Separation of deuterium from H–D gas mixture by thermal diffusion in the devices of multi concentric-tube columns with total sum of column heights fixed

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ABSTRACT

The equation for predicting the degrees of separation for deuterium recovery from the H_2–HD–D_2 system using thermal diffusion in single-column, double-column and triple-column devices are derived. The column number effect on separation efficiency with a fixed total sum of column heights is then investigated. Considerable improvement in recovery can be achieved in multi-column devices, instead of a single-column device with the column height equal to the same total sum of column heights, especially for the cases of higher flow-rate operation and larger total sum of column heights.

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1. Introduction

Nuclear energy supplied by fission reactors with uranium as the nuclear fuel, now plays an important role in meeting our energy need. In the distant future the applications of thermonuclear fusion with deuterium (D) may become a reality. In addition to being the fusion energy resource, heavy water is also the most feasible moderator and coolant for fission reactors. Lewis and Mac Donald [1] concentrated a large quantity of water into a small amount of nearly pure heavy water by electrolysis. Between 1940 and 1945, four heavy water production plants were placed in operation by the US Government under the Manhattan Program [2,3]. Thermal diffusion is a well-established method for separating isotopes. It was used to separate uranium isotopes at Oak Ridge Laboratory during World War II. This method is particularly attractive for the separation of hydrogen isotopes (H–D–T) because of the large molecular weight ratio [4,5]. Verhagen [6] used this method for routine tritium (T) sample enrichment. Using suitable arrangement of two diffusion columns and a container, 10-times enrichment with better than 95% recovery was achieved in about 20 h.

Recently, several investigators [7–13] employed the cryogenic-wall thermal diffusion column successfully separating H–D and H–T mixtures. The deuterium (D) recovery from an H–D gas mixture in the cryogenic-wall thermal diffusion columns was estimated [14–16] using the modeling prediction method [14] with the transport coefficients determined from the experimental data of Arita et al. [13].

The degrees of separation are very small for separating isotope mixtures using thermal diffusion, as well as by other means. In industrial applications, therefore, thermal diffusion should be applied in the multi-column devices, instead of the single-column one, with columns connected in series as shown in Figs. 2 and 3. The reason for this is that to obtain a larger production rate, although increasing the column height L in a single-column increases the effective device separation section, the increment of separation efficiency by increasing L has a limited value, especially for larger volumetric flow rates. The purpose of this study is to compare the separation efficiencies for recovery of deuterium from the H_2–HD–D_2 system using thermal diffusion in single-, double-, and triple-column devices at a fixed total sum of column heights under various volumetric flow rates V_F, operating pressures P and total sums of column heights. The separation theories are based on one column design developed in previous works [14–16].

2. Separation theory

Fig. 1 shows a single concentric-tube thermal diffusion column for separation of the H_2–HD–D_2 system with feed introduced at the column middle point. A temperature gradient applied between the hot and cold walls has two effects: a flux (J_{X-TD}) of deuterium (D) relative to others is brought to the cold surface by thermal diffusion, and (2) the natural convective currents are produced in the z-axis parallel to the wall surfaces owing to density differences. The combined result of these effects is to produce a concentration difference between the two ends of the column [15].

2.1. Transport equation

The transport equation for deuterium (D) recovery from the H_2–HD–D_2 system in a batch-type concentric-tube thermal diffusion column with inner tube outside radius R_1 and outer tube inside radius R_2, may be expressed with temperature difference, ΔT, as [15]

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Nomenclature

A_F	product form of feed concentration
B	column width (cm)
C	fractional mass concentration of deuterium in ith column
C_i	C in ith column
C_B	C in the bottom product of the single-column device
$C_{B,I}$	C in the bottom of ith column
C_F	C in the feed streams
C_T	C in the top product of the single-column device
$C_{T,I}$	C in the top product of ith column
D	ordinary diffusion coefficient (cm^2/s)
g	gravitational acceleration (cm/s^2)
H	system constant defined by Eq. (2) (cm^3/s)
h	column height (cm)
I_d, I_d	improvement in recovery of deuterium defined by Eq. (39), by Eq. (40)
J_{X-OD}	mass flux of deuterium in x-direction owing to ordinary diffusion (g/cm^{2}s)
J_{Z-OD}	mass flux of deuterium in z-direction owing to ordinary diffusion (g/cm^{2}s)
K	system constant defined by Eq. (3) (cm^4/s)

