

# **CHAPTER 6**

**Thermal Diffusion Factors of  
Hydrogenic Trace Mixtures  
with Helium by Column  
Calibration Factor**

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

### **6.1. Introduction**

In the existing column theory as developed by Furry and others<sup>1-3)</sup> the column geometry plays an important role in determining the exact value of thermal diffusion factor  $\alpha_T$  of 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

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

is very large even in the case of small mass difference between the components of a mixture. Here,  $x_i$  and  $x_j$  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<sup>4)</sup> with known reliable  $\alpha_T$  of He -  $T_2$  mixture to arrive at the column calibration factor (CCF)  $F_s$  from the relation:

$$\ln q_{max} = \alpha_T F_s (r_c, r_h, L, \bar{T}) \quad \dots \dots \dots \quad (6.1)$$

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<sup>5-7)</sup> and Navarro et al<sup>8)</sup> 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<sup>4)</sup> 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 Fig. 6.1 and 6.2 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<sup>7)</sup>.

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

$$\begin{aligned} p^2/\ln q_e &= 0.7758 + 0.8161 p^4 \text{ at } 338 \text{ K,} \\ &= 0.4938 + 0.7294 p^4 \text{ at } 378 \text{ K,} \\ &= 0.3964 + 0.6034 p^4 \text{ at } 423 \text{ K and} \end{aligned}$$

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

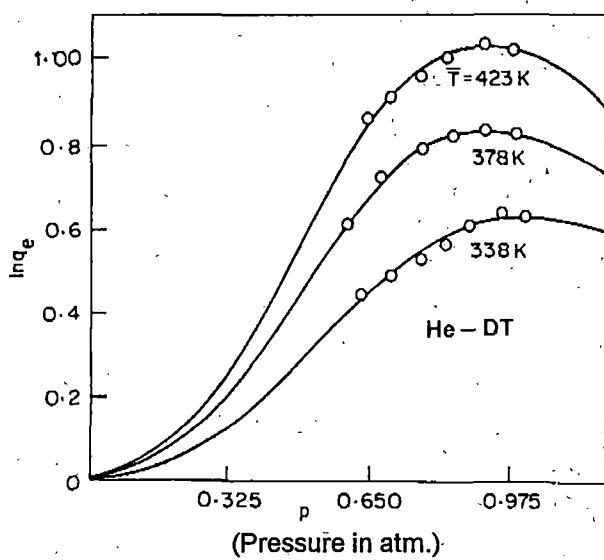
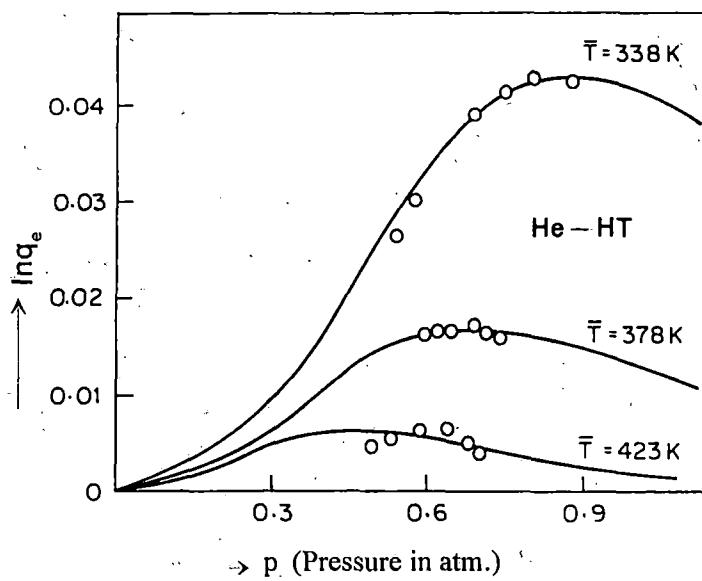
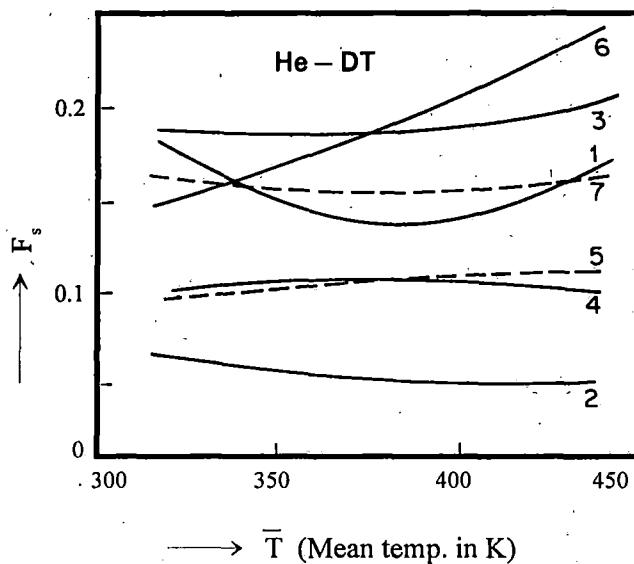


