shape factors taking account of inherent asymmetry of column geometry. The Lennard-Jones shape factor, however, becomes inapplicable when T_c is held fixed. The mass density ρ, the coefficient of viscosity η and the diffusion coefficient D are calculated from MTGL of Hirschfelder *et al.*[9] The column shape factors and force parameters necessary for the present work are shown in Table II.

Now the important parameters a' and b' of eq. (5) govern the nature of $\ln q_e$ versus pressure curve obtained at any experimental temperature. It is found out that in most cases, as the pressure increases, $\ln q_e$ increases and

Table II. Molecular parameters and shape factors utilised to evaluate α_T.

System	ε/k' in K	σ in Å	Interaction model	Shape factors'		$\bar{T}$ in K	Molecules	$\bar{T}$ in K	$\eta\times 10^5$ gm/cm /sec.	Z_{rot}		$C^*_{int/R}$
				h	k_d					Barua *et al.*	Parkers formula	
T$_2$, HT or DT	37.3	2.928	M	0.99102	9.97775	338						
			A				T$_2$	338	16.756	4.78[†]		2.085
			X					378	18.026	3.80		2.216
			W	1.06388	0.96775	378		423	19.396	3.05		2.375
			E				HT	338	13.681	4.78	2.78**	2.085
			L					378	14.718	3.80	2.91	2.216
			L	1.14584	0.95650	423		423	15.837	3.05	3.05	2.375
			S			338	DT	338	15.296	4.78	4.78**	2.085
			L	$\frac{0.5433}{6!}\pi(1-a^2)$		378		378	16.455	3.80	5.01	2.216
			I			423		423	17.706	3.05	5.23	2.375
He	10.22	2.556	E				He	338	21.754			0
			K					378	23.388			0
			E					423	25.148			0
			R									

[†] A. K. Barua, A. Manna, P. Mukhopadhyay & A. Das Gupta (1970).
[*] N. B. S. Circular 564 (1955).
[**] J. G. Parker (1959).

becomes maximum at $p=(b')^{1/4}$ where $\partial \ln q_e/\partial p$ is zero. However, at the point of maximum, eq. (5) takes the form:

$$\ln q_{\max}=\frac{a'}{2\sqrt{b'}}, \tag{8}$$

where a' and b' are estimated by fitting the following equations with the experimental data measured at different pressures in atmosphere:

$$\begin{aligned}\sum p^4 \ln q_e&=a'\sum p^2-b'\sum \ln q_e,\\ \sum p^6 \ln q_e&=a'\sum p^4-b'\sum p^2 \ln q_e.\end{aligned} \tag{8a}$$

Knowledge of a' and b' at different experimental temperatures helps calculate the corresponding $\ln q_{\max}$ values which, in conjunction with reliable α_T values, enables us to fix the values of F_s for a column at experimental temperatures. Finally, the temperature dependence of F_s can be expressed by the relation

$$F_s=A+B\bar{T}+C\bar{T}^2,$$

where A, B and C are the constants to be determined for a given column.

For the calibrating gas mixture He–T$_2$, a' and b' at $\bar{T}=338.0$, 378.0 and 423 K are calculated to obtain the corresponding $\ln q_{\max}$ values. With these $\ln q_{\max}$ values and the reliable α_T values of He–T$_2$ mixture,[8] the experimental F_s values are computed. All the values of a', b' and F_s are shown in Table I.

§3. Theoretical Formulations

The Chapman-Enskog expression for the first approximation of theoretical α_T is given by[9]

$$\alpha_T=A(6C_{12}^*-5), \tag{9}$$

where A is a complicated function of composition, masses and thermal conductivities of the mixture components and $(6C_{12}^*-5)$ is the temperature dependent factor. C_{12}^* is the ratio of collision integrals, a function of $T^*=T/(\varepsilon/k)$, where T is he temperature in K and ε/k is the depth of the potential well. Using L–J(12:6) potential (Table II), α_T values of He–T$_2$, He–HT and He–DT mixtures having hydrogenic components as traces less than 5% are calculated from eq. (9). These elastic theoretical α_T are shown in Table I for comparison.

While taking account of only the classical theory, we fully ignore the internal degrees of freedom of the colliding molecules which, in many cases, are capable of transporting appreciable amount of energy. However, with regard to inelastic collision effect, Monchick *et al.*[10] assume that the differential cross-section for all the entrance and exit channels are not the same except for an angle dependent factor which is equal to the probability of a change in the internal energy state. The expression for the theoretical inelastic thermal diffusion factor α_{ij} is given by

$$\alpha_{ij}=\frac{(6C_{ij}^*-5)\,\mu_{ij}}{5nk[D_{ij}]_1}\left[\frac{\lambda_{j\,\text{trans}}^{\infty}}{x_jM_j}-\frac{\lambda_{i\,\text{trans}}^{\infty}}{x_iM_i}\right]+(5nk[D_{ij}])^{-1}\left[\frac{(6\tilde{C}_{ji}-5)\lambda_{j\,\text{int}}^{\infty}}{x_j}-\frac{(6\tilde{C}_{ij}-5)\lambda_{i\,\text{int}}^{\infty}}{x_i}\right], \tag{10}$$

where the subscripts 'trans' and 'int' indicate the contributions of translational and internal degrees of freedom respectively, and the superscript ∞ indicates steady state values for thermal conductivities λ. x_i and x_j are the mole fractions of ith and jth molecules of molecular weights M_i and M_j respectively. μ_{ij} is the reduced mass of the system, n the number density and $[D_{ij}]_1$ the binary diffusion coefficient. The collision integral ratio $\tilde{C}_{ji}$ differs from C_{ij}^*. In fact, $\tilde{C}_{ij}$ is not symmetric with respect to the interchange of the indices i and j and it is very sensitive to inelastic collisions.

