Improvement in Enrichment of Heavy Water from Water-Isotopes Mixture in Flat-Plate Thermal-Diffusion Columns with Optimal Plate Spacing

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Abstract

The optimun plate spacings for maximum separation, maximum production rate and minimum column length in a flat-plate thermal diffusion column for the improvement in separation of heavy water (D_2O) from water – isotopes mixture (H_2O-HDO-D_2O) have been determined. Considerable improvement in performance is obtainable if the plate spacing is suitably adjusted. The appropriate temperature differences between two vertical plates of a thermal diffusion column for keeping the total expense fixed are also delineated.

***Key Words*:** Heavy Water, Thermal Diffusion, Plate Spacing

1. Introduction

Thermal diffusion process is one of the feasible methods for separation of isotope mixtures. For separation of hydrogen isotopes, this method is particularly attractive because of the large ratio in molecular weights [1–3]. The first complete presentation of the separation theory of thermal diffusion was that of Furry and coworkers [4,5]. The enrichment of heavy water by thermal diffusion was studied both theoretically and experimentally [6–8].

It was great achievement of Clusius and Dickel [1,2] to point out that a horizontal temperature gradient produces not only thermal diffusion in the direction of the temperature gradient, but also natural convection of the fluid upward near the hot surface and downward near the cold surface. These convective currents produce a cascading effect analogous to the multistage effect of a countercurrent extraction, and as a result a considerably greater separation may be obtained.

In addition to the desirable cascading effect, the convective currents arisen due to the density difference in a Clusius-Dickel column also produce an undesirable remixing effect [1,2,9]. Therefore, proper control of the convective strength might effectively suppress this undesirable remixing effect while still preserving the desirable cascading effect, and thereby lead to improved separation. One of the feasible ways for properly controlling the convective strength is suitably adjusting the plate spacing [10]. It is the purpose of this work to investigate the effect of plate spacing on the improvement in performance for separation of heavy water from water-isotopes mixture in flat-plate thermal-diffusion columns with total expense fixed.

2. Separation Equations

We will first review an analysis of the enrichment of heavy water (D_2O) from water-isotopes mixture (H_2O-HDO-D_20) in a continuous thermal-diffusion column previously made by Yeh et al. [6–8]. A schematic representation of the thermal diffusion process under consideration is given in Figure 1. As shown in this figure, an applied temperature gradient between the two prarllel

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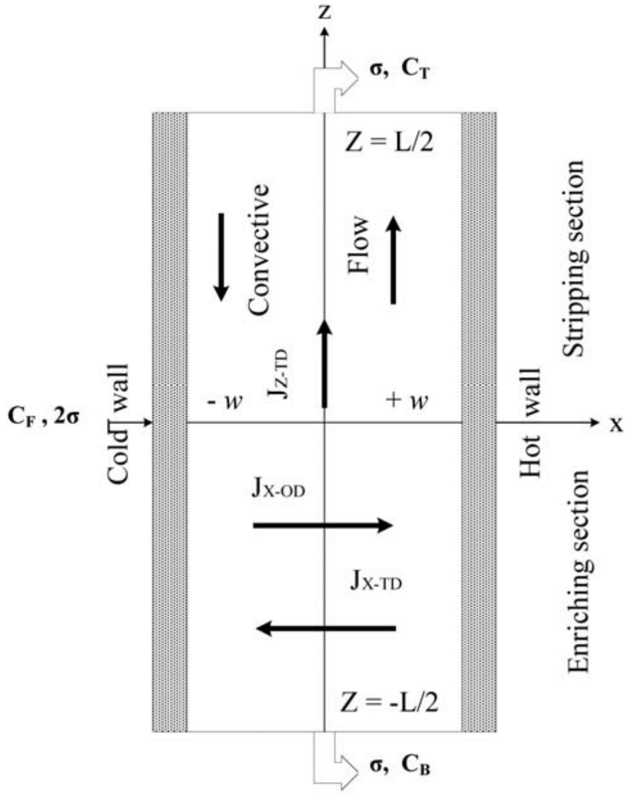

Figure 1. Flows and fluxes in a flat-plate thermal-diffusion column.

plates results in a D_2O flux, $J_{x\text{-TD}}$, moving toward the cold plate by thermal duffusion, setting up natural convective current parallel to the plate due to density difference. There are also two ordinary-diffusion fluxes, $J_{X,OD}$, and $J_{Z,OD}$, compensating the thermal-diffusion and convective mass-transfer effects.