L	total sum of column heights (cm)
P	operating pressure (kPa)
R_1	outside radius of inner tube (cm)
R_2	inside radius of outer tube (cm)
$\overline{T}$	mean absolute temperature (K)
ΔT	difference in temperature between hot and cold surfaces (K)
V_F	volumetric flow rate of feed streams (cm^3/s)
x	axis perpendicular to hot and cold surfaces (cm)
z	axis parallel to the surfaces of column wall (cm)

Greeks symbols

α	thermal diffusion constant, <0 for H$_2$–HD–D$_2$ system
$\beta_{\overline{T}}$	$(-(1/\rho)(\partial\rho/\partial T))$ evaluated at $\overline{T}$ (K^{-1})
$\Delta_s, \Delta_{d-i}, \Delta_{t-i}$	degree of separation obtained in single-column, double-column and triple-column devices of ith column.
ρ	mass density at $\overline{T}$ (g/cm^3)
μ	absolute viscosity (g/cm s)
σ	mass flow rate (g/s)
τ	transport of deuterium in a column (g/s)

$$\tau = -(H\rho/8) - (K\rho/2)\frac{dC}{dz} < 0$$

(since deuterium is transferred toward opposite direction
of z-axis)   (1)

where τ and C are the transport and mass fraction of deuterium
while the transport coefficients, H and K, are defined as

$$H = \frac{8(-\alpha)(2\pi R_1)(R_2 - R_1)(\Delta T)^2 A_F F'(k)}{6!\mu\overline{T}}$$ (2)

$$K = \frac{2g^2\beta_{\overline{T}}^2(2\pi R_1)(R_2 - R_1)^7(\Delta T)^2 G'(k)}{9!\mu^2 D}$$ (3)
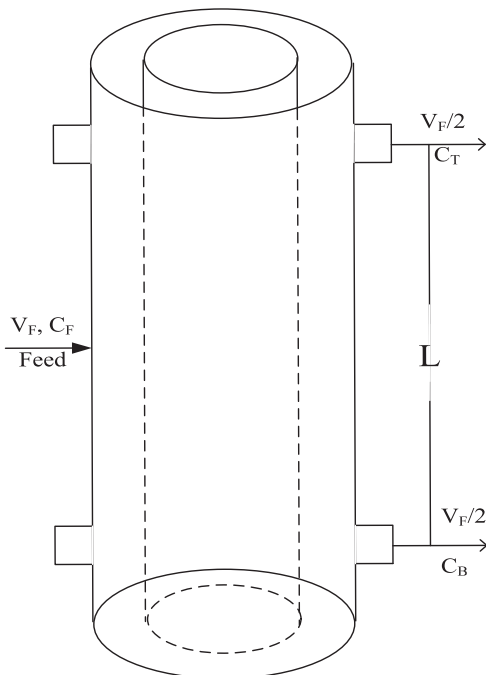

Fig. 1. Single concentration-tube column device with column height L.

In Eq. (1), the term H represents the separation effectiveness
using thermal diffusion and the term K represents the counter ef-
fect of remixing due to convection in a vertical column. The most
important assumptions in deriving the above equation are that
the flow is laminar, that the physical properties (mass density ρ,
expansion coefficient $\beta_{\overline{T}}$, diffusivity D, viscosity μ, average absolute
temperature $\overline{T}$, ...) are constant, and the concentrations are lo-
cally in equilibrium at every point in the column for the following
reversible reaction:

$$H_2 + D_2 \Longleftrightarrow 2HD$$ (4)

The modified factors, $F'(k)$ and $G'(k)$, in Eqs. (2) and (3) for the
tube curvature effect were derived in the previous works [15,17],
defined by very long and complicated equations and expressed
graphically. As mentioned before, since the degree of separation
for the separation of isotope mixtures in a thermal diffusion col-
umn is generally very small, as well as in other separation devices,
the pseudo product-form concentration, A_F, in Eq. (2) was also as-
sumed to be constant for simplicity and convenience while still
preserving the precision of the predicted results [15,16].

