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Estimation of deuterium recovery from H–D gas mixture by thermal diffusion

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ABSTRACT

The recovery of deuterium from hydrogen isotope mixture in continuous-type cryogenic-wall thermal diffusion columns was calculated by the modeling prediction modified from the previous studies. The transport coefficients in the correlation equation were determined with the use of the experimental results obtained by Arita et al., and along the method performed in the previous works. The relation between the separation factor and degree of separation is delineated. The experimental results conform well to the predictions.

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1. Introduction

The thermogravitational thermal diffusion column introduced by Clusius and Dickel [1,2] is a powerful device for the separation of isotope mixtures. For separation of hydrogen isotopes (H, D, T), this method is particularly attractive because of the large ratio in molecular weights [3,4]. Yamamoto et al. [5–10] used the cryogenic-wall thermal diffusion columns successfully separating H–D and H–T mixtures. The separations of water–isotope mixture by the thermal diffusion were also carried out by the present author, and the recovery of deuterium thus obtained was also estimated [11–15]. It was realized that heavy water (D_2O) is the most feasible moderator and coolant for fission reactors to furnish excess neutrons which may be absorbed in materials other than uranium, while deuterium (D) is the optimal nuclear fuel for fusion reactors, which may play an important role in fulfilling the world's energy requirements in the distant future. It is the purpose of present study to develop a correlation model for estimating the degree of separation, as well as the separation factor, for deuterium from H–D gases in thermal diffusion columns by employing the experimental data obtained by Arita et al. [16].

2. Modeling study

2.1. Recovery of deuterium from water–isotope mixture

The equation for estimating the recovery of deuterium from the separation of water–isotope mixture in a continuous-type concentric-tube thermal diffusion column, with outside radius of inner tube R_1, and inside radius of outer tube R_2, was derived with the temperature difference, ΔT, and with the neglect of the tube-curvature effect for small annular spacing, $(R_2–R_1)$, [15,17], as

$$\Delta_D = C_{D,B} - C_{D,T} \tag{1}$$

$$= \frac{2F(-H_0)}{\sigma}\left[1 - \exp\left(-\frac{\sigma L}{2K_0}\right)\right], \tag{2}$$

where $C_{D,B}$ and $C_{D,T}$ are the mass fractions of deuterium in the bottom and top products, and the transport coefficients, H_0 and K_0, are defined as

$$H_0 = \frac{\alpha\beta_{\overline{T}}\rho g(R_2 - R_1)^3(2\pi R_1)(\Delta T)^2}{6!\mu\overline{T}} < 0,$$

(since the thermal diffusion constant $\alpha < 0$ for H_2O—HDO—D_2O system) (3)

$$K_0 = \frac{\beta_{\overline{T}}^2\rho^2 g^2(R_2 - R_1)^7(2\pi R_1)(\Delta T)^2}{9!D\mu^2}, \tag{4}$$

while the concentration terms are defined by

$$F = A[0.2 - (K_{eq}/19) + (K_{eq}/C_{3,F})^{1/2}/19] \tag{5}$$

$$A = C_{3,F}[0.05263 - (0.05263 - 0.0135K_{eq})C_{3,F}^{1/2}] - 0.027\{C_{3,F}K_{eq}[1 - (1 - 0.25K_{eq})C_{3,F}]^{1/2}\}, \tag{6}$$

in which $C_{3,F}$ denotes the feed concentration of heavy water in H_2O–HDO–D_2O system. The most important assumption in deriving above equations are that the flow rates σ are the same in the enriching and stripping sections of same length, $L/2$, that the physical properties (mass density ρ, expansion coefficient $\beta_{\overline{T}}$, diffusivity D, viscosity μ, average absolute temperature $\overline{T}$,.....) are constant, and that the concentration is locally in equilibrium with the equilibrium constant, at every point in the column [11,12], i.e

$$H_2O + D_2O \leftrightarrow 2HDO. \tag{7}$$

Since the top and bottom products are withdrawn at the same rate with the feed mass rate 2σ, σ is related to the feed volumetric rate V_F with density as

$$\sigma = \rho V_F/2. \tag{8}$$

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2.2. Recovery of deuterium from H–D system