Accordingly, the equation of separation for enrichment of heavy water from water-isotopes mixture was obtained from momentum, heat and mass balances. The degree of separation is [6–8]

$$\Delta = C_B - C_T = \frac{2A(-H)}{\sigma}\left[1-\exp\left(-\frac{\sigma L}{2K}\right)\right] \tag{1}$$

where C_B and C_T denote the fractional mass concentrations of heavy water in the bottom and top products, respectively, σ is the feed flow rate, and L is column length, while

$$H = \frac{\alpha\bar{\rho} g\bar{\beta}_T B(2w)^3(\Delta T)^2}{6!\mu\bar{T}} < 0 \tag{2}$$

$$(\because \sigma < 0 \text{ for } H_2O\text{-}HDO\text{-}D_2O \text{ system})$$

$$K = \frac{\bar{\rho} g^2\bar{\beta}_T^2 B(2w)^7(\Delta T)^2}{9!\mu^2 D} \tag{3}$$

$$A = C_F\{0.05263 - (0.052630 - 0.0135K_{eq})\,C_F - 0.027\{C_F K_{eq}\,[1 - (1 - 0.25K_{eq})\,C_F]\}^{1/2}\} \tag{4}$$

in which C_F is the fractional mass concentration of heavy water in the feed stream. The meanings of the other symbols are given in the nomenclature.

The most important assumptions for obtaining above results were that since in general the feed and withdrawal rates are extremely slow, the total reflux is ignored, and that the concentrations of water isotopes are locally in equilibrium at every point in the Clusius-Dickel column, i.e.

$$H_2O + D_2O \Leftrightarrow 2HDO \tag{5}$$

with the equilibrium constant defined as

$$K_{eq} = \frac{[HDO]^2}{[H_2O][D_2O]} = 3.793\ (\bar{T} = 30.5\ °C) \tag{6}$$

These facts were confirmed experimentally in the previous work [6].

3. Optimum Plate Spacing for Best Performance

The plate spacing ($2w$) in a flat-plate thermal-diffusion column is general so small that changing it will not cause any additional fixed charge. The expenditure of making a separation by thermal diffusion essentially includes two parts: a fixed charge and an operating expense. The fixed charge is roughly proportional to the equipment cost, while the operating expense is chiefly heat. The heat-transfer rate is obtainable from the expression, $kBL/(\Delta T/2w)$. Based on these terms, we shall take account of the influence of plate-spacing change on the enrichment of heavy water, the output and the column length with the consideration of fixed operating expense (i.e. $\Delta T/2w$ is constant, where ΔT denotes the temperature difference between the two vertical plates).

For this purpose, Eq. (1) is better rewritten with the use of Eqs. (1)–(3) as

$$\Delta_D = \frac{2\text{A}a(2w)^5}{\sigma}\left[1-\exp\left\{\frac{-\sigma L}{2b(2w)^9}\right\}\right] \tag{7}$$

where a and b are constants defined as

$$a = \frac{(-\alpha)\bar{\rho}\,\bar{\beta}_T gB(\Delta T/2w)^2}{6!\mu\bar{T}} = (-H)/(2w)^5 \tag{8}$$

$$b = \frac{\bar{\rho}\,\bar{\beta}_T^2 g^2 B(\Delta T/2w)^2}{9!\mu^2 D} = K/(2w)^9 \tag{9}$$

3.1 Maximum Separation

The optimum plate spacing $(2w)_\Delta$ for a maximum separation $\Delta_{\max}$ with the production rate fixed, is obtained by partially differentiating Eq. (7) with respect to $(2w)$ and setting $\partial\Delta/\partial(2w)$. After differentiation and simplification we obtain

$$e^X = 1+\frac{9}{5}X \tag{10}$$

$$X = \frac{\sigma L}{2b(2w)_\Delta^9} = 1.08 \tag{11}$$

Solving for $(2w)_\Delta$, one obtains the optimum plate spacing for maximum separation as

$$(2w)_\Delta = \left(\frac{\sigma L}{2.16b}\right)^{1/9} \tag{12}$$

Consequently, the maximum recovery may be obtained from Eq. (4) by substitution of Eq. (12). The result is

$$\Delta_{\max} = 0.86(\text{A}a/\sigma)(\sigma L/b)^{5/9} \tag{13}$$

It should be noted from Eqs. (12) and (13) that whereas $\Delta_{\max}$ depends on the thermal diffusion constant α, $(2w)_\Delta$ is independent of α. The problem of finding the maximum separation and optimum plate spacing for a specified flow rate σ can readily be estimated by using Eqs. (12) and (13) since a, b, and L are known constants for a given column and system.