For a pure gas, within the framework of Wang Chang, Uhlenbeck and deBoer form of kinetic theory, the exact value for $\lambda_{j\,\text{trans}}^{\infty}$ or $\lambda_{i\,\text{trans}}^{\infty}$[12] is given by

$$\lambda_{i\,\text{trans}}^{\infty}=\frac{\eta}{M}\left[\left\{\frac{5}{2}C_{v\,\text{trans}}+\frac{\rho D_{\text{int}}}{\eta}C_{\text{int}}\right\}-\left(\frac{2}{\pi}\frac{C_{i\,\text{int}}}{Z_{\text{rot}}}\right)\left(\frac{5}{2}-\frac{\rho D_{\text{int}}}{\eta}\right)^2\left\{1+\frac{2}{\pi Z_{\text{rot}}}\left(\frac{5}{3}\frac{C_{\text{int}}}{R}+\frac{\rho D_{\text{int}}}{\eta}\right)\right\}^{-1}\right], \tag{11}$$

where η is the coefficient of viscosity, M the molecular weight, $C_{v\,\mathrm{trans}}=3R/2$ the constant value for the translational heat capacity, Z_{rot} the rotational translational collision number for inelastic collision, ρ the mass density and D_{int} the diffusion coefficient for the transfer of internal energy. $\rho D_{\mathrm{int}}/\eta=(6/5)A^*$, where A^* is a weak function of temperature and intermolecular force.

For the non-spherical term of eq. (10), we use the Hirschfelder-Euken expressions[13] for the partial internal thermal conductivity $\lambda_{i\,\mathrm{int}}^{\infty}$ given by

$$\lambda_{i\,\mathrm{int}}^{\infty}=\frac{n[D_{ii}]c_{\mathrm{int}}}{1+(x_j/x_i)[D_{ii}/D_{ij}]_1}\,. \qquad (12)$$

The calculated inelastic theoretical α_{ij} thus obtained from eq. (10) with the help of eqs. (11) and (12) are shown in Table I for comparison with our experimental α_T values. These are also shown in Figs. (4)–(6). The necessary molecular parameters to calculate α_{ij} are shown in Table II.

§4. Results and Discussions

Following Furry and Jones,[2] the experimental α_T values of a He–T_2 mixture at $\bar{T}=338.0$, 378.0 and 423.0 K were computed from eq. (7) using both Maxwell and Slieker shape factors. Theoretical α_T values of the same mixture at the same temperatures (5% T_2 in 95% He) were also calculated from eq. (9) based on the elastic collision theory. The theoretical calculation was repeated using eq. (10) based on the inelastic collision theory[10] with rotational translational collision number $Z_{\mathrm{rot}}=300$, and using those of A. K. Barua *et al.*[14] Finally our calibration factor method[4,5] was utilized to calculate the experimental α_T values for a He–T_2 mixture directly from eq. (1) with the help of F_s values and the corresponding $\ln q_{\max}$ values obtained from eq. (8) in terms of a' and b' of Table I at different $\bar{T}$. All the experimental and theoretical α_T thus obtained for the He–T_2 mixture are indicated in Table I and their temperature dependence is shown in Fig. 4 for comparison. The estimated errors in our regression technique in obtaining $\ln q_{\max}$ through eq. (8) from the experimental $\ln q_e$ data at different pressures in atm were only 1.14%, 0.159% and 0.107% at three experimental temperatures. These are well within the limit of tolerance.

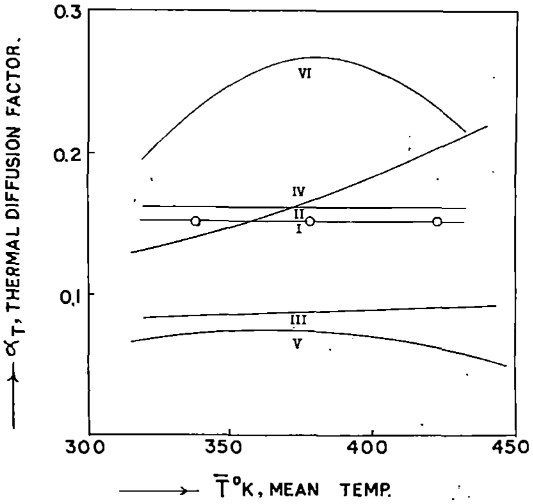

Fig. 4. Temperature dependence of α_T of He–T_2 mixture:

I —o—o— expt. α_T (our method).
II ——— theor. α_T (elastic).
III ——— theor. α_T (inelastic, with $Z_{\mathrm{rot}}=300$).
IV ——— theor. α_T (inelastic, with Z_{rot} A. K. Barua *et al.*, 1970).
V ——— expt. α_T (Maxwellian case) and
VI ——— expt. α_T (Sliekerian case).