The predicting equation for the recovery of deuterium from hydrogen–isotope mixture may be simulated from Eq. (2) with the considerations of the tube-curvature effect, and the following equilibrium condition:

$$H_2 + D_2 \leftrightarrow 2HD \tag{9}$$

i.e.

$$\Delta_D = \frac{2F(-H_0)f(k)}{\sigma}\left[1 - \exp\left(-\frac{\sigma L}{2K_0 g(k)}\right)\right], \tag{10}$$

where $k(=R_2/R_1)$ is the ratio of the inside radius (R_2) of outer tube to the outside radius (R_1) of inner tube, and the functions of $f(k)$ and $g(k)$ were derived in the previous work [18], defined by the very long and complicate equations, and thus the application for calculation is cumbersome. For a system specified, Eq. (10) coupled with Eq. (8), may be simply rewritten as

$$\Delta_D = \frac{H}{2V_F}\left[1 - \exp\left(-\frac{V_F L}{2K}\right)\right], \tag{11}$$

where

$$H = 8F(-H_0)f(k)/\rho \tag{12}$$

$$K = 2K_0 g(k)/\rho, \tag{13}$$

and the system constants, H and K, can be determined by the experiment data, as to be illustrated in next section.

3. Correlation prediction

3.1. Numerical example

The experimental results obtained by Arita et al. [16] for the separation of H–D gas in a cryogenic-wall thermal diffusion column will be employed for confirming the correlation predictions based on the present model.The apparatus they used mainly consists of a stainless steel column of 29.4 mm in inner diameter as the cold wall, inserted concentrically with a tungsten wire of 0.5 mm diameter as a heater. The effective heat length is 1500 mm. The feed with unity atomic ratio of H and D (mass fraction of deuterium $C_{D,F} = 2/(1+2) = 2/3$) was introduced at the middle point of the column. The temperatures of heater were 1273, 973 and 773 K, while the cold wall was cooled by the liquid nitrogen. The feed volumetric rates V_F were 25, 50 and 100 cm^3/min, and the operating pressures were in the range of 13–60 kPa. The experimental results thus obtained for the separation factor in Fig. 3 of Arita et al.'s paper [16] for H–D at 1273 K of heater temperature were employed and listed in Table 1.

3.2. Relation between the degree of separation and separation factor

Let 2σ be the feed mass flow rate while σ is the same mass flow rate of bottom and top products, then a total mass balance for deuterium is readily obtained as

$$2\sigma C_{D,F} = \sigma C_{D,B} + \sigma C_{D,T}, \tag{14}$$

Table 1
Experimental results for H–D system with $C_{D,F} = 2/3$ [18]

V_F (cm^3/min)	26.36 (kPa)		33.18 (kPa)		40 (kPa)		53.18 (kPa)	
	γ	Δ	γ	Δ	γ	Δ	γ	Δ
25	13.26	0.4825	16.31	0.5066	12.34	0.4728	6.15	0.3692
50	5.69	0.3560	9.38	0.4353	8.46	0.4201	5.08	0.3362
100	2.46	0.1956	4.00	0.2923	5.69	0.3560	4.15	0.2992

where $C_{D,F}$ denotes the mass fraction of deuterium in the feed stream. Solving Eqs. (1) and (13) for $C_{D,B}$ and $C_{D,T}$, one has

$$C_{D,B} = C_{D,F} + \Delta_D/2 \tag{15}$$

$$C_{D,T} = C_{D,F} - \Delta_D/2. \tag{16}$$

Accordingly, the mass fractions of hydrogen are

$$C_{H,B} = 1 - (C_{D,F} + \Delta_D/2) \tag{17}$$

$$C_{H,T} = 1 - (C_{D,F} - \Delta_D/2). \tag{18}$$

The separation factor is defined as

$$\gamma = (D/H)_{bottom}/(D/H)_{top}. \tag{19}$$

From Eqs. (15)–(19) becomes

$$\gamma = \frac{(C_{D,F} + \Delta_D/2)/(1 - C_{D,F} - \Delta_D/2)}{(C_{D,F} - \Delta_D/2)/(1 - C_{D,F} + \Delta_D/2)} = \frac{(C_{D,F} + \Delta_D/2)(1 - C_{D,F} + \Delta_D/2)}{(C_{D,F} - \Delta_D/2)(1 - C_{D,F} - \Delta_D/2)}. \tag{20}$$

Solving Δ_D from Eq. (20) for the degree of separation of deuterium related to the separation factor, we have

$$\Delta_D = \left(\frac{\gamma+1}{\gamma-1}\right) - \sqrt{\left(\frac{\gamma+1}{\gamma-1}\right)^2 - 4C_{D,F}(1 - C_{D,F})}, \tag{21}$$

in which only the minus sign in the second term of the right side is taken because $\Delta_D < 1$.