3.2 Maximum Output

The plate spacing for maximum separation of heavy water $\Delta_{\max}$ with σ fixed is also the plate spacing required to obtained the maximum production rate $\sigma_{\max}$ for given column which is to give a specified value of Δ. Although Eq. (4) cannot be put into a form explicit in σ, it is nevertheless possible to maximize σ with respect to (2w) at constant Δ and L. The maximization yields an expression which is identical to that given by Eqs. (12) and (13) when σ is represented by $\sigma_{\max}$ and when $\Delta_{\max}$ is replaced by Δ, as well as when $(2w)_\Delta$ is replaced by $(2w)_\sigma$ The results are

$$(2w)_\sigma = (\sigma_{\max} L/2.16b)^{1/9} \tag{14}$$

$$\sigma_{\max} = 0.71(\text{A}a/\Delta_D)^{9/4}(L/b)^{5/4} \tag{15}$$

It may be more convenient to eliminate $\sigma_{\max}$ in Eq. (14) by substitution of Eq. (15), i.e.

$$(2w)_\sigma = 0.88(\text{A}aL/b\Delta_D)^{1/4} \tag{16}$$

3.3 Minimum Column Length

To find the minimum column length $L_{\min}$ required to accomplish the specified values of Δ and σ, we rearrange Eq. (4) into a form explicit in the column length

$$L = \frac{-2b(2w)^9}{\sigma}\ln\left[1-\frac{\sigma\Delta_D}{2\text{A}a(2w)^5}\right] \tag{17}$$

Minimization of L with respect to (2w) at constant Δ and σ yields an expression identical with Eq. (10). Therefore, the solution for this optimum condition is identical with Eqs. (12) and (13) when L is replaced by $L_{\min}$ and when $\Delta_{\max}$ is replaced by Δ, as well as when $(2w)_\Delta$ is replaced by $(2w)_L$. The results are

$$(2w)_L = (\sigma L_{\min}/2.16b)^{1/9} \tag{18}$$

$$L_{\min} = 1.31(\text{A}\Delta_D/\text{A}a)^{9/5}(b/\sigma) \tag{19}$$

Similarly, Eq. (18) may be rewritten, with the use of Eq. (19), as

$$(2w)_L = 0.946(\text{A}\Delta_D/\text{A}a)^{1/5} \tag{20}$$

4. The Improvement in Performance

4.1 Numerical Example

The improvement in performance resulting from operating at the optimum plate spacing with fixed operating expense may be illustrated numerically by using the experimental data of previous work [6]. The conditions are: water-isotopes mixture (H_2O-HDO-D_2O system); $\Delta T = 47 - 14 = 33$ °C, $\overline{T} = 30.5$ °C, (2w) = 0.016 in. = 0.0406 cm, L = 177 cm, B = 10 cm, $-H = 1.47 \times 10^{-4}$ g/s = 0.53 g/h, $K = 1.549 \times 10^{-3}$ g cm/s = 5.58 g cm/h, K_{eq} = 3.793 at 30.5 °C, $a = 4.807 \times 10^{6}$ g/cm^3 h, $b = 1.86 \times 10^{13}$ g/cm^8 h, $\Delta T/2w = 751.23\ K/cm$. A = 0.359 ($C_F = 0.1$), 0.709 ($C_F = 0.3$), 0.761 ($C_F = 0.5$), 0.591 ($C_F = 0.7$), 0.237 ($C_F = 0.9$).

4.2 Result and Discussion

The improvement in separation of heavy water by operating at the optimum plate spacing $(2w)_\Delta$ is best illustrated by calculating the percentage increase in separation based on the specified column with 2w = 0.0406 cm, which was employed in previous experimental work [6]

$$I_D = \frac{\Delta_{\max} - \Delta_O}{\Delta_O} \tag{21}$$

Similarly, the improvement in output and column length may be defined as

$$I_\sigma = \frac{\sigma_{\max} - \sigma_O}{\sigma_O} \tag{22}$$

$$I_L = \frac{L_O - L_{\min}}{L_{\min}} \tag{23}$$

where Δ_o, σ_o and L_o are the performance obtained in the specified column with 2w = 0.0406 cm.

From the numerical values, the optimum plate spacings [$(2w)_\Delta$, $(2w)_\sigma$, $(2w)_L$] and the corresponding performances ($\Delta_{\max}$, $\sigma_{\max}$, $L_{\min}$, I_Δ, I_σ, I_L), as well as performances obtained in the specified column (2w = 0.0406 cm), are calculated from the appropriate equations. The results are shown in Tables 1–3.

