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TECHNICAL NOTE

Separation of Heavy Water by Vapor-Phase Thermal Diffusion Coupled with Distillation and Condensation

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ABSTRACT

A study on the enrichment of heavy water in a vapor-phase thermal-diffusion column has been conducted. With the combination of the effects of distillation, vapor-phase thermal diffusion, and partial condensation, considerable improvement in the degree of enrichment has been achieved in a vapor-phase column rather than in a liquid-phase column. It was also found that even the part of enrichment contributed only by vapor-phase thermal-diffusion effect is much higher than that obtained by liquid-phase thermal diffusion.

Key Words. Enrichment; Heavy water; Vapor phase; Thermal diffusion

INTRODUCTION

Thermal diffusion is a well-established method for separating isotopes either in the liquid state or in the gaseous state under the influence of a temperature gradient. It was used to separate uranium isotopes in the

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gaseous state at Oak Ridge National Laboratory in World War II. For separation of hydrogen isotopes in the gaseous state, this method is particularly attractive because of the large ratio in molecular weights (1). It has also been shown that heavy water can be effectively concentrated in liquid-phase thermal diffusion columns (2). Later, the separation of a liquid mixture of heavy water and ordinary water in liquid-phase thermal-diffusion columns was extensively studied (3–6). Separation equations have been derived, and experimental work with various feed concentrations of the H_2O–HDO–D_2O system have also been conducted; the results quantitatively confirm the prediction of the theory. However, the enrichment of heavy water by thermal diffusion in the vapor state has never been conducted. It is the purpose of this study to investigate the separation of heavy water by vapor-phase thermal diffusion in a Clusius-Dickel column.

SEPARATION OF HEAVY WATER IN A VAPOR-PHASE COLUMN

The thermal diffusion effect occurs both in the liquid phase and in the gas phase under the influence of a temperature gradient. However, a limitation of temperature difference applicable for liquid-phase operations exists. The reason why this limitation exists is that application of a large temperature difference to a liquid mixture to secure a high degree of enrichment may cause either evaporation on the hot surface or freezing on the cold surface. These phase changes will result in attenuating or even completely eliminating the thermal diffusion effect.

An alternative method for enrichment of heavy water by thermal diffusion is introduced in this study. In this method, thermal diffusion is carried out in the vapor phase instead of in the liquid phase, with a high temperature gradient used to achieve a high degree of enrichment. It should be mentioned here that thermodiffusion work has previously been carried out for liquids in the liquid state, and for gases in the gaseous state, but never for liquids in the vapor state. Figure 1 illustrates the flows and fluxes in a vapor-phase thermal-diffusion column.

For enrichment of heavy water by vapor-phase thermal diffusion, a liquid mixture of ordinary water and heavy water must be vaporized in advance. The vapor produced, in which ordinary water is richer than in the liquid mixture, is then introduced into the vapor-phase thermal-diffusion section, where a temperature gradient is established and thus thermal diffusion occurs between the hot and cold surfaces. In addition to the thermal diffusion effect which causes heavy water to diffuse toward the cold surface, the temperature gradient also causes convection currents of vapor up the hot surface and down the cold surface to produce a cascading

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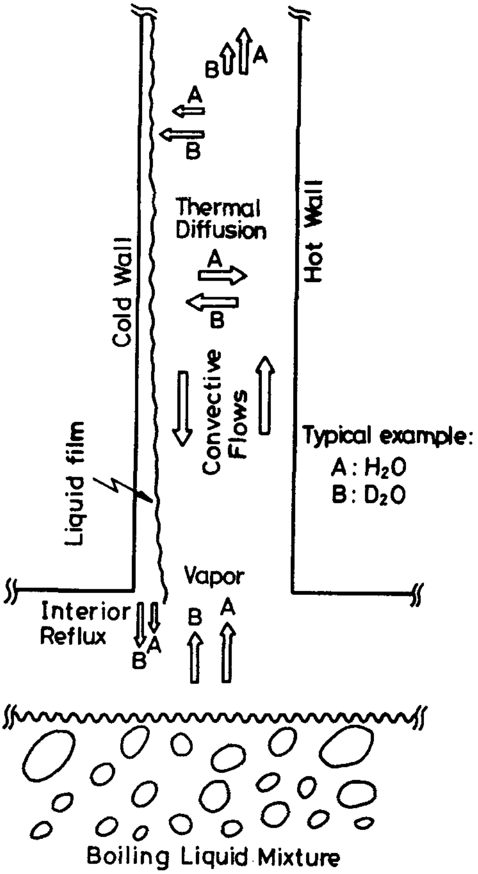