2.2. Single-column device with column height L

The transport equations for deuterium recovery from the H$_2$–
HD–D$_2$ system in a continuous-type concentric-tube thermal diffu-
sion column with feed introduced at the column middle point
($z = 0$), as shown in Fig. 1, may be modified from Eq. (1) with the
addition of a forced convection stream for continuous operation,
$\sigma C = (V_F/2)\rho C$, in which the feed volume rate V_F is related to the
mass flow rate σ in each transport section as

$$V_F = 2\sigma/\rho$$ (5)

The results are

$$\tau = -(V_F/2)\rho C - (H\rho/8) - (K\rho/2)\frac{dC}{dz},$$
$$-L/2 \leqslant Z \leqslant 0 \text{ (enriching section)}$$ (6)

$$\tau = (V_F/2)\rho C - (H\rho/8) - (K\rho/2)\frac{dC}{dz},$$
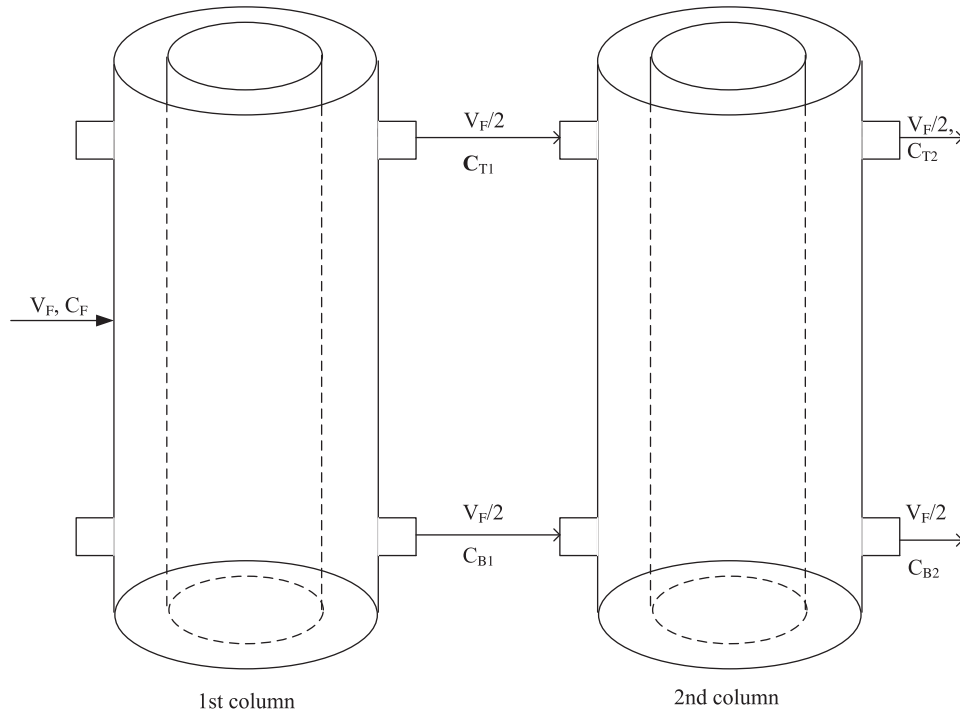$$0 \leqslant Z \leqslant L/2 \text{ (stripping section)}$$ (7)