It is seen in Table 1 that the degrees of separation increases when the flow rate decreases, while the best feed concentration exists at $C_F = 0.5$. The comparison of separation, $\Delta_{\max}$ and Δ, obtainable at the optimum corresponding plate spacing $(2w)_\Delta$ and at (2w) = 0.0406 cm, respectively, under various flow rates and feed concentrations, is also shown in Table 1. It is seen from this table as well as from Eq. (12) that the optimum plate spacing for maximum separation though is independent of

Table 1. Comparison of the degree of separation obtained at $(2w)_\Delta$ and at (2w) = 0.0406 cm

C_F	σ (g/h)	Δ_O/A	Δ_O (%)	$(2w)_\Delta$ (cm)	$(\Delta T)_\Delta$ (K)	$\Delta_{\max}$ (%)	I_Δ (%)
0.1	0.01	15.56	5.586	0.0328	24.64	8.656	55
0.1	0.02	14.42	5.177	0.0354	26.59	6.360	23
0.1	0.04	12.46	4.473	0.0383	28.77	4.675	5
0.1	0.08	9.54	3.425	0.0413	31.03	3.436	0
0.3	0.01	15.56	11.032	0.0328	24.64	17.09	55
0.3	0.02	14.42	10.227	0.0354	26.59	12.564	23
0.3	0.04	12.46	8.834	0.0383	28.77	9.229	5
0.3	0.08	9.54	6.759	0.0413	31.03	6.786	0
0.5	0.01	15.56	11.841	0.0328	24.64	18.351	55
0.5	0.02	14.42	10.974	0.0354	26.59	13.486	23
0.5	0.04	12.46	9.482	0.0383	28.77	9.908	5
0.5	0.08	9.54	7.260	0.0413	31.03	7.280	0
0.7	0.01	15.56	9.196	0.0328	24.64	14.246	55
0.7	0.02	14.42	8.522	0.0354	26.59	10.469	23
0.7	0.04	12.46	7.364	0.0383	28.77	7.693	5
0.7	0.08	9.54	5.638	0.0413	31.03	5.658	0
0.9	0.01	15.56	3.688	0.0328	24.64	5.718	55
0.9	0.02	14.42.	3.418	0.0354	26.59	4.196	23
0.9	0.04	12.46	2.953	0.0383	28.77	3.089	5
0.9	0.08	9.54	2.261	0.0413	31.03	2.269	0

feed concentration, but decreases with the flow rate and, therefore, the temperature difference $(\Delta T)_\sigma$ between two vertical plates needed to fix operating cost, also decreases. The improvement in recovery I_Δ is really obtained, especially for low flow-rate operation. The improvement in recovery can reach 55% as $\sigma = 0.01$ g/h.

Table 2 shows that the product rates decrease when the degree of separation increases. The comparison of production rates, σ_{max} and σ, obtainable at the optimum corresponding plate spacing $(2w)_\sigma$ and at (2w) = 0.0406 cm, respectively, under various feed concentrations and separation values of Δ is also presented in Table 2 It is shown in this table as well as in Eq. (16) that the optimum plate spacing, as well as$(\Delta T)_\sigma$, for maximum production rate decreases when the specified recovery (Δ/A) increases. The improvement in production rate I_σ is really obtained, especially for higher value of (Δ/A). The improvement in production rate is higher than 170% as $\Delta/A > 15.56$.

Table 3 illustrates the minimum column length L_{min} and the corresponding optimum plate spacing $(2W)_L$ under various flow rates, feed concentrations and specified values of Δ. It is seen from this table and Eq. (20) that the optimum plate spacing, as well as $(2W)_L$, for minimum column length decreases when the specified value of ($\sigma\Delta$/A) decreases. The improvement in column length I_L is really obtained, especially for low value of ($\sigma\Delta$/A). I_L is high as 120% when $(\Delta/A) = 15.56$ and $\sigma = 0.07\sigma$.

It is also shown in Tables 1–3 that the optimum plate spacings $[(2w)_\Delta, (2w)_\sigma, (2w)_L]$ decreases while the improvements in performance $(I_\Delta, I_\sigma, I_L)$ increases. Although the plate spacing in a thermal diffusion column is generally so small that changing (2w) will not cause any additional or deductible fixed charge. However, decreasing (2w) will also lead to decreasing the suitable temperature differences $[(\Delta T)_\Delta, (\Delta T)_\sigma, (\Delta T)_L]$ between two vertical plates of the column in order to maintain the operating cost $(\alpha\Delta T/2w)$ constant and, therefore, some operating cost may be deducted to maintain the lower temperature differences. The appropriate temperature differences for maintaining the constant values of $(\Delta T/2w)$ are also listed in the tables.