The curves III and IV in Fig. 4 obtained by the crude inelastic collision theory (eq. (10)) showed the positive temperature dependence of α_T, whereas the curves V and VI obtained by the experimental α_T using the existing column theoretical formulations of Maxwell & Slieker respectively from eq. (7) were found to be convex in nature. As evident from the Table I, the Slieker formulations in a rough estimation of experimental α_T is one order of magnitude higher while the experimental α_T due to the Maxwellian model is one order of magnitude less than our experimental α_T curve I in Fig. 4. But in view of both trend and magnitude, the curve I obtained from our calibration factor method fairly well corresponds with the curve II to support the elastic collision effect in a He–T_2 mixture. This is what is usually expected on a symmetric diatomic molecule like T_2 where the angle dependent part of molecular potential is trivial in comparison with those of eccentrically loaded sphere molecules like HT and DT.

Now to verify the trustworthiness of the role of experimental F_s, we calculate the theoretical F_s values from theoretically obtained elastic α_T (eq. (9)) at different $\bar{T}$. These are indicated in Table I and shown by the curve II in Fig. 3, which is expressed by the following fitted equation:

$$F_s^{\text{theo}} = -62.43218 + 0.3286909\,\bar{T} - 3.93039 \times 10^{-4}\,\bar{T}^2. \qquad (13)$$

The curves I and II in Fig. 3 are almost identical, showing the same temperature dependence; thus signifying that the role of F_s is correct and hence the choice of a He–T_2 mixture as calibration gas is valid.

Both mass and size differences play a key role in yielding the magnitude of α_T. For a He–HT mixture, the magnitude of α_T should be small because mass difference between He and HT is practically nil. Moreover, in addition to the other influencing factors, eccentricity of the loaded sphere molecules like HT or DT affects the thermal diffusion through the inelastic collision. Consequently the α_T values of the latter two mixtures are expected to be temperature dependent. The Table I as well as the curves I of Figs. 5 and 6 respectively proves that the magnitude and trend of experimental α_T obtained from our calibration factor method are in line with our expectation. The experimental α_T of a He–DT mixture first decreases with $\bar{T}$ to assume a minimum value at about 375.0 K and then begins to increase, while those of a He–HT mixture show a monotonic increase with $\bar{T}$. The α_T values of a H_2–He(1:1) mixture, as reported elsewhere,[15] are then plotted into the curve VI in Fig. 6, showing the temperature dependence similar to He–DT. Although H_2 is a symmetric molecule, still it shows the inelastic collision in helium: This is perhaps due to concentration effect. Had H_2 been a trace component in He, it would have shown the elastic collision effect like a trace component T_2 in helium (Curve I, Fig. 4).

For an eccentrically loaded sphere type colliding molecules like HT or DT, the angle dependent part of molecular potential has a great influence over thermal diffusion phenomenon. This is better realised when the concentration of HT or DT is very low.

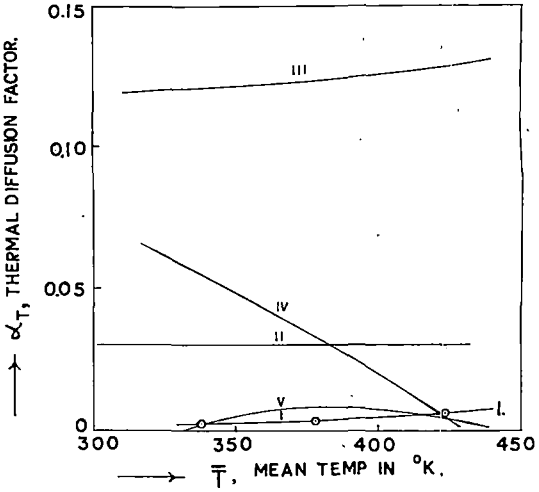

Fig. 5. Temperature dependence of α_T of He–HT mixture:

I —o—o— expt. α_T (our method).
II ——— theor. α_T (calculated with elastic theory).
III ——— theor. α_T (calculated with inelastic theory with $Z_{\text{rot}}=300$).
IV ——— theor. α_T (inelastic, with Z_{rot} A. K. Barua *et al.,* 1970).
V ——— theor. α_T (inelastic with Z_{rot} Parker, 1959).

