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Experimental Studies on the Separation of Deuterium Oxide in Continuous Thermal Diffusion Column for Low Concentration Range

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Abstract

Separation equations for the enrichment of heavy water in a continuous-flow thermal diffusion column have been derived for low-concentration operations. Experimentals on two feed concentrations of the H_2O-HDO-D_2O system have also been conducted, and the results quantitatively confirm the predictions of theory.

INTRODUCTION

The application of the principle of thermal diffusion to the practical separation of isotopes was devised by Clusius and Dickel (*1, 2*). In World War II, thermal diffusion was used to separate uranium isotopes at Oak Ridge Laboratory. Anderson and Libby applied the technique to the enrichment of ^{14}C in sewage methane in 1947 (*3*). For the separation of hydrogen isotopes, this method is effective because of the large ratio in molecular weights (*4, 5*).

It has been shown that heavy water can be concentrated in a thermal diffusion column (*1, 2, 6, 7*). The enrichment of heavy water in a batch-type thermal diffusion column has been studied both theoretically and experimentally by the present authors (*8*). It is the purpose of this work to investigate both theoretically and experimentally the continuous-throughput rectification of D_2O with a thermal diffusion column in the low concentration range.

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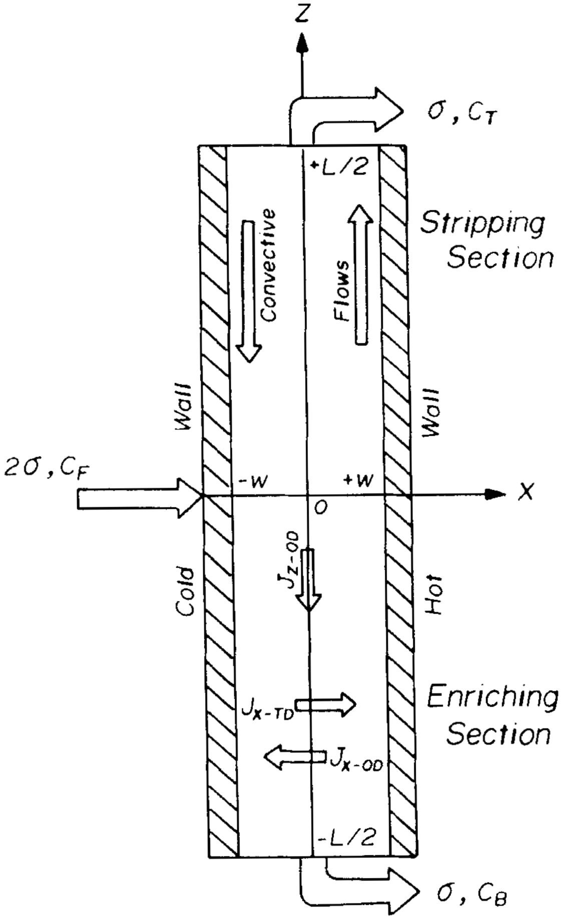

FIG. 1. Schematic diagram of the Clusius-Dickel column.

SEPARATION THEORY

The separation theory of thermal diffusion for a multicomponent isotopic liquid mixture in a Clusius-Dickel column was presented by Jones, Furry, and Onsager (*9–12*). Figure 1 illustrates the flows and fluxes prevailing in a continuous flow column. By integrating the transport equations or modifying from previous results, two ordinary differential equations for D_2O under steady continuous operation were obtained:

$$\tau = \sigma c_T = \sigma c + H_0 c\hat{c} - K \frac{dc}{dz} \tag{1}$$

for the stripping section and

$$\tau = -\sigma c_B = -\sigma c + H_0 c\hat{c} - K \frac{dc}{dz} \tag{2}$$

for the enriching section. The transport constants are defined by

$$H_0 = \alpha_0 \bar{\rho} g \bar{\beta}_T (2\omega)^3 (\Delta T)^2 / 6!\mu \bar{T} \tag{3}$$

$$K = \bar{\rho} g^2 \bar{\beta}_T^2 (2\omega)^7 B (\Delta T)^2 / 9!\mu^2 D + 2\omega \bar{\rho} D B \tag{4}$$

and the pseudoconcentration product, $c\hat{c}$, for low concentration is

$$c\hat{c} = c[0.05263 - (0.05263 - 0.0135K_{\text{eq}})c - 0.027c^{1/2}K_{\text{eq}}^{1/2}] \tag{5}$$

where α_0, the reduced thermal diffusion constant, is the same for all isotopic pairs.