The degrees of separation for deuterium defined by Eq. (1), were calculated from Eq. (21) with the use of $C_{D,F} = 2/3$ and the experimental values of γ in Table 1, and the results are also listed in Table 1.

Table 2
System constants of present interest for various pressures

P (kPa)	26.36	33.18	40	53.18
H (cm^3/min)	39.506	66.254	137.66	152.74
K (cm^4/min)	162.1	3504	10300	15085

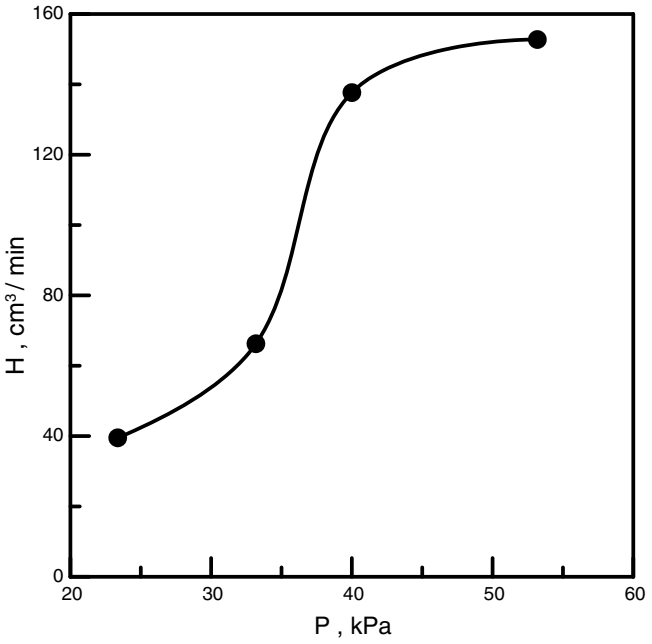

Fig. 1. H vs. P.

3.3. System constants

If Eq. (11) is applied to two sets of the experimental data with the condition that $(V_F)_2 = 2(V_F)_1$, then

$$(\Delta_D)_1 = \frac{H}{2(V_F)_1}\left[1 - \exp\left\{-\frac{(V_F)_1 L}{2K}\right\}\right], \tag{22}$$

$$(\Delta_D)_2 = \frac{H}{2(V_F)_2}\left[1 - \exp\left\{-\frac{(V_F)_2 L}{2K}\right\}\right]. \tag{23}$$

Solving Eqs. (22) and (23) for H and K since $(V_F)_2 = 2(V_F)_1$, gives

$$H = \frac{(V_F)_1 (\Delta_D)_1^2}{(\Delta_D)_1 - (\Delta_D)_2} \tag{24}$$

$$K = \frac{(V_F)_1 L}{2\ln\left[\frac{(\Delta_D)_1}{2(\Delta_D)_2 - (\Delta_D)_1}\right]} \tag{25}$$

Two data points of $(V_F)_1 = 50\ \mathrm{cm^3/min}$ and $(V_F)_2 = 100\ \mathrm{cm^3/min}$ for each operating pressure were applied to Eqs. (24) and (25) to calculate the corresponding values of H and K with $L = 150$ cm. The results are listed in Table 2 and also plotted in Figs. 1 and 2, respectively.