Neither the elastic collision theory eq. (9) nor the inelastic collision theory eq. (10), i.e. the curve II or III in Figs. 5 and 6 could not explain our experimental α_T, although the curve III of Fig. 5 shows the $\bar{T}$ dependence similar to the curve I for the experimental α_T of He–HT. Thus the role of F_s in favour of inelastic collision effect on thermal diffusion of a He–HT mixture is quite reasonable when $Z_{\text{rot}}=300$. $Z_{\text{rot}}=300$ is of the right order of magnitude[10] when we remember that we have not quantised the rotational contribution. Due to lack of accurate and extensive data of Z_{rot} we are compelled to calculate α_{ij} (inelastic) with available Z_{rot} for the hydrogenic gas[13] (Table I). Fortunately for the case of He–HT and He–DT, one value of the theoretical α_T obtained from the theoretical estimation (eq. (10)) coincides with the experimental points at 423 K and 338 K, as illustrated from the curve IV in Figs. 5 and 6. This coincidence immediately prompts us to adjust Z_{rot}^{∞}, i.e., the translational rotational collision number of hydrogenic isotopes at a higher temperature and Z_{rot} as given by the Perkar's formula,[16] though it is valid for

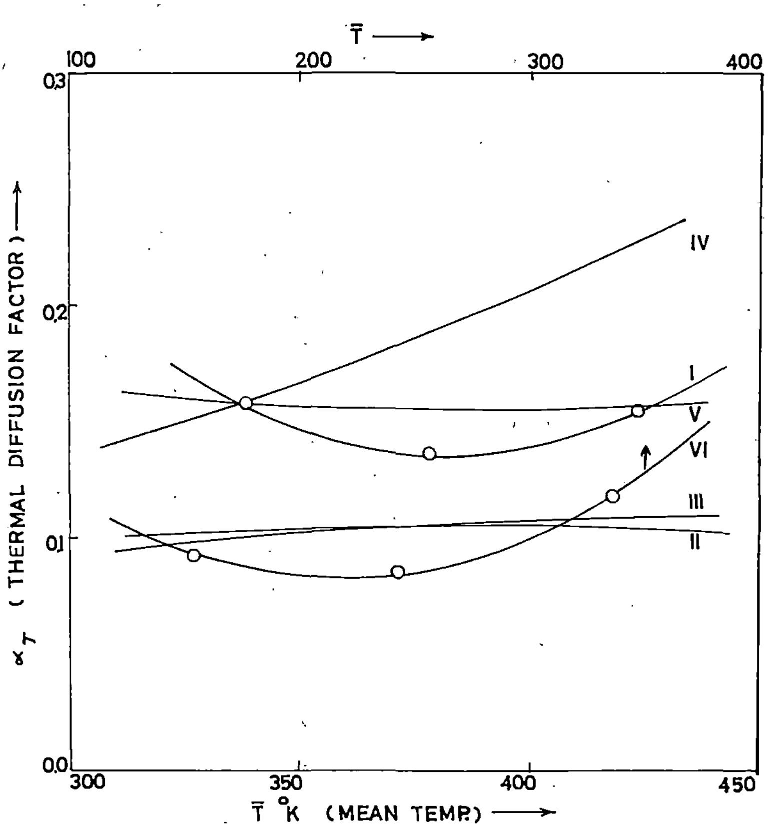

Fig. 6. Temperature dependence of α_T of He–DT mixture:
I —○—○— expt. α_T (our method).
II ——— theor. α_T (elastic theory).
III ——— theor. α_T (inelastic, with $Z_{rot}=300$).
IV ——— theor. α_T (inelastic, with Z_{rot} A. K. Barua *et al.*, 1970).
V ——— theor. α_T (inelastic with Z_{rot} Parker, 1959).
VI ——— temperature dependence of expt. α_T of He–H_2 (1:1) mixture (Ghosh *et al.*, 1968).

homonuclear diatomic molecule:

$$Z_{rot}=Z_{rot}^{\infty}\left[1+\frac{\pi^{3/2}}{2}\left(\frac{\varepsilon}{kT}\right)^{\frac{1}{2}}+\left(\frac{\pi^2}{4}+\pi\right)\left(\frac{\varepsilon}{kT}\right)\right]^{-1}, \qquad (14)$$

where ε is the maximum energy of attraction between the two molecules. The values turn out to be $Z_{rot}^{\infty}=12.15$ and 7.08 for DT and HT respectively. The corresponding Z_{rot} at other temperatures are then calculated and placed in Table I to compute α_{ij} from the theoretical inelastic formulation (eq. (10)). The curves V in Figs. 5 and 6 are now in excellent agreement with our experimental α_T. This study is finally substantiated with the calculated values of moment of inertia I_j of HT and DT molecules from their eccentricity and bond length data.[6] The values of K turn out to be 10.5378 and 5.914538 by the method of successive approximation to yield the theoretical moment of inertia $I_j=0.2424\times10^{-40}$ gm·cm^2 and $I_j=0.6774\times10^{-40}$ gm·cm^2, which are close to the experimental $I_j=0.2727\times10^{-40}$ gm·cm^2 and $I_j=0.6896\times10^{-40}$ gm·cm^2 respectively, giving $Z_{rot}=4.78$ and 3.05 at $\bar{T}=338$ K and 423 K for DT and HT molecules respectively. The close agreement of the theoretical I_j with the experimental ones thus establishes that the choice of the magnitude of Z_{rot} for HT and DT molecules (Table II) used to calculate α_{ij}'s (inelastic) from eq. (10) is correctly performed.