The assumptions made in obtaining the above results were that the concentrations were locally in equilibrium at every point in the column, that the flow rates were the same in both the enriching and stripping sections, and that physical properties were constant. In addition, only low concentration heavy water was considered in this study.

The pseudoproduct form of concentration dependence of the thermal diffusion effect defined by Eq. (5) could be approximated by a straight line within the low-concentration range

$$c\hat{c} \approx a + bc \tag{6}$$

in which

$$\begin{aligned} b &= \frac{d}{dc}(c\hat{c})|c = c_F \\ &= 0.05263 - (0.10526 - 0.027K_{\text{eq}})c_F - 0.0405K_{\text{eq}}^{1/2}c_F^{1/2} \end{aligned} \tag{7}$$

$$\begin{aligned} a &= c_F\hat{c}_F - bc_F \\ &= (0.05263 - 0.0135K_{\text{eq}})c_F^2 + 0.0135K_{\text{eq}}^{1/2}c_F^{3/2} \end{aligned} \tag{8}$$

Consequently, Eqs. (1) and (2) can be rewritten as

$$H_0[(a + bc) - n(c_T - c)] = K\frac{dc}{dz} \tag{9}$$

$$H_0[(a + bc) + n(c_B - c)] = K\frac{dc}{dz} \tag{10}$$

where

$$n = \sigma/H_0 \tag{11}$$

The degree of separation may be obtained from Eqs. (9) and (10) associated with the boundary conditions:

$$c = c_F \qquad \text{at } z = 0 \tag{12}$$

$$c = c_T \qquad \text{at } z = L/2 \tag{13}$$

$$c = c_B \qquad \text{at } z = -L/2 \tag{14}$$

The solution is

$$\begin{aligned}\Delta &= c_B - c_T \\ &= \frac{-\Delta_a}{2bA}\left[\frac{1 - e^{bA(1-n/b)}}{e^{bA(1-n/b)} - n/b} - \frac{1 - e^{-bA(1+n/b)}}{e^{-bA(1+n/b)} + n/b}\right]\end{aligned} \tag{15}$$

where

$$\Delta_a = -2bA(c_F + a/b) \tag{16}$$

$$A = H_0L/2K \tag{17}$$

For batch operation, $c_F = c_i$, thus

$$\Delta_a = -2bA\left(c_i + \frac{a}{b}\right)\Big|_{c_F=c_i} = \Delta_b \tag{18}$$

and Eq. (15) becomes, by setting $n = 0$,

TABLE 1
Values of $(bA)^2/3!$ and $(bA)^4/5!$ at Various c_F with $A = -8.416$ and $K_{eq} = 3.793$ Taken from Previous Work (*8*)

c_F	$b \times 10^2$, Eq. (7)	$[(bA)^2/3!] \times 10^3$	$[(bA)^4/5!] \times 10^5$
0.05	3.485	14.333	6.163
0.15	2.165	5.533	0.919
0.25	1.248	1.838	0.101
0.50	−0.457	0.246	0.002
0.75	−1.782	3.746	0.421
0.95	−2.696	8.575	2.206

$$\frac{\Delta}{\Delta_b} = \frac{-1}{2bA}\left[\frac{1 - e^{bA}}{e^{bA}} - \frac{1 - e^{-bA}}{e^{-bA}}\right] = \frac{1}{2bA}\left[e^{bA} - e^{-bA}\right]$$

$$= \frac{1}{2bA}\left[2(bA) + 2\frac{(bA)^3}{3!} + 2\frac{(bA)^5}{5!} + \cdots\right]$$

$$= 1 + \frac{(bA)^2}{3!} + \frac{(bA)^4}{5!} + \cdots \tag{19}$$

Usually, $(bA)^2 \ll 1$ for the entire range as shown in Table 1. Therefore, we conclude from Eqs. (18) and (19) that

$$\Delta = \Delta_a = \Delta_b \tag{20}$$

for batch operation. In other words, Eq. (15) reduced to Eq. (26) obtained in the previous work (*8*) for batch operation ($n = 0$). Some graphical representations of Eqs. (15) and (16) are given in Figs. 2 and 3, respectively.

EXPERIMENTAL STUDIES

A concentric tube thermal diffusion column was constructed with two stainless steel tubes with an annular space of 0.016 in., for hot and cold surfaces. Hot water was circulated through the inner tube while cold water was circulated through the jacket on the outside of the outer tube. Hot and cold water were supplied from two temperature controlled tanks.