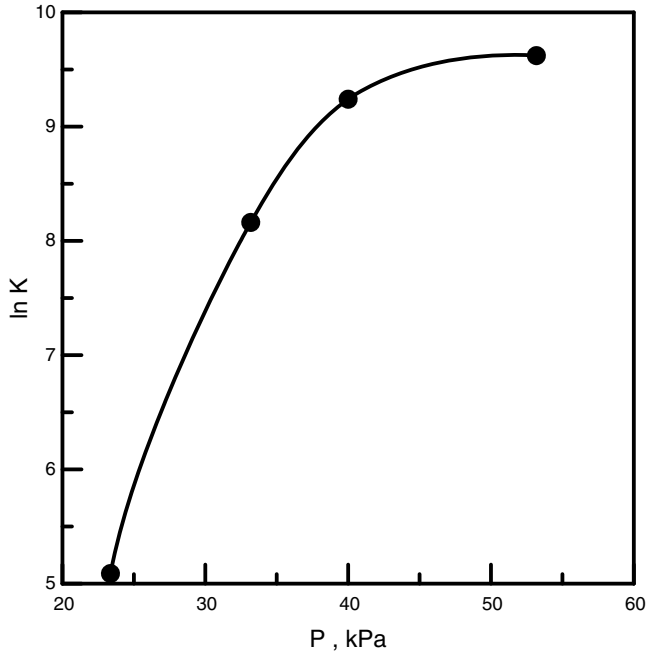

Fig. 2. ln$K$ vs. P.

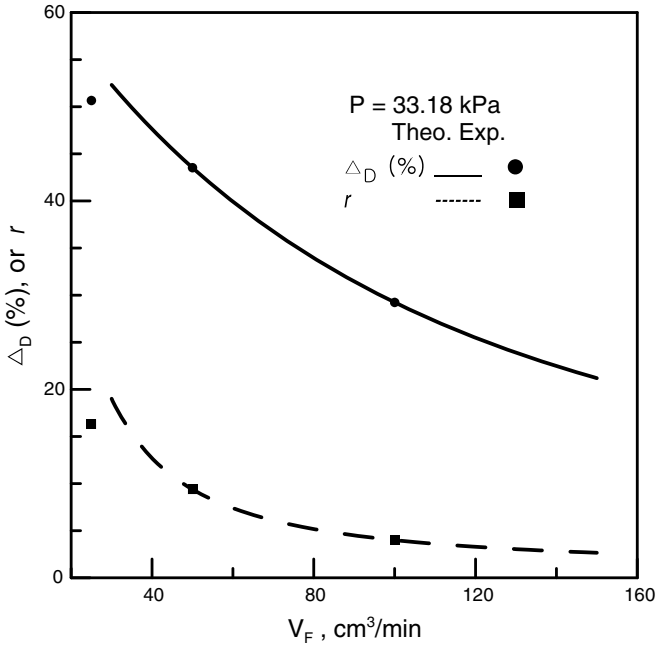

Fig. 4. Degree of separation and separation factor for $P = 33.18$ kPa.

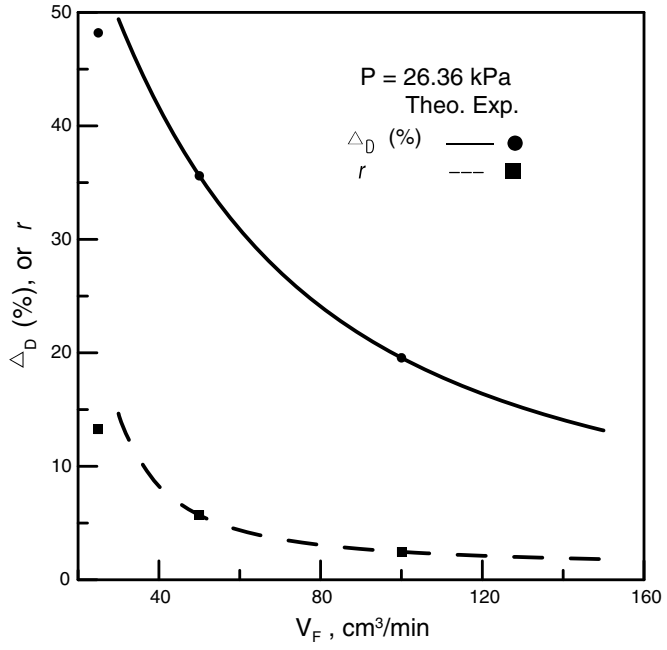

Fig. 3. Degree of separation and separation factor for $P = 26.36$ kPa.