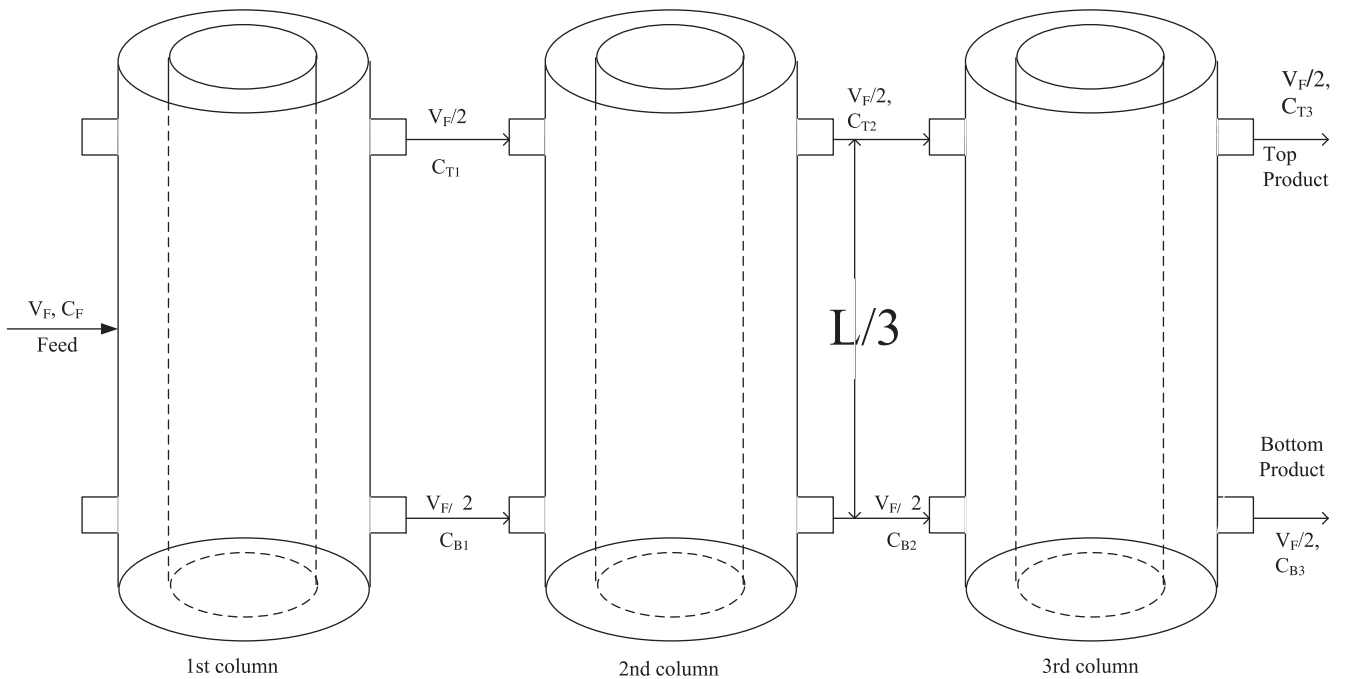**Fig. 2.** Double concentration-tube column device with column height $L/2$.

Fig. 3. Triple concentration-tube column device with column height $L/3$.

At steady state, the deuterium mass transport τ is constant and $\tau = -(V_F/2)\rho C_B$ and $\tau = (V_F/2)\rho C_T$ in the enriching and stripping section, respectively, Eqs. (6) and (7) become

$$-(H/4) + V_F(C_B - C) = K\frac{dC}{dz}, \quad -L/2 \leqslant Z \leqslant 0 \tag{8}$$

$$-(H/4) - V_F(C_T - C) = K\frac{dC}{dz}, \quad 0 \leqslant Z \leqslant L/2 \tag{9}$$

The deuterium concentrations at the bottom (C_B) and top (C_T) ends of a single-column are readily obtained by integrating Eqs.

(8) and (9), respectively, using of the following boundary conditions:

$$C = C_B \text{ at } z = -L/2 \tag{10}$$

$$C = C_F \text{ at } z = 0$$

(middle point of a single-column where the feed streamright is introduced) (11)

$$C = C_T \text{ at } z = L/2 \tag{12}$$

The results are

$$C_B - C_F = \frac{H}{4V_F}(1 - e^{-V_F L/2K}) \tag{13}$$

$$C_T - C_F = \frac{-H}{4V_F}(1 - e^{-V_F L/2K}) \tag{14}$$

The degree of separation is finally obtained by combining Eqs. (13) and (14), as

$$\Delta_S = C_B - C_T \tag{15}$$

$$= \frac{H}{2V_F}(1 - e^{-V_F L/2K}) \tag{16}$$

Eq. (16) is exactly the same equation as Eq. (11) in previous work [14].

2.3. Double-column device with uniform column height L/2

The equation for the concentration difference in the first column of a double-column device (Fig. 2) is readily modified from Eq. (16) with Δ_S and L replaced by Δ_{d-1} and $L/2$, respectively

$$\Delta_{d-1} = C_{B,1} - C_{T,1} \tag{17}$$

$$= \frac{H}{2V_F}(1 - e^{-V_F L/4K}) \tag{18}$$

Making material balance for deuterium at the top and bottom ends of the second column, respectively, one has

