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The Simplified Equation of Separation for the Enrichment of Heavy Water in a Batch-Type Thermal Diffusion Column

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Abstract

A simple but precise equation of separation for the enrichment of heavy water in a batch-type thermal diffusion column has been derived with the consideration of a pseudobinary mixture. The experiment has also been conducted for various initial concentrations of D_2O and the results are in agreement with the prediction of the theory.

INTRODUCTION

The idea of using a thermogravitational thermal diffusion apparatus for separating the isotopes of a certain element in the gas or liquid state was disclosed by Clusius and Dickel in 1939. Many investigators (*1, 4*) have reported that heavy water can be concentrated by thermal diffusion. Recently, the enrichment of heavy water in C-D columns has been investigated intensively (*7–9*). The theoretical equations for separating D_2O from the H_2O–HDO–D_2O system have been derived with consideration of a ternary system and with the use of equilibrium relation. However, the resultant equation, expressed in Fourier series, is complicated in form and converges very slowly for small time.

It is reported (*5*) that the separation of multicomponent isotopic mixtures might be approximately treated as binary systems. The purpose of this work is to investigate, both experimentally and theoretically, the separation of a H_2O–HDO–D_2O mixture with the consideration of a pseudobinary mixture. It is expected that the resultant equation will be simple for analysis and precise for calculation.

SEPARATION THEORY OF A PSEUDOBINARY MIXTURE

The transport equation for the H_2O-HDO-D_2O system in a batch-type thermogravitational thermal diffusion column was given with the assumption that the concentrations are locally in equilibrium at every point in the column as (7)

$$\tau_3 = H_0 c_3 \hat{c}_3 - K \frac{\partial c_3}{\partial z} \tag{1}$$

in which

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

$$K = (2\omega)^7 g^2 \beta_T^2 \bar{\rho} B (\Delta T)^2 / 9! \mu^2 D + 2\omega \bar{\rho} D B \tag{3}$$

$$\hat{c}_3 = 0.05263 - (0.05263 - 0.0135 K_{eq}) c_3 - 0.027 \{c_3 K_{eq} [1 - (1 - 0.25 K_{eq}) c_3]\}^{1/2} \tag{4}$$

Equation (1) may be rewritten in the form of a binary system as (2)

$$\tau_3 = H_{3A} c_3 (1 - c_3) - K \frac{\partial c_3}{\partial z} \tag{5}$$

where

$$H_{3A} = H_0 \hat{c}_3 / (1 - c_3) = \alpha_{3A} \bar{\rho} g B \beta_T (2\omega)^3 (\Delta T)^2 / 6! \mu \bar{T} \tag{6}$$

$$\alpha_{3A} = \alpha_0 \hat{c}_3 / (1 - c_3) \tag{7}$$

The degree of separation of the H_2O-HDO-D_2O system obtainable by thermal diffusion, as well as by other means, in a single column is so slight (7) that H_{3A} and α_{3A} may be assumed to be constant within the operation range of concentration. Accordingly, Eq. (7) may be approximated as

$$\alpha_{3A} \approx \alpha_0 \hat{c}_{3i}/(1 - c_{3i}) \tag{8}$$

If a differential mass balance is made within the column for unsteady-state operations, one obtains

$$m \frac{\partial c_3}{\partial t} = - \frac{\partial \tau_3}{\partial z} \tag{9}$$

Substitution of Eq. (5) into Eq. (9) results in

$$m \frac{\partial c_3}{\partial t} = -H_{3A}(1 - 2c_3)\left(\frac{\partial c_3}{\partial z}\right) + K \frac{\partial^2 c_3}{\partial z^2} \tag{10}$$