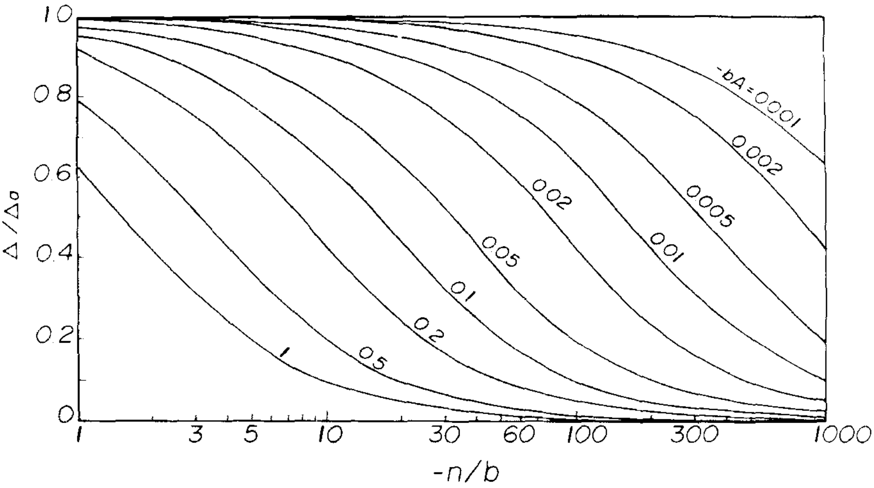

FIG. 2. Effect of flow rate on separation at various feed concentrations, Eq. (15).

The mean temperatures of the hot and cold tubes were 47 and 14°C, respectively, and thus the mean temperature of solution in the annulus was 30.5°C. The tube temperature was kept constant within ±1°C at all times.

The feed flowed steadily from a constant-head tank by gravity into the midpoint of the column. The flow rates of the two product streams were controlled by adjustable needle valves and withdrawn continuously at constant and equal rates to the accumulators. Samples of products were analyzed at 25 ± 0.05°C by an automatic density meter, model DA-101B, Kyoto Electronics Manufacturing Co., Ltd. This instrument can measure specific gravity with a precision of ±0.00001. Samples of both streams were analyzed at 30 min intervals until steady-state was reached as indicated by no change in the specific gravity reading. The flow rate was changed after each run. After the desired range of flow rates was covered, the feed concentration, c_F, was changed and new runs were carried out in the same manner.

Most of the experiments employed in this study are the same as those in Yeh and Ward's work (*13*), except that no wire spiral was inserted in the annulus. Furhter, the column dimensions and the experimental procedures performed in this study were the same as those in previous work (*8*), except that the products were withdrawn from the top and bottom of column steadily, and that the fractionating section was changed to 69.5

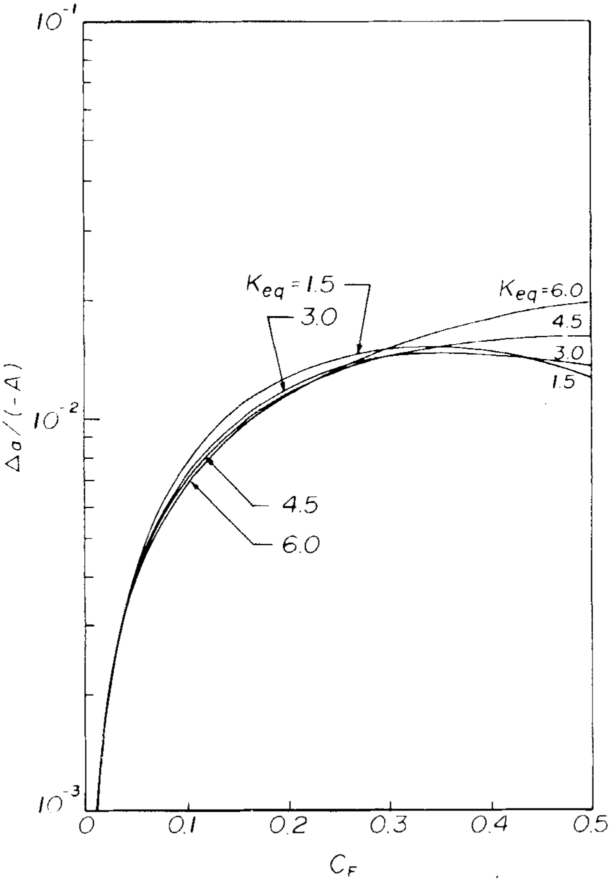

FIG. 3. Some graphical representations of Eq. (16).

in. Figure 4 shows the flow diagram of a continuous-type concentric-tube thermal diffusion column.