$$\sigma C_{T,1} = (-\tau) + \sigma C_{T,2} \tag{19}$$

$$\sigma C_{B,2} = (-\tau) + \sigma C_{B,1} \tag{20}$$

The combination of Eqs. (1) and (19) using Eq. (5) yields

$$C_{T,1} - C_{T,2} = (H/4V_F) + (K/V_F)\frac{dC}{dz} \tag{21}$$

Similarly, the combination of Eqs. (1) and (20) results in

$$C_{B,2} - C_{B,1} = (H/4V_F) + (K/V_F)\frac{dC}{dz} \tag{22}$$

The integration of Eqs. (21) and (22) from the bottom ($z = -L/4$) to the top ($z = L/4$) of the second column satisfies the boundary conditions:

$$C = C_{B,2} \text{ at } z = -L/4 \text{ (the bottom of second column)} \tag{23}$$

$$C = C_{T,2} \text{ at } z = L/4 \text{ (the top of second column)} \tag{24}$$

are

$$C_{T,2} - C_{B,2} = \left(\frac{V_F L}{2K}\right)[(C_{T,1} - C_{T,2}) - (H/4V_F)] \tag{25}$$

$$C_{T,2} - C_{B,2} = \left(\frac{V_F L}{2K}\right)[(C_{B,2} - C_{B,1}) - (H/4V_F)] \tag{26}$$

The addition of Eqs. (25) and (26) using Eq. (17) gives the equation for calculating the degree of deuterium recovery in a double-column device as

$$\Delta_d = C_{B,2} - C_{T,2} \tag{27}$$

$$= \frac{(H/2V_F) + \Delta_{d-1}}{1 + (4K/V_F L)} \tag{28}$$

2.4. Triple-column device with uniform column height L/3

The equation for the concentration difference in the first column of the triple-column device (Fig. 3) is readily obtained by modifying Eq. (16) with Δ_S and L replaced by Δ_{t-1} and $L/3$, respectively

$$\Delta_{t-1} = C_{B,1} - C_{T,1} \tag{29}$$

$$= \frac{H}{2V_F}(1 - e^{-V_F L/6K}) \tag{30}$$

The equation for the second column is modified from Eq. (28) with $L/2$, Δ_{d-1} and Δ_d replaced by $L/3$, Δ_{t-1} and Δ_{t-2}, respectively

$$\Delta_{t-2} = C_{B,2} - C_{T,2} \tag{31}$$

$$= \frac{(H/2V_F) + \Delta_{t-1}}{1 + (6K/V_F L)} \tag{32}$$

Making the material balances for deuterium at the top and bottom ends of the third column, respectively, one has

$$\sigma C_{T,2} = (-\tau) + \sigma C_{T,3} \tag{33}$$

$$\sigma C_{B,3} = (-\tau) + \sigma C_{B,2} \tag{34}$$

Substituting Eq. (1) into Eqs. (33) and (34) to eliminate τ and then integrating, subject to the following boundary conditions for the third column:

$$C = C_{B,3} \text{ at } z = -L/6 \text{ (the bottom of third column)} \tag{35}$$

$$C = C_{T,3} \text{ at } z = L/6 \text{ (the top of third column)} \tag{36}$$

one has the degree of deuterium recovery in a triple-column device by following the same procedure from Eq. (19) through Eq. (28). The result is

$$\Delta_t = C_{B,3} - C_{T,3} \tag{37}$$

$$= \frac{(H/2V_F) + \Delta_{t-2}}{1 + (6K/V_F L)} \tag{38}$$

3. Numerical calculation

3.1. Numerical example

The experimental data obtained by Arita et al. [13] for the separation of the H–D gas mixture in a continuous-type cryogenic-wall thermal diffusion column will be employed to predict the deuterium recovery in the multi-column devices with a fixed total sum of column heights ($L = 300, 600$ and 900 cm). The apparatus used consists of a stainless steel column 2.97 cm inside diameter ($2R_2$) as the cold wall, inserted concentrically with a tungsten wire 0.05 cm in diameter ($2R_1$) as a heater. The stainless steel column and the tungsten wire may be considered as the outer and inner tubes, respectively, of a concentric-tube thermal diffusion column. The effective heat length was 150 cm. The feed with unity atomic ratio of H and D (mass fraction of deuterium $C_F = 2/(1 + 2) = 2/3$) was introduced. The heater temperature was 1273 K, while the cold wall was cooled using liquid nitrogen with the temperature under the operating pressures (P) of 26.36, 33.18, 40 and 53.18 kPa. The transport coefficients H and K, for deuterium were determined [14] by using the experimental data of Arita et al.'s

Table 1
Transport coefficients of deuterium in H_2–HD–D_2 system [14].