Equation (10) is subject to the following initial and boundary conditions:

$$\text{I.C.:} \quad t = 0, \qquad \tau_3 = H_{3A}c_{3i}(1 - c_{3i}) \tag{11}$$

$$\text{B.C.1,2:} \quad z = 0, L, \qquad \tau_3 = 0 \tag{12}$$

Solving Eq. (10) associated with Eqs. (11) and (12) results in (*6*)

$$\begin{aligned}
\Delta &= c_{3B} - c_{3T} \\
&= \left\{\left(\frac{2}{\sqrt{\pi\theta}}\right)(e^{0.25\theta} - e^{\sigma^2\theta})\left[-1 + 2e^{-\sigma\lambda} \sum_{n=0}^{\infty} e^{-0.25(2n+1)^2\lambda^2\theta^{-1}}\right.\right. \\
&\quad \left.\left. - 2 \sum_{n=0}^{\infty} e^{-0.25(2n+2)^2\lambda^2\theta^{-1}}\right] - 2\sigma e^{\sigma^2\theta}\right\} \cdot e^{-0.25\theta} \\
&\quad - \left\{\left(\frac{2}{\sqrt{\pi\theta}}\right)(e^{0.25\theta} - e^{\sigma^2\theta})\left[e^{-\sigma\lambda}\left(1 + 2 \sum_{n=1}^{\infty} e^{-n^2\lambda^2\theta^{-1}}\right)\right.\right. \\
&\quad \left.\left. - 2 \sum_{n=0}^{\infty} e^{-0.25(2n+1)^2\lambda^2\theta^{-1}}\right] - 2\sigma e^{\sigma^2\theta - \sigma\lambda}\right\} \cdot e^{-0.25\theta + \sigma\lambda}
\end{aligned} \tag{13}$$

where

$$\theta = H_{3A}^2 t/mK = \frac{0.7(\Delta T)^2 D\alpha_{3A}^2 t}{\bar{T}^2(2\omega)^2} \tag{14}$$

$$\sigma = 0.5 - c_{3i} \tag{15}$$

$$\lambda = H_{3A}L/K \tag{16}$$

Although Eq. (13) is complicated in form, it converges very rapidly, especially as θ approaches zero.

SIMPLIFIED EQUATION OF SEPARATION FOR SUFFICIENTLY SMALL θ

For θ sufficiently small, Eq. (13) can be simplified. With this restriction,

$$e^{0.25\theta} \cong 1 + 0.25\theta \tag{17}$$

$$e^{\sigma^2\theta} \cong 1 + \sigma^2\theta \tag{18}$$

$$\sum_{n=1}^{\infty} e^{-n^2\lambda^2\theta^{-1}} \cong \sum_{n=0}^{\infty} e^{-0.25(2n+1)^2\lambda^2\theta^{-1}} \cong \sum_{n=0}^{\infty} e^{-0.25(2n+2)^2\lambda^2\theta^{-1}} \cong 0 \tag{19}$$

and

$$\frac{1}{\sqrt{\pi\theta}}(e^{0.25\theta} - e^{\sigma^2\theta}) \cong \sqrt{\frac{\theta}{\pi}}(0.25 - \sigma^2) \tag{20}$$

Equation (13) becomes

$$\Delta = \left(\frac{-4}{1 + 0.25\theta}\right)\sqrt{\frac{\theta}{\pi}}(0.25 - \sigma^2) \cong \sqrt{\frac{\theta}{\pi}}(-1 + 4\sigma^2) \tag{21}$$

Substituting Eqs. (14) and (15) into Eq. (21) to eliminate θ and σ, one obtains

$$\Delta = \frac{1.888c_{3i}(1 - c_{3i})(\Delta T)(-\alpha_{3A})}{\bar{T}(2\omega)}\sqrt{Dt} \tag{22}$$

DETERMINATION OF α_{3A}

An experimental study for the enrichment of D_2O in a batch-type concentric-tube thermal diffusion column was carried out previously for

c_{3i} = 0.636, 0.0975, 0.1804, and 0.3011 (7). The experimental conditions were: $2R_1 = 3.18$ cm, $2R_2 = 3.26$ cm, $2\omega = 0.04$ cm, $L = 144.78$ cm, $\Delta T = 33$ K, $\bar{T} = 303.5$ K, and $D = 3.9 \times 10^{-5}$ cm^2/s = 3.37 cm^2/day (3). $K_{eq} \cong 3.8$ (7). The results are shown in Fig. 1.