5. Conclusion

The equations which may be employed to predict the optimum plate spacing for recovery of deuterium from water-isotopes mixture in a flat-plate thermal-diffusion column, have been derived. They are Eqs. (12) and (13) for the maximum separation, Eqs. (15) and (16) for the maximum production rate, and Eqs. (19) and (20) for minimum column. The improvement in performance was illustrated by employing the experimental data obtained in previous work, and the results are presented in Tables 1–3.

It has been shown in these tables that substantial improvement in performances for enrichment of heavy water from water-isotopes mixture in a flat-plate thermal diffusion column can be achieved if the plate spacing is suitably adjusted. Since changing plate spacing (2w) will also lead to change the difference of plate temperatures ΔT in order to maintain the operating cost $(kBL\Delta T/2w)$ constant, the appropriate values of ΔT for such purpose are also presented in Tables 1–3.

Table 2. Comparison of production rates obtained at $(2w)_\sigma$ and at (2w) = 0.0406 cm

Δ/A	σ_o (g/h)	$(2w)_\sigma$ (cm)	$(\Delta T)_\sigma$ (K)	σ_{max} (g/h)	I_σ (%)
15.56	0.01	0.0364	27.34	0.027	170
14.42	0.02	0.0371	27.87	0.032	60
12.46	0.04	0.0385	28.92	0.044	10
9.54	0.08	0.0423	31.78	0.080	0

Table 3. Comparison of column length obtained at $(2w)_L$ and at (2w) = 0.0406 cm

Δ/A	σ (g/h)	L_0 (cm)	$(2w)_L$ (cm)	$(\Delta T)_L$ (K)	L_{min} (cm)	I_L (%)
15.56	0.07	177	0.0300	22.54	80.36	120
14.42	0.02	177	0.0340	25.54	121.99	45
12.46	0.04	177	0.0379	28.47	163.30	8
9.54	0.08	177	0.0413	31.03	175.82	0

Nomenclature

a	constant defined by Eq. (8), g/cm^5s
B	column width cm
b	constant defined by Eq. (9), g/cm^8s
C	fractional mass concentration of heavy water
C_B, C_T	C in the product streams exiting from bottom end, from top end
C_F	C in feed stream
A	pseudo-production form of concentration for D_2O defined in Eq. (4)
D	mass diffusivity, cm^2/s
g	gravitational acceleration, cm/s^2
H	transport coefficient defined by Eq. (2), g/s
I_D, I_σ, I_L	improvement in performances defined by Eqs. (21)–(23)
$J_{x,od}$, $J_{X,TD}$	mass flux in x direction due to ordinary diffusion, thermal diffusion, g/m^2s
$J_{Z,OD}$	mass flux in z direction due to ordinary diffusion, g/m^2s
L	column length, cm
L_{min}	minimum value of L, cm
L_0	L obtained in a column with 2w specified, cm
K	transport coefficient defined by Eq. (3), g cm/s
K_{eq}	mass fractional equilibrium constant of H_2O-HDO-D_2O system
$\overline{T}$	average absolute temperature of fluid, K
ΔT	temperature difference between hot and cold surfaces, K
$(\Delta T)_\Delta$, $(\Delta T)_{2w}$, $(\Delta T)_L$	ΔT for the best performances, K
z	axis parallel to the transport direction, cm

Greek Letters

α	reduced thermal diffusion constant, < 0
$\overline{\beta}$	$-(1/\rho)(\partial\rho/\partial T)$ evaluated at $\overline{T}$, 1/K
Δ_i	$C_B - C_T$, degree of separation for heavy water
Δ_{max}	maximum value of Δ
Δ_0	Δ obtained in a column with 2w specified
2w	plate spacing of the column, cm
$(2w)_\Delta$, $(2w)_\sigma$, $(2w)_L$	optimal value of (2w) for Δ_{max}, for σ_{max}, for L_{min}, cm
σ	mass flow rate, g/s
σ_{max}	maximum value of σ, g/s
σ_0	σ obtained in a column with 2w specified, g/s
$\overline{\rho}$	fluid density at $\overline{T}$, g/cm^3
μ	fluid viscosity, cP

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