FIG. 1 The flows and fluxes in a vapor-phase thermal-diffusion section.

effect. Combining the effects of distillation and thermal diffusion as well as the cascading effect, a concentration difference of the vapor mixture will be created, with ordinary water rich at the top and heavy water at the bottom of the column. Furthermore, partial condensation of the vapor mixture may also happen on the cold surface if the surface temperature is set below the dew point of the vapor mixture. The condensate, in which heavy water is richer than in the vapor mixture, will form a liquid film and flow down to the bottom of the column, acting as an interior reflux of the column, which enhances separation. Consequently, with the combination of thermal-diffusion, distillation, and condensation effects, a vapor-phase thermal-diffusion column may be a feasible devise for enriching heavy water.

EXPERIMENTAL METHOD

Apparatus and Materials

The apparatus used in this investigation is shown schematically in Fig. 2. It consists essentially of a boiler and a vapor-phase thermal-diffusion section. Their dimensions are illustrated in Fig. 3. The vapor-phase thermal-diffusion section, made of a glass tube with a water jacket outside and an electrically high temperature rod inside, has an annular space of 0.5 cm. The outside diameter of the electrically heated rod is 3.5 cm, while the inside diameter of the glass tube is 4.5 cm. The length of the test section is 55 cm. The temperature of the electrical rod is controlled by a temperature controller, model RKC PF-62, Japan, with a precision of ±0.1°C.

Experimental Conditions and Procedure

During operation, heavy water of 99.75 atom% deuterium from Baker Chemical Co. was employed. Liquid mixtures of 1500 g with 19% (or 33%) deuterium oxide were initially fed to the bolier where a vapor mixture of

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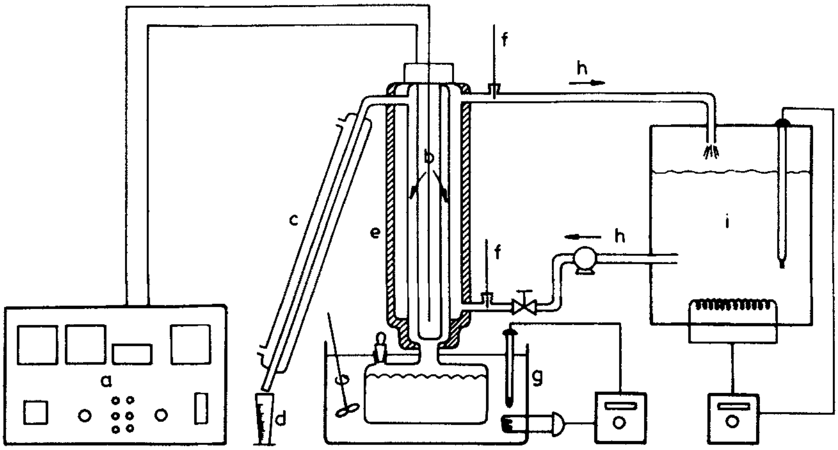

FIG. 2 Schematic diagram of a vapor-phase thermal diffusion system: (a) temperature controller, (b) annular space, (c) total condenser, (d) collector, (e) vapor-phase thermal-diffusion column, (f) thermometer, (g) thermostat, (h) water circulation, (i) constant-temperature water tank.