P (kPa)	26.36	33.18	40	53.18
H (cm3/min)	39.506	66.254	137.66	152.74
K (cm4/min)	1621	3504	10,300	15,085

Table 2
Comparison of deuterium recoveries in single-column, double-column and triple-column devices: (a) $L = 300$ cm; (b) $L = 600$ cm; (c) $L = 900$ cm.

V_F (cm³/min)	26.36 kPa			33.18 kPa			40 kPa			53.18 kPa		
	Δ_s	Δ_d	Δ_t	Δ_s	Δ_d	Δ_t	Δ_s	Δ_d	Δ_t	Δ_s	Δ_d	Δ_t
(a)												
100	0.198	0.987	0.562	0.327	0.425	0.396	0.528	0.440	0.327	0.481	0.353	0.251
200	0.098	0.195	0.289	0.166	0.267	0.299	0.325	0.361	0.305	0.330	0.310	0.242
400	0.049	0.098	0.146	0.083	0.148	0.190	0.172	0.249	0.253	0.187	0.237	0.216
(b)												
100	0.198	0.391	0.577	0.331	0.533	0.598	0.642	0.720	0.605	0.659	0.621	0.485
200	0.099	0.197	0.292	0.166	0.297	0.380	0.341	0.498	0.502	0.375	0.473	0.433
400	0.049	0.099	0.147	0.083	0.157	0.216	0.172	0.291	0.350	0.191	0.302	0.333
(c)												
100	0.198	0.392	0.580	0.331	0.573	0.663	0.680	0.891	0.836	0.725	0.812	0.690
200	0.099	0.197	0.293	0.166	0.307	0.400	0.344	0.560	0.627	0.381	0.558	0.569
400	0.049	0.099	0.147	0.083	0.159	0.222	0.172	0.309	0.397	0.191	0.327	0.394

Table 3
Improvement of deuterium recoveries in multi-column devices: (a) $L = 300$ cm; (b) $L = 600$ cm; (c) $L = 900$ cm.

V_F (cm³/min)	26.36 kPa		33.18 kPa		40 kPa		53.18 kPa	
	I_d (%)	I_t (%)	I_d (%)	I_t (%)	I_d (%)	I_t (%)	I_d (%)	I_t (%)
(a)								
100	95.77	184.50	30.10	21.32	−16.67	−38.07	−26.60	−47.88
200	97.86	192.08	61.04	80.60	11.08	−6.15	−5.84	−26.48
400	98.93	195.99	79.07	129.66	44.77	47.09	26.34	15.53
(b)								
100	7.86	192.08	61.04	80.60	12.11	−5.76	−5.84	−26.48
200	98.93	195.99	79.07	129.66	46.04	47.21	26.34	15.53
400	99.46	197.99	88.96	161.02	69.19	103.49	58.38	74.42
(c)								
100	98.57	193.63	72.91	100.05	31.03	22.94	11.93	−4.80
200	99.28	196.79	85.55	141.51	62.79	82.27	46.37	49.42
400	99.64	198.39	92.59	168.09	79.65	130.81	71.07	106.42

work [13]. Some values for various operating pressures are listed in Table 1.

3.2. Results and discussion

The degrees of deuterium recovery in single-column, double-column and triple-column devices with fixed total sum of column heights (L), were calculated from the appropriate equations with various operating pressures and volumetric flow rates. The results are listed in Table 2. From this table, the degree of recovery increases when the total sum of column heights increases, while as the volumetric flow rate decreases. The best recoveries for larger L were obtained under operating pressures of 40 kPa. The order of operating pressures for better recovery is 40 kPa, 53.18 kPa, 33.18 kPa and 26.36 kPa.