Our calibration factor method is so sensitive and reliable that it can detect the collision effect of even trace hydrogenic isotopes in helium, giving at the same time the actual magnitude of α_T. It also unambiguously points out that the so-called existing crude inelastic theoretical formulations eq. (10) with proper choice of $Z_{\rm rot}$ or alternative molecular model could also explain the temperature dependence of α_T of He–DT and He–HT trace mixtures, as shown by the curve V in Figs. 5 and 6 respectively.

§5. Conclusions

Thus the role of F_s in the study of temperature dependence of thermal diffusion factor of He–T_2, He–HT and He–DT mixtures appears conspicuous. This study clearly indicates that a more refined theoretical approach is yet to be developed for proper explanation of the temperature dependence of α_T. We may conclude that the calibrated T.D. column is a reliable α_T measuring instrument. The process adopted here is a straightforward one. Too much attention to the column geometry through the rigorous formulations of column theory is, therefore, shifted to a simple F_s which, being free from a binary molecular interaction model, depends entirely on the geometry of the column. The study also suggests that there exist some functional relationships between F_s and the column parameters.

Acknowledgement

The authors are grateful to Mr. A. Sen, I. A. S., District Magistrate, West Dinajpur, and Principal S. N. Roy, University College, Raiganj for their generous help in the work.

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Journal of the Physical Society of Japan
Vol. 56, No. 7, July, 1987, pp. 2381–2386

Composition Dependence and Inversion of α_T of N_2–CO Gas Mixture

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(Received April 28, 1986)

The available concentration variation on ln q_e data of isobaric N_2–CO gas mixtures in a hot wall thermal diffusion column has been utilised to calculate the composition dependence of thermal diffusion factor α_T at three experimental temperatures 350.1, 368.1 and 432.0 K. It is found that there is always an inversion of α_T as a function of composition for these experimental temperatures, indicating further that this inversion phenomenon occurs in a well-defined temperature range 248.6 K to 610.1 K. If the experimental conditions on composition and temperature fall within the area enclosed by the inversion curve and the temperature axis, in general, N_2 enriches at the top of the column; if they are outside, then N_2 enriches at the bottom.

§1. Introduction

During the past few years, the thermal diffusion phenomenon in the isotopic or nonisotopic gas mixture was regarded as a sensitive tool to investigate binary interactions between like and unlike molecules. Both experimental and theoretical investigations were performed by a number of workers[1,2] in this field. But the measured results on α_T could hardly be explained by the existing theories based on either elastic[4] or inelastic[3] collisions. This is because of the inadequate assumptions made on various kinds of molecular cross sections. Chattopadhyay and Acharyya[5] had also shown that the recent theory of inelastic collisions on thermal diffusion was not widely applicable; the present N_2–CO system fails to fit.[5] However, the N_2–CO system is an interesting binary gas mixture, having components of nearly identical mass, size and molecular force field. The elastic theory obviously yields a vanishingly small α_T of the order of 10^{-4} for the system of interest, since α_T depends on the mass difference, size difference and the dynamics between colliding molecules. But, in practice, the result is quite different. Several workers[6-8] observed higher thermal equilibrium separation factors q_e, as well as higher thermal diffusion factors α_T for the same system. Moreover, perplexing and contradictory informations on the enrichment of N_2 between at the top and at the bottom of a column were reported.

The thermal diffusion phenomenon in a gas mixture is usually studied by the observation of α_T either by varying the temperature for a fixed composition or by varying the composition at a fixed temperature. However, the temperature dependence of α_T of N_2–CO(1:1) mixture in a TD column had already been analysed using a method prescribed by Acharyya *et al.*[9] In this note, an attempt has been made to analyse the composition dependence and inversion of both ln q_e and α_T of a N_2–CO gas mixture at three experimental temperatures 350.1, 368.1, and 432.0 K and to explore the actual situation of enriching either N_2 or CO at the top of a TD column. In fact, no extensive measurement have yet been done on N_2–CO system regarding the composition dependence of α_T. Müller[6] used a TD column of length 260 cm with a hot wire temperature $T_h=1058.0$ K and the cold wall temperature $T_c=300.2$ K yielding the mean gas temperature $\bar{T}=679.1$ K, and found N_2 always enriched at the bottom. deVries[7] used a TD column of length 1000 cm containing N_2–CO(1:1) system at $\bar{T}=350.0$ K found N_2 enriched at the top of the column, despite the fact that mass of N_2(28.016) > mass of CO(28.011). On the other hand, Bhattacharyya[8] *et al.* measured the composition dependence of α_T on the same mixture in a trenschaukel apparatus at $\bar{T}=299.0$ K using N_2 as the heavier component. We, thus, intend to avail ourselves of the opportunity to utilise the unpublished I.A.C.S. TD column data on ln q_e of N_2–CO mixtures at different compositions of CO, in conjunction with those reported by Müller,[6] deVries[7] and Bhattacharyya[8] *et al.*, in order to estimate the composition dependence of α_T and to compare and study the general behaviour of equilibrium separation including inversion.