Fig. 6.1.  $\ln q_e$  against pressure  $p$  in atmosphere for He-DT trace mixture at  $T = 338, 378$  and  $423$  K, 'O' experimental points.



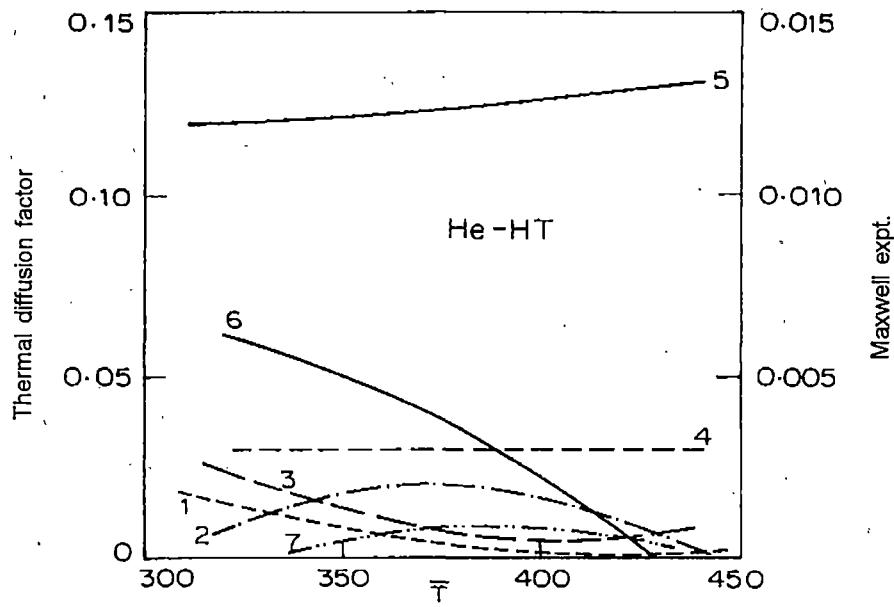
**Fig. 6.2:**  $\ln q_e$  against pressure  $p$  in atmosphere for He-HT trace mixture, at  $\bar{T} = 338$  and  $423$  K, 'O' experimental points.



**Fig. 6.3.** 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  $\alpha_T$  (Slieker case); 4. Theor  $\alpha_T$  (elastic) from eq (6.7); 5. Theor  $\alpha_T$  (inelastic) with  $Z_{rot} = 300$  from eq (6.7); 6. Theor  $\alpha_T$  (inelastic) with  $Z_{rot}$  calculated from Barua et al (1970) from eq (6.8); 7. Theor  $\alpha_T$  (inelastic) with  $Z_{root}^{\alpha}$  calculated from Parkers<sup>12)</sup> formula with adjustable  $Z_{root}^{\alpha} = 7.08^{13)}$ .

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<sup>7)</sup>,

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



(Mean temp. in K)

**Fig. 6.4.** 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 (6.7); 5. Theor  $\alpha_T$ (inelastic) with  $Z_{\text{rot}} = 300$  from Eq(6.8) 6. Theor  $\alpha_T$ (inelastic) with  $Z_{\text{rot}}$  calculated from Baura et al<sup>12)</sup> from Eq(6.8) 7. Theor  $\alpha_T$ (inelastic) with  $Z_{\text{rot}}$  calculated from Parker<sup>13)</sup> formula with adjustable  $Z_{\text{rot}} = 12.15$ .

Now  $\alpha_T$ 's of He-DT and He-HT were obtained from eq(6.1) and compared with those by the existing methods using column theory as well as the theoretical  $\alpha_T$  based on elastic and inelastic<sup>9)</sup> collisions in Fig 6.3 and 6.4 respectively in order to reveal the existence of inelastic collisions in these mixtures.