RESULTS AND DISCUSSION

Once the specific gravities of the products were measured, the mass % of D_2O in the products could be easily determined from the calibration curves constructed in previous work (*8*). The experimental results thus

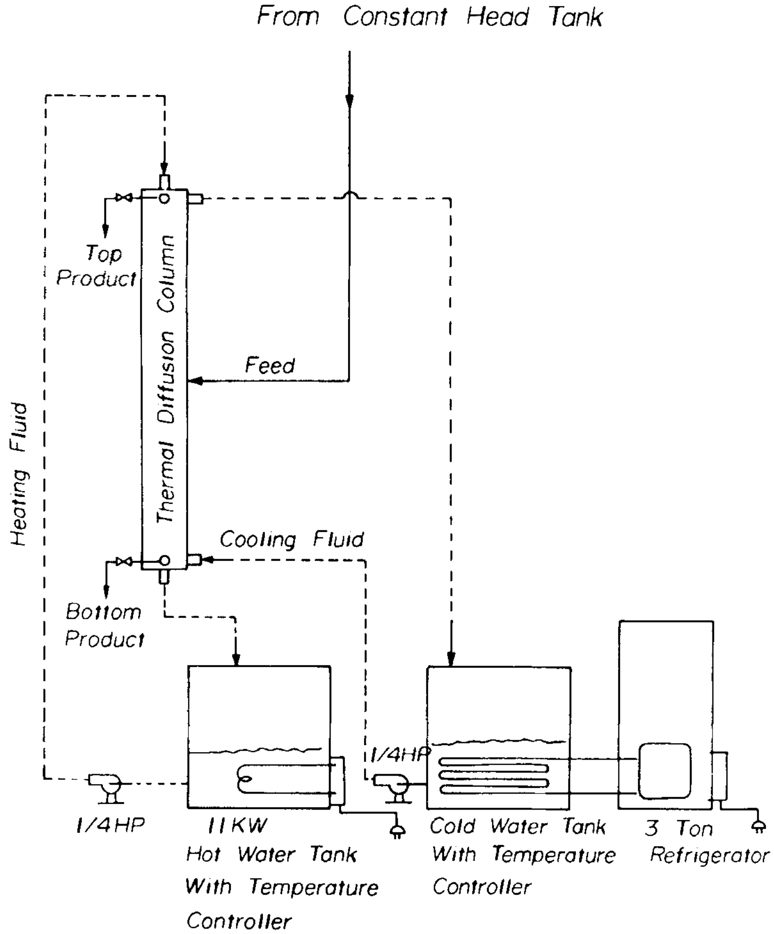

FIG. 4. Flow diagram of concentric tube thermal diffusion column.

obtained are plotted in Figs. 5 and 6. The theoretical values of separation for these two feed concentrations were calculated from Eq. (15) by using the following transport coefficients and equilibrium constant (*8*):

$$H_0 = -1.473 \times 10^{-4} \text{ g/s}$$

$$K = 1.549 \times 10^{-3} \text{ g}\cdot\text{cm/s}$$

$$K_{eq} = 3.793 \ (\bar{T} = 30.5°\text{C})$$

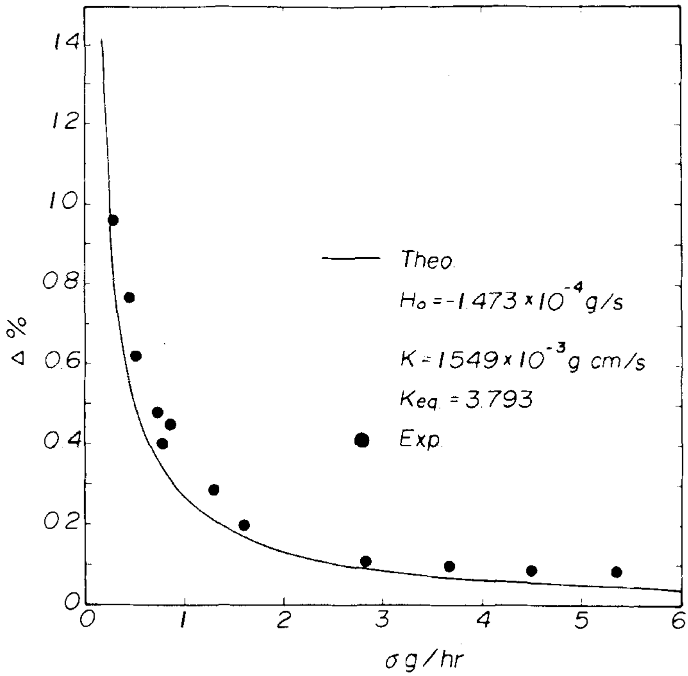

FIG. 5. Comparison of separation obtained from experimental work and theoretical equations for $c_F = 0.0650$.

and the column length

$$L = 69.5 \text{ in.} = 177 \text{ cm}$$

The theoretical results thus obtained are also plotted in Figs. 5 and 6. The experimental results are in good agreement with the prediction of theory.