The experimental equilibrium thermal separation factor q_e was measured by

$$q_e=\frac{(x_{N_2}/x_{CO})_{Top}}{(x_{N_2}/x_{CO})_{Bottom}}, \qquad (1)$$

of a N_2–CO mixture at various compositions, but at different experimental temperatures 350.1, 368.1 and 432.0 K, in an all metal concentric tube type hot wall TD column described elsewhere.[10] This column had the cold wall redius $r_c=1.1113$ cm, the hot wall radius $r_h=0.5556$ cm and the length $L=305.2$ cm. The experimental ln q_e, unpublished hitherto, are shown in Table I with their respective standard deviations. N_2 was supplied by Indian Oxygen Ltd, Calcutta, while CO was prepared in I.A.C.S. laboratory, the purity of which was better than 99.5% as proved by a mass spectrometer (Model MS-3, Associated electrical Industries, U.K.). The pressure of the mixture was kept at 0.60 atm in the column for overnight run. At all the experimental temperatures $\bar{T}=305.1$, 368.1 and 432.0 K, N_2 was found enriching at the top of the column until CO reached a certain percentage in the mixture. When the CO concentration was increased further, nitrogen enriched at the bottom.

§2. Theoretical Formulations

At any mean gas temperature $\bar{T}=[\frac{1}{2}(T_h+T_c)]$, the equilibrium thermal separation factor q_e of a binary gas mixture in an ideal column of length L closed at both ends is given by

$$q_e=\exp(HL/K_c+K_d), \qquad (2)$$

where H is the transport coefficient, and K_c and K_d respectively are the convective and diffusive remixing coefficients. They are proportional to p^2, p^4 and p^0 respectively, p being the pressure. Thus eq. (2) becomes

$$\ln q_e=\frac{ap^2}{b+p^4}, \qquad (3)$$

Table I. I.A.C.S. Column data on ln q_c for different compositions of N_2–CO at constant pressure and temperatures.

Pressure (atm)	Cold-wall temperature T_c (K)	Hot-wall temperature T_h (K)	Mean temperature T (K)	Mole fraction of CO (x_{CO})	ln q_c
0.60	305.2	395.1	350.1	24.8	0.053±0.004
				33.0	0.050±0.004
				63.0	0.017±0.005
				76.0	−0.040±0.003
				89.1	−0.198±0.005
				76.0	
0.60	305.2	431.0	368.1	20.1	0.077±0.005
				33.0	0.067±0.006
				48.8	0.060±0.005
				69.2	0.005±0.009
				85.9	−0.128±0.006
0.60	305.2	558.8	432.0	24.8	0.081±0.003
				32.8	0.082±0.004
				62.8	0.074±0.003
				69.2	0.049±0.006
				79.9	0.000±0.007
				88.8	−0.067±0.005

where $a=(HL/K_c)p^2$ and $b=(K_d/K_c)p^4$. But in a practical column, due to the presence of asymmetries in the column geometry, parasitic remixing usually occurs. The aftermath of this parasitic remixing is the reduction in separation. Nevertheless, according to Furry and Jones,[11] the quilibrium separation factor for this realistic situation is obtained by simply adding a term K_p, proportional to p^4, to the denominator of eq. (2) and hence eq. (2) becomes

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

or

$$p^2/\ln q_e=\frac{b'}{a'}+\frac{1}{a'}p^4. \tag{5}$$

Equation (5) is thus a straight line between $p^2/\ln q_e$ and p^4, having a certain slope and an intercept. In fact eq. (5) proclaims the nature on the variation of $p^2/\ln q_e$ with respect to p^4 as demanded by the column theory.[11-13] Taking β as the ratio between the intercept and slope of the straight line, we have

$$H=\frac{K_d}{L}\left(1+\frac{1}{|\beta|}\right)\ln q_e. \tag{6}$$

Having been expressed in the unit of p^4, the magnitude of β becomes equal to b'. Equation (6) is finally written as

$$H=\frac{K_d}{L}\left(1+\frac{1}{b'}\right)\ln q_e,$$

or

$$\alpha_T=\frac{K_d}{H_0L}\left(1+\frac{1}{b'}\right)\ln q_e, \tag{7}$$

since $H=H_0\alpha_T$. α_T can be obtained at different compositions of the mixture, provided that the value of b' be known from the variation of $\ln q_e$ against pressure, at least at one composition[14] of the mixture. For H, K_c and K_d, in practice, we can proceed in three ways where the $L-J$ model is not applicable to a problem where T_c is held fixed. However in the Maxwell case ($n=1$ and α_T is assumed to be temperature independent), we have

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

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

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

and in the Slieker-case (interaction model independent):

$$H=c_1=[SF]_1r_c^4\left\{\frac{\rho^2g\alpha_T}{\eta}\right\}_1\left(\frac{\Delta T}{\bar{T}}\right)^2,$$

$$K_c=c_3=[SF]_3r_c^8\{\rho^3g^2/\eta^2D\}_1\left(\frac{\Delta T}{\bar{T}}\right)^2,$$

$$K_d=c_2=\pi\left(1-\frac{r_h}{r_c}\right)r_c^2\{\rho D\}_1 \quad \text{respectively.}$$

Here h', k_c', k_d', $[SF]_1$, $[SF]_3$ and $(1-r_h/r_c)$ are the Maxwell and Slieker dimensionless shape factors. η the coefficient of viscosity, ρ the mass density, and D the diffusion coefficient of a binary mixture like N_2–CO which are found to be composition independent due to the same masses and force parameters were calculated from ref. 4. Here $u=[(T_h-T_c)/(T_h+T_c)]$, $\Delta T=T_h-T_c$ and g is the acceleration of gravity.