## **6.2. Theoretical Formulation to Estimate Experimental $\alpha$ .**

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

$$\ln q_e = HL/(K_c + K_d) \quad \dots \dots \dots \quad (6.2)$$

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<sup>2)</sup> simply added a term  $K_0$  proportional to  $p^4$  to the denominator when eq.(6.2) becomes

which is also written as

$a'$  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 eq. (6.4) we have

the exact expressions for  $H$ ,  $K_c$  and  $K_d$  are given in our previous publications<sup>5-7)</sup>

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<sup>10</sup>, the column shape factors and the force parameters required had already been reported earlier<sup>7</sup>.

It is observed in Fig.6.1 - 6.2, that as the pressure increases  $\ln q_e$  increases and becomes maximum when  $p = (b')^{1/4}$  for which  $\frac{\delta}{\delta p} (\ln q_e) = 0$ .

We then have from eq (6.3)

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 eq (6.6).

Table 6.1 and the graphs of Figs 6.1 and 6.2 revealed that  $\ln q_{\max}$  from eq (6.6) in terms of  $a'$  and  $b'$  are in good agreement with the graphically determined values earlier<sup>7</sup>. 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.

### **6.3. Theoretical Formulations to Calculate $\alpha_T$**

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

$$\alpha_T = \frac{1}{6[\lambda_{ij}]_1} \cdot \frac{S^{(0)} x_i - S^{(0)} x_j}{[X_\lambda + Y_\lambda]} (6C^*_{ij} - 5) \quad \dots \quad (6.7)$$

where  $(6C_{ij}^* - 5)$  depends mainly on the temperature while the other factors involved in eq (6.7) are the complicated functions of composition, masses and thermal conductivities of gases and gas mixtures. The  $\alpha_T$  calculated from eq (6.7) is presented in the 12th column of Table 6.1, and shown graphically in Figs 6.3 and 6.4 for He-DT and He-HT respectively.

The inelastic thermal diffusion factor  $\alpha_{ii}$  is given by Monchick et al<sup>11</sup>.

$$\alpha_{ij} = \frac{(6C_{ij}^* - 5)\mu_{ij}}{5nk[D_{ij}]_1} \left( \frac{\lambda_{j \text{ trans}}^\alpha}{x_j m_j} - \frac{\lambda_{i \text{ trans}}^\alpha}{x_i m_j} \right) + \frac{1}{5nk [D_{ij}]_1} \left[ \frac{(6\tilde{C}_{ij} - 5)\lambda_{j \text{ int}}^\alpha}{x_j} - \frac{(6\tilde{C}_{ij} - 5)\lambda_{i \text{ int}}^\alpha}{x_i} \right]. \quad (6.8)$$

where the symbols have their usual meanings only the collision integral ratio

Table 6.1. Experimental and Theoretical  $\alpha_T$  values of binary gas mixtures with temperature.

System	$T_h$ in K	$T_c$ in K	Hot wall temp	Cold wall Temp	Mean $\bar{T}$ in K	$a'$ in (atm) <sup>2</sup>	$b'$ in (atm) <sup>4</sup>	In $q_{\max}$ computed from eq(6.5)	Expt $F_s$ Ref (6)	Expt $\alpha_T$ with		Our calibration factor method eq(6.1)	Maxwell shape factor	Slicker shape factor	Theoretical $\alpha_T$ from eq(6.7) with $Z_{\text{rot}}$		
										Theor. $\alpha_T$ from eq(6.6) elastic theor. method	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			

$\tilde{C}_{ij}$  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

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

$$\left\{ 1 + \frac{2}{\pi Z_{\text{rot}}} \left( \frac{5}{3} \frac{C_{\text{int}}}{R} + \frac{\rho D_{\text{int}}}{\eta} \right) \right\}^{-1} \quad \dots \dots \dots (6.9)$$

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 eq (6.8), we used Hirschfelder-Eucken expression<sup>10</sup> to calculate the thermal conductivity  $\lambda_{\text{int}}^\alpha$  from

$$\lambda_{\text{int}}^\alpha = \frac{n[D_{ii}]_1 C_{\text{int}}}{1 + (x_j/x_i)(D_{ii}/D_{jj})_1} \quad \dots \dots \dots (6.10)$$

Theoretical inelastic  $\alpha_T$ 's for He-DT and He-HT thus calculated from eq (6.8) with the help of eq (6.9) and eq (6.10) are shown in Table 6.1 and also in Figs 6.3 and 6.4 respectively for comparison with other experimental  $\alpha_T$  values.