The improvement in performance by operating with multi-column devices is best illustrated using the calculated percentages of increased performance based on the single-column device:

$$I_d = \frac{\Delta_d - \Delta_s}{\Delta_s} \tag{39}$$

$$I_t = \frac{\Delta_t - \Delta_s}{\Delta_s} \tag{40}$$

The results are listed in Table 3 and Fig. 4. This table shown that considerable improvements, I_d and I_t, can be achieved if the deuterium recovery from the H_2–HD–D_2 system by thermal diffusion is operated using multi-column devices, instead of a single-column device, of same total sum of column heights. A larger value for the column number is needed for better recovery for higher value of volumetric flow rate V_F, as well as for a larger total sum of column heights (L). Further, the improvements in recovery, I_d and I_t, increase when V_F or L increases. The order of operating pressures for better improvement recovery is 23.36 kPa, 33.18 kPa, 53.18 kPa and 40 kPa, which is the opposite order for operating pressures for better recoveries, Δ_s, Δ_d and Δ_t. This fact is evident because the higher-separation operation has smaller room for improvement. For the case of smaller volume flow rate and smaller total sum of column heights, say $V_F = 100$ cm³/min and $L = 300$ cm, we even obtain the minus sign of improvements for higher-pressure operation, as shown in Table 3 and Fig. 4. In this typical case, the single-column device is rather suggested to be employed.

Actually, when thermal diffusion is operated in a single-column device, increasing the column height, h (=L), increases the effective separation section of the device, leading to an increased degree of separation,

$$\Delta_s \text{ i.e. } \frac{d\Delta_s}{dL} = \frac{HK}{(V_F + 2K)^2} > 0 \tag{41}$$

However, the increment of Δ_s by increasing L has a limiting value, i.e.

$$\frac{d}{dL}\left(\frac{d\Delta_S}{dL}\right) = -\frac{2HKV_F}{(V_F + 2k)^3} < 0 \tag{42}$$

Taking the case of $P = 26.36$ kPa and $V_F = 400$ cm³/min for instance, $\Delta_s = 0.049$ for $L = 300$–900 cm. Therefore, the multi-column devices should be employed for a higher flow-rate operation.
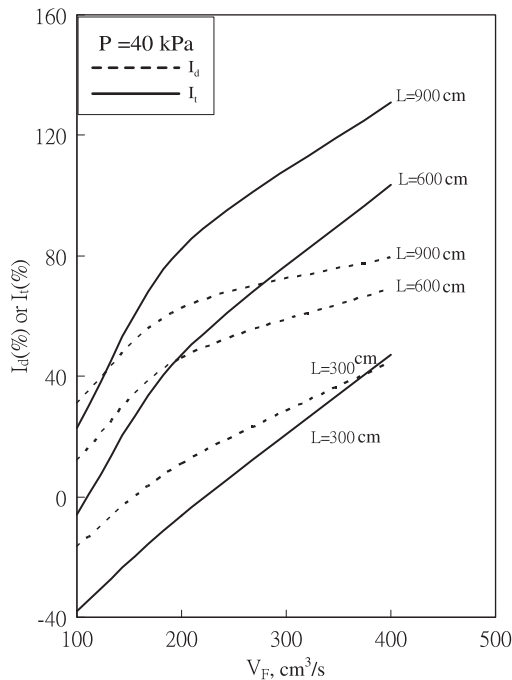
Fig. 4. Comparison of I_d and I_t at $P = 40$ kPa with various L and V_F.

4. Conclusion

The equations for predicting the deuterium recovery from the H_2–HD–D_2 system using thermal diffusion in single-column, double-column and triple-column devices with a fixed total sum of column heights, have been derived. They are Eqs. (16), (28), and (38), respectively. The most important assumption is that the concentrations are under locally-equilibrium at every point in the column, i.e. $H_2 + D_2 \leftrightarrow 2HD$. The degrees of deuterium recovery (Δ_s, Δ_d and Δ_t) were predicted numerically using the transport coefficients, H and K, determined in the previous work [14] using the

experimental data of Arita et al. [13]. Some of the H and K values for various operating pressures are listed in Table 1, while the degrees of deuterium recovery (Δ_s, Δ_d and Δ_t) for various operating pressures and volumetric flow rates are given in Table 2. The improvement in separation by operating multi-column devices was also calculated based on the recovery in a single-column device. The results are presented in Table 3. These tables show that considerable improvement in performance can be achieved if a multi-column device is used, instead of single-column device of same total sum of column heights, especially for the case of higher flow-rate operation and larger total column heights. The reason for that is because when obtaining a larger production rate (higher flow-rate operation), the total separation section in a thermal diffusion column should be longer. Because the separation efficiency increment by increasing the effective separation section in a single-column has a limited value, in this case, therefore, a multi-column device should be employed for improved performance.

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