The values of b' for a N_2–CO(1:1) gas mixture at different temperatures had already been obtained in our previous work.[9] As K_p/K_c is nearly composition independent,[14] the graphical extrapolation technique is used in getting the b' values 1.3338, 1.5771 and 1.5651 at $\bar{T}=350.1$, 368.1 and 432.0 K respectively, in order to estimate α_T from eq. (7).

§3. Results and Discussions

The experimental points of $\ln q_e$ for N_2–CO mixtures with their standard deviations are shown in Fig. 1 at $\bar{T}=350.1$, 368.1 and 432.0 K respectively, for different CO concentrations; they are reproduced in Table I. From Fig. 1 it is clear that as the concentration of carbon monoxide increases, $\ln q_e$ decreases down to negative values through zero. In fact, this involves inversion of α_T of the system due to variation of composition. However, unlike the present case, the measurements of Müller[6] exhibit no such changes as shown in Fig. 1.

From the curves of $\ln q_e$ against the CO concentration (Fig. 1), the special values of x_{CO} undergoing no separation were found out to be 65.25, 71.50 and 80.75% at 350.1, 368.1

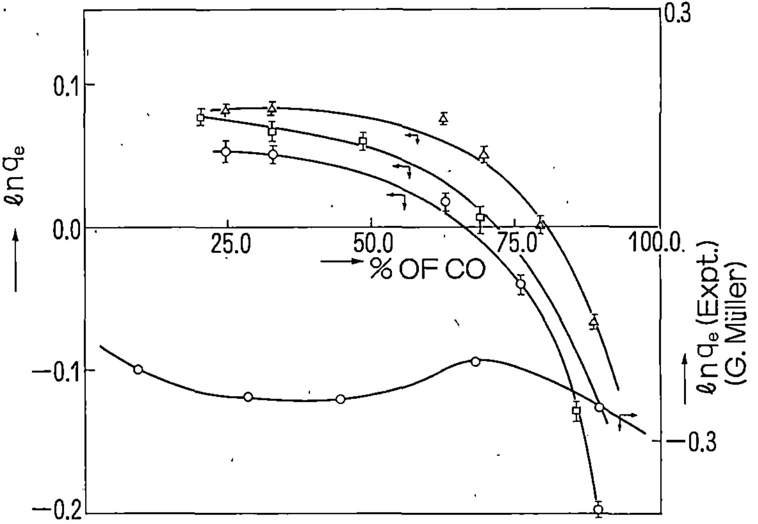

Fig. 1. ln q_e of N_2-CO gas mixtures against x_{CO}.
—○—○— at $\bar{T}$=350.1 K, —□—□— at $\bar{T}$=368.1 K. —△—△— at $\bar{T}$=432.0 K. —o—o— Müller.

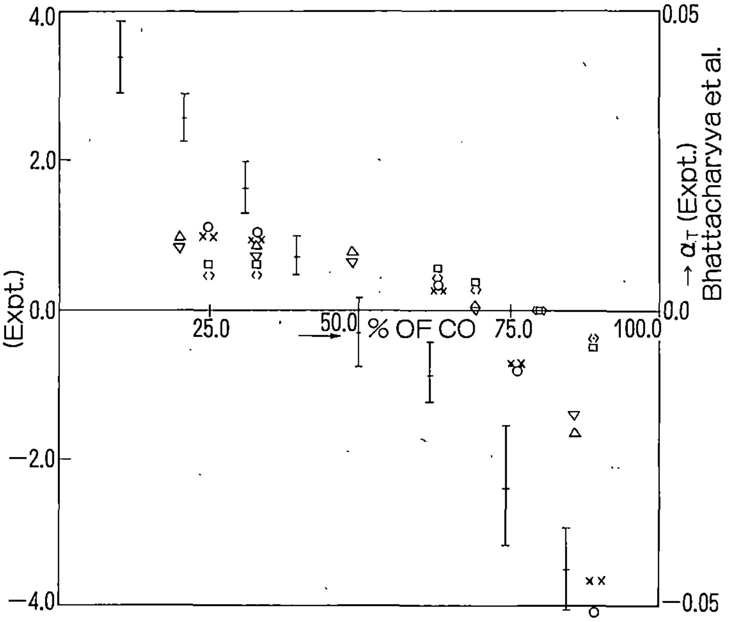

Fig. 2. Experimental α_T against CO concentrations at different mean temperatures $\bar{T}$ in the N_2-CO mixture. ⊡→(Slieker at $\bar{T}$=432.0 K), △→(Slieker at $\bar{T}$=368.1 K), ⊙→(Slieker at $\bar{T}$=350.1 K), <•>→(Maxwell at $\bar{T}$=432.0 K), ▽→(Maxwell at $\bar{T}$=368.1 K), >(•)<→(Maxwell at $\bar{T}$=350.1 K), I→(Bhattacharyya *et al.* at $\bar{T}$=299.0 K).