#### 6.4. Results and Discussion

The inherent asymmetry in the column geometry is however, taken into account by Maxwell, Sileker and Lennard - Jones dimensionless shape factors<sup>7</sup>. We calculated the experimental  $\alpha_T$ 's of He-HT and He-DT trace mixtures at  $T=338, 378$  and  $423\text{K}$  respectively for eq (6.5) using those shape factors. Slieker's case does not involve any molecular model and it gives rather a rough estimation of the experimental  $\alpha_T$  due to L-J case cannot be applicable here. The  $\alpha_T$  thus obtained due to Maxwell and Slieker cases is presented in table 6.1 and shown graphically by the curves 2 and 3 respectively of Figs 6.3 and 6.4.

The experimental  $\alpha_T$  from eq (6.1) as obtained in terms of  $\ln q_{\max}$  of eq(6.8) and  $F_s$  is shown by curve 1 in Fig. 6.3 and 6.4. When they are compared with those due to Maxwell (curve 2) and Slieker (curve 3) it is found that so far as the trend is concerned the data due to Slieker agree better than those due to Maxwell's shape factors. This is perhaps due to the fact that both Slieker 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 of eq (6.7), as shown by curve 4 in Figs 6.3 and 6.4 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 eq (6.8) with  $Z_{\text{rot}} = 300$ , show its positive temperature dependence as represented by curve 5 in Figs 6.3 and 6.4.

When  $\alpha_{ij}$  were calculated with the available rotational translational collision number of Barua et. al<sup>12)</sup> an interesting feature is that the curve 6 of Figs 6.3 and 6.4 coincide with  $\alpha_T$ 's of our CCF method. This fact prompted us to adjust  $Z_{\text{rot}}$  from Parker's formula<sup>12)</sup>. Using  $Z_{\text{rot}} = 2.78, 2.91$  and  $3.05$  for HT and  $Z_{\text{rot}} = 4.78, 5.01$  and  $5.23$  for DT at  $338, 378$  and  $423\text{K}$  respectively inelastic  $\alpha_{ij}$ 's are then estimated for both He-DT and He-HT trace mixtures and were shown by curve 7 in Figs 6.3 and 6.4 respectively for comparison with other  $\alpha_T$ 's.

With  $Z_{\text{rot}}$  determined by us inelastic theoretical  $\alpha_T$ 's curve 7 (15th column of table 6.1) 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 6.1) and only in trend with  $\alpha_T$ 's due to Slieker (11th column of Table 6.1). 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 mixtures. Again the variation of  $\ln q_{\max}$  against  $T$  for He-HT is given by

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

showing that at  $\bar{T} \sim 429\text{K}$ ,  $\ln q_{\max}$  may be zero as shown in Fig. 6.5. 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  $\text{N}_2\text{-CO}$  as studied in our recent publication of Saha et.al<sup>[4]</sup>. The system He-HT deserves a detailed study of measurements of  $\ln q_e$  against pressure for its different composition and temperatures.

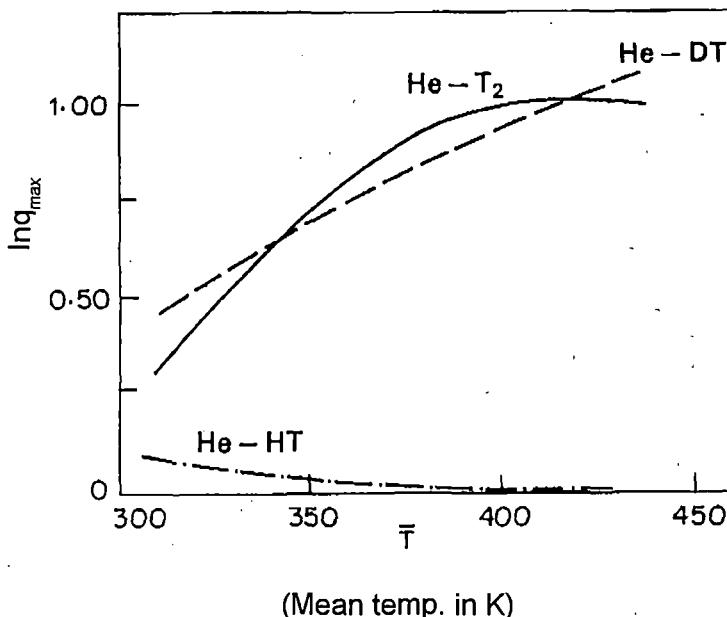


Fig. 6.5. Variation of  $\ln q_{\max}$  with temperature  $\bar{T}$  in K for He-DT, He-T<sub>2</sub> and He-HT mixtures.

We are, therefore, now in a position to conclude that CCF is an accurate  $\alpha_T$  determining factor of isotopic, nonisotopic and isobaric  $\alpha_T$  for 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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