CONCLUSION

On the basis of the results of this study, the following conclusions were reached.

(1) Separation equations for the enrichment of heavy water in a continuous-type thermal diffusion column have been derived. Some graphical representations are given in Figs. 2 and 3.

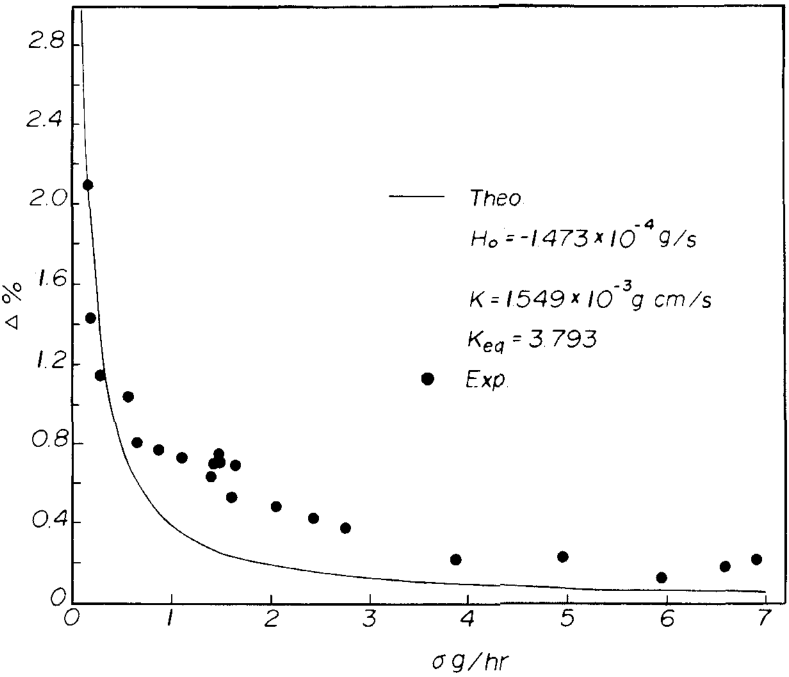

FIG. 6. Comparison of separation obtained from experimental work and theoretical equations for $c_F = 0.0995$.

(2) The most important assumption made in this work was that the concentrations were locally in equilibrium at every point in the column. A linear approximation to concentration product, $c\hat{c}$, was also made for low-concentration operations.

(3) Experimental results of H_2O-HDO-D_2O system were carried out for $c_F = 0.0650$ and 0.0995. The results quantitatively confirm the prediction of theory as shown in Figs. 5 and 6.

Acknowledgment

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SYMBOLS

A	$H_0L/2K$
a	constant defined by Eq. (8)

B	column width; $2\pi R$ for concentric-tube column, cm
b	constant defined by Eq. (7)
c	fractional mass concentration of D_2O in H_2O-HDO-D_2O system
c_F	fractional mass concentration of D_2O in feed stream
c_i	initial fractional mass concentration of D_2O in batch operation
c_B, c_T	c obtained at the bottom and the top of the column, respectively
D	mass diffusivity, cm^2/s
g	gravitational acceleration, cm/s^2
H_0	transport coefficient defined by Eq. (3), g/s
K	transport coefficient defined by Eq. (4), $g \cdot cm/s$
K_{eq}	mass-fractional equilibrium constant of H_2O-HDO-D_2O system
L	column length, cm
n	system constant defined by Eq. (11)
$\bar{T}$	mean temperature, °K
ΔT	difference in temperature of hot and cold surface, °C
x	axis normal to the plates
z	axis parallel to transport direction
$c\hat{c}$	pseudoconcentration product

Greek Letters

α_0	reduced thermal diffusion constant
$\bar{\beta}_T$	$(\partial\rho/\partial T)$ evaluated at $\bar{T}$, $g/cm^3 \cdot K$
Δ	$c_B - c_T$
Δ_a	defined by Eq. (16)
Δ_b	$\Delta_a \big|_{c_F=c_i}$, i.e., $\Delta_{3\infty}$ in Ref. *8*, Δ obtained in batch operation
$\bar{\rho}$	mass density evaluated at $\bar{T}$, g/cm^3
μ	absolute viscosity, $g \cdot cm/s$
τ	transport of D_2O along z-direction, g/s
σ	mass flow rate, g/s
ω	half of plate spacing, or half of annular space, cm

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