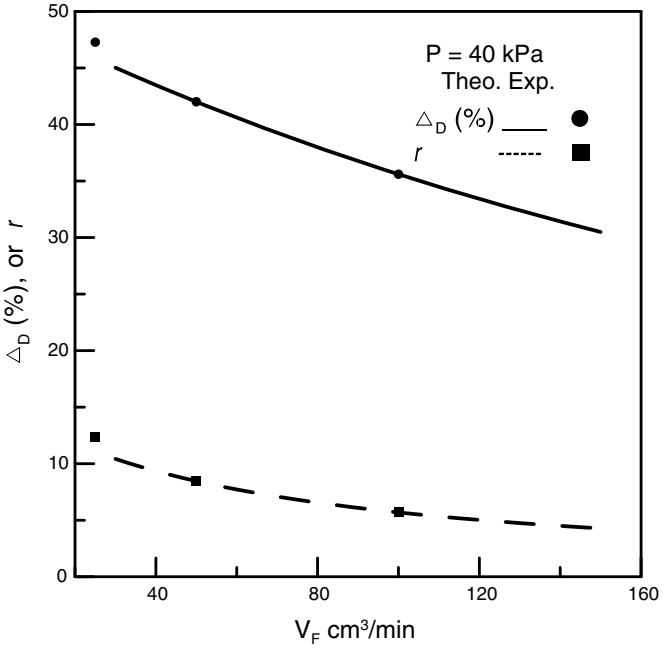

Fig. 5. Degree of separation and separation factor for $P = 40$ kPa.

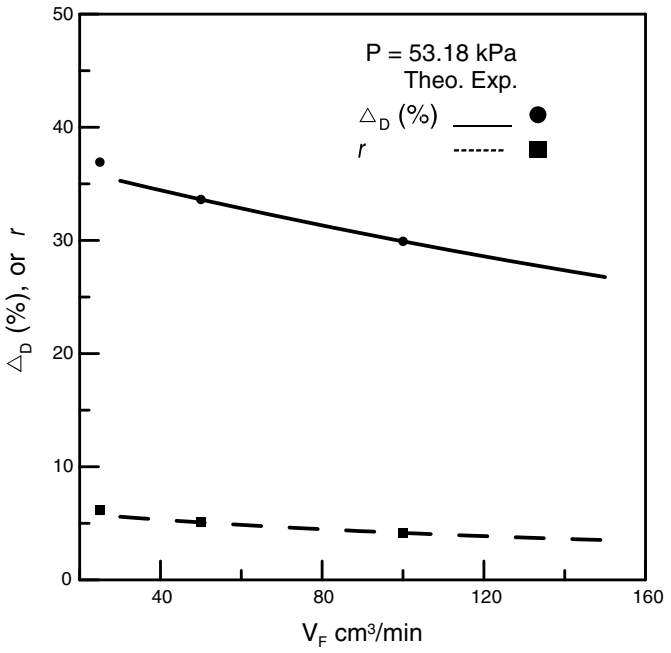

Fig. 6. Degree of separation and separation factor for $P = 53.18$ kPa.

3.4. Comparison of the correlation predictions with experimental results

The correlation predictions for the degrees of separation of deuterium were obtained from Eq. (11) coupled with the use of Table 2, or Figs. 1 and 2, and the results are compared with the experimental data as shown in Figs. 3–6. The correlation predictions for the separation factor of deuterium γ were also calculated from Eq. (20) with the known values of, and the comparisons of correlated prediction of γ with the experimental data are also given in Figs. 3–6. It is seen that the experimental results confirm well to the correlation predictions.

4. Discussion and conclusion

The studies on the enrichment of heavy water, as well as the recovery of deuterium, from water–isotope mixture in concentric-tube thermal diffusion columns were carried out theoretically and experimentally in the previous works. The separation equations derived in these works were simulated and modified in present study for the correlation predictions of deuterium recovery from hydrogen–isotope mixture in the continuous-type cryogenic-wall thermal diffusion columns. The transport coefficients, as well as the system constants in the correlation equation, were determined from the two sets of experimental data for each operating pressure, along the method performed in the previous works. The separation efficiencies are expressed by the separation factor and the degree of separation, and the experimental results obtained by Arita et al. [18] confirm well to the correlation predictions of both efficiencies.

The present nuclear energy supplied by fission reaction may be replaced in the near future by that supplied by fusion reaction with deuterium as the nuclear fuel. If this happens, enrichment of deuterium from hydrogen–isotope mixture will be an important event, and the thermal diffusion process will play an important role for separating these mixtures.

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