and 432.0 K respectively. In order to focus our attention on the inversion and enrichment of a mixture component, an empirical relation between $\bar{T}$ and x_{CO} satisfying $\ln q_e=0$ was derived as

$$(x_{CO})_{\ln q_e=0} = -374.8806+2.122604\bar{T} -2.472\times 10^{-3}\bar{T}^2. \quad (8)$$

Equation (8) shows that the highest CO concentration having no separation was found to be nearly 80%, as evident from Fig. 3. The

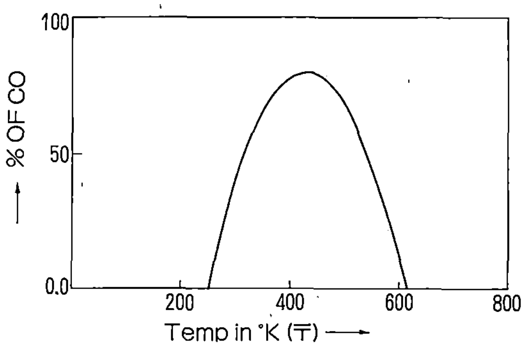

Fig. 3. CO concentration x_{CO} against mean temperature $\bar{T}$ of N_2–CO mixtures satisfying $\ln q_e=0$.

minimum and maximum temperatures for which $\ln q_e=0$ are 248.6 and 610.1 K. These are the special percentage and temperatures for the N_2–CO system. Nature of variation of x_{CO} with respect to $\bar{T}$ for which $\ln q_e=0$ is shown in Fig. 3. It has a well-defined temperature domain ranging from 248.6 to 610.1 K and a composition range of CO from 0 to 81.32%. This is called the inversion curve (IC) which has an interesting field of application. It can unambiguously predict the nature of enriching a component in a N_2–CO mixture simply by knowing $\bar{T}$ and x_{CO} in an experiment. For example, if the experimental conditions regarding the temperature $\bar{T}$ and composition x_{CO} fall within the area enclosed by the IC and the temperature axis (Fig. 3), N_2 will enrich at the top of the column. If they lie outside, on the other hand, N_2 will enrich at the bottom. These are the cases in the Müller and deVries experiments using N_2–CO systems. But when they fall on the IC itself, there will be no separation. The effectiveness of the IC was also tested by applying it to conjecture the enrichment of N_2 in the different experimental observations[6-8] already reported in the literatures. The successful results are summarised in Table II. But when $x_{CO}>81.32\%$, neither $\ln q_e$ nor α_T will experience inversion.

Lastly, the α_T values of N_2–CO mixtures were estimated from eq. (7). The α_T thus obtained for the cases of the Maxwellian model and the Slieker case were shown in Fig. 2, in order to compare with those of Bhattacharyya *et al.*[8] But no smooth α_T against x_{CO} curves could be drawn with certitude over their data, which still showed inversion at about 45% of CO as shown in Fig. 2. This fact is corroborated also

Table II. Nature of enrichment as predicted by IC of Fig. 3.

References	$\bar{T}$ in K	% of CO in the mixture	Position of ($\bar{T}$, x_{CO}) in Fig. 3	Enrichment of N_2	
				Predicted	Observed/Reported
Present work (I.A. C.S. Column)	350.1	Below 65.25 Above 65.25 Just 65.25	Under I.C. Above I.C. On I.C.	Top Bottom Nil	Top Bottom Nil
〃	368.1	Below 71.50 Above 71.50 Just 71.50	Under I.C. Above I.C. On I.C.	Top Bottom Nil	Top Bottom Nil
〃	432.0	Below 80.75 Above 80.75 Just 80.75	Under I.C. Above I.C. On I.C.	Top Bottom Nil	Top Bottom Nil
Müller (1962) (column)	679.1	Any percentage.	Above I.C.	Bottom	Bottom
deVries (1956) (column)	350.0	50.0	Under I.C.	Top	Top
Bhattacharyya *et al.* (1975) (Trenschaukel)	299.0	Below 45.0 Above 45.0 Just 45.0	Under I.C. Above I.C. On I.C.	Top Bottom Nil	Top Bottom Nil

by our inversion curve of Fig. 3.

§4. Conclusion

The inversion curve thus plays a vital role in showing an interesting state of interacting molecules in a binary gas mixture particularly at the specific temperature and specific mole fraction. The inversion phenomenon observed in the thermal diffusion of a N_2–CO system invokes a thorough study inasmuch as it is capable of throwing much light into the collision processes. To further our knowledge in this field, both the experimental as well as theoretical investigations are of necessity.

Acknowledgement

We are grateful to Professor A. K. Barua, Director and Dr. A. K. Batabyal, I.A.C.S.Cal-32 for their kind permission to utilise the unpublished experimental data on ln q_e of N_2–CO gas mixtures. Finally, we are indebted to Professor D. B. Datta, Vice-Chancellor, N. B. U., and Principal, S. N. Roy, University College, Raiganj (West Dinajpur) for their kind support in this work.

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