By using the experimental results in Fig. 6 in Yeh and Yang's work (7), a plot of $\Delta/[c_{3i}(1 - c_{3i})]$ vs $\sqrt{t}$ is made as shown in Fig. 1. Statistical analysis using the least-squares method showed, indeed, a good linear regression between $\Delta/[c_{3i}(1 - c_{3i})]$ and $\sqrt{t}$. If the linear regression with the line passing through the origin is employed, one obtains

$$\Delta/[c_{3i}(1 - c_{3i})] = (9.65 \times 10^{-2} \pm 1.75 \times 10^{-2})\sqrt{t} \tag{23}$$

This is exactly the same form as Eq. (22), and thus sufficiently small θ may be assumed for separation of the H_2O-HDO-D_2O system in a thermal diffusion column. Accordingly, the effective thermal dfifusion constant, α_{3A}, can be determined from Eqs. (22) and (23) as follows:

$$\alpha_{3A} = \frac{-9.65 \times 10^{-2}\bar{T}(2\omega)}{1.888(\Delta T)\sqrt{D}} = -1.00 \times 10^{-2} \pm 0.19 \times 10^{-2}$$

Furthermore, substituting the appropriate values into Eq. (14) yields

$$\theta = 1.828 \times 10^{-3}t$$

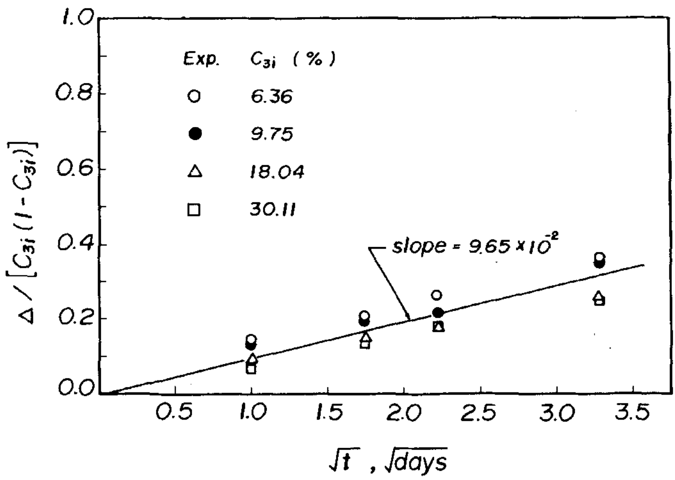

FIG. 1. Experimental results of $\Delta/[c_{3i}(1 - c_{3i})]$ vs $\sqrt{t}$ at various initial feed concentrations.

It is obvious, therefore, that even for 10-day operation, θ is still sufficiently small and the assumption we made is quite correct.

One may also calculate the Soret coefficient for a H_2O–D_2O mixture from the definition of $\alpha_0(20 - 18)/[(20 + 18)\bar{T}]$. Hence, combining Eqs. (4) and (7) gives the result as $-4.8 \times 10^{-5} \pm 0.3 \times 10^{-5}$ K^{-1}, which is quite in agreement with that ($-7.0 \times 10^{-5} \pm 3.0 \times 10^{-5}$ K^{-1}) obtained by Prigogine et al. (*4*) in which they neglected the formation of HDO.

EXPERIMENTAL

In order to investigate the enrichment of heavy water thoroughly for a whole range of concentrations, additional 'experimental studies for c_{3i} = 0.4880 and 0.7018 have been made. The experimental equipment employed and the experimental procedure performed are exactly the same as those in our previous work (*7*). The experimental data are shown in Fig. 2. The theoretical values estimated by Eq. (22) with the substitution of the experimental conditions, or directly by Eq. (23), are also plotted in Fig. 2 for comparison. It is concluded from Fig. 2 that the simplified equation of separation, Eq. (22), is precise for the H_2O–HDO–D_2O system in a batch-type thermal diffusion column.

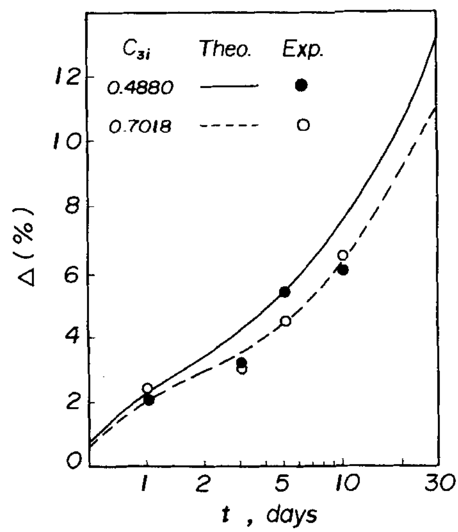

FIG. 2. Comparison of separation obtained from theoretical and experimental results for c_{3i} = 0.4880 and 0.7018.

CONCLUSION

The enrichment of heavy water from a H_2O–HDO–D_2O mixture in a batch-type thermal diffusion column has been further investigated both theoretically and experimentally. The simplified equation of separation, Eq. (22), applicable to a whole range of concentrations, has been derived with consideration of a pseudobinary mixture.

The experimental data obtained in previous work (*7*) for c_{3i} = 0.0636, 0.0975, 0.1804, and 0.3011 are replotted in Fig. 1. It is found from the figure that a good linear regression of $\Delta/[c_{3i}(1 - c_{3i})]$ vs $\sqrt{t}$ with the line passing through the origin can be obtained by the method of least squares. The effective thermal diffusion constant, α_{3A}, is then determined by employing Eq. (22) with the use of experimental results.

The assumption of sufficiently small θ was also verified by Eq. (24). It is believed from Eq. (24) that this assumption is acceptable even for extremely long-term operation.

The experimental work done previously has further been extended for c_{3i} = 0.4880 and 0.7018. The theoretical predictions obtained from Eq. (22) with the substitution of appropriate values, or directly from Eq. (23), are compared with the present experimental data as shown in Fig. 2. It is found that the theoretical prediction values confirm experimental results very well.

SYMBOLS

B	column width; $2\pi R_1$ for concentric-tube column
c_3	fractional mass concentration of D_2O in the H_2O–HDO–D_2O system
c_{3B}, c_{3i}, c_{3T}	c_3 at bottom of the column, at initial state, and at top of the column, respectively
$\hat{c}_3$	constant defined in Eq. (4)
$\hat{c}_{3i}$	$\hat{c}_3$ with c_3 equal to c_{3i}
D	mass diffusivity
g	gravitational acceleration
H_0	transport constant defined by Eq. (2)
H_{3A}	constant defined in Eq. (6)
K	transport constant defined by Eq. (3)
K_{eq}	mass-fractional equilibrium constant of H_2O, HDO, and D_2O system
L	column length
m	mass of solution per unit length ($= 2B\omega\bar{\rho}$)

R_1, R_2 outer radius of inner tube and inner radius of outer tube, respectively
$\tilde{T}$ mean temperature
ΔT difference in temperature of hot and cold plate
t time
z axis parallel to the transport direction

Greek Letters

α_0 reduced thermal diffusion constant which is defined as negative when the heavier component of a mixture tends to migrate toward the hot wall
α_{3A} constant defined in Eq. (7)
$\bar{\beta}_T$ $=_{,}(\partial\rho/\partial T)$ evaluated at $\tilde{T}$
Δ degree of separation defined as $(c_{3B} - c_{3T})$
θ constant defined in Eq. (14)
λ constant defined in Eq. (16)
μ viscosity
$\bar{\rho}$ mass density evaluated at $\tilde{T}$
σ constant defined in Eq. (15)
τ_3 transport of D_2O along z-direction
ω half of plate spacing, or half of annulus space

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