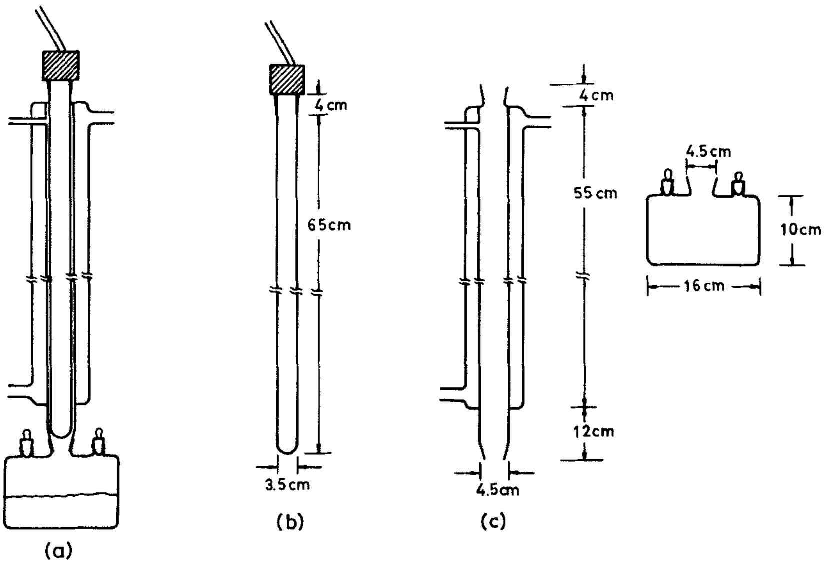

FIG. 3 Dimensions of a vapor-phase thermal-diffusion column: (a) vapor-phase thermal-diffusion column, (b) high temperature rod, (c) glass tube with water jacket, (d) boiler.

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D_2O, HDO, and H_2O was steadily generated, and its evaporation rates (V = 300, 450, and 600 g/h) were controlled by electrical heating at the boiling point of the liquid mixture. Vapor was then passed through the annular region between the tube wall and the electrically high temperature rod in which thermal diffusion took place due to the temperature gradient, while some amount of vapor mixture was condensed on the cold surface, forming a liquid film which flowed down to the boiler as an interior reflux. In addition, cold water with its temperature controlled by a thermostat was circulated at a sufficiently high rate through the outside jacket of the column, and thus the cold surface was maintained at a near constant temperature to obtain uniform condensation over the test section. The vapor was partially condensed on the surface of the liquid film at a constant rate controlled by the temperature of the cold surface, while the vapor that did not condense in the test section was conducted out of the column steadily and was perfectly liquefied in the total condenser. Six temperature differences (ΔT = 0, 100, 150, 200, 250, and 300°C) between the hot and cold surfaces were used in this study.

Four calibrated copper-constantan thermocouples with a precision of ±0.1°C were located on the surface of the glass tube and the electrical rod at the inlet and outlet, respectively, to measure the surface temperatures. The experiment were carried out as batch operations. After 1 hour of operation, the samples were analyzed at 25°C by an automatic density meter, model DA-101B, Kyoto Electronic Manufacturing Co. The specific gravity was measured with a precision corresponding to ±0.001% in composition. The relation between specific gravity and mass% for each component in the H_2O–HDO–D_2O system at 25°C is presented in Fig. 4 (3).

RESULTS AND DISCUSSIONS

Many experimental runs were carried out as 1-hour batch-type operations. The experimental results for $V = 300$ g/h (with a steady evaporation rate of 5 g/min) are presented in Tables 1 and 2 for $C_F = 19$ and 33%, respectively, in which the degree of enrichment is defined as

$$\Delta_v = C_v - C_F$$

Many other results for different evaporation rates ($V = 450$ and 600 g/h) were also obtained but are not presented here. It was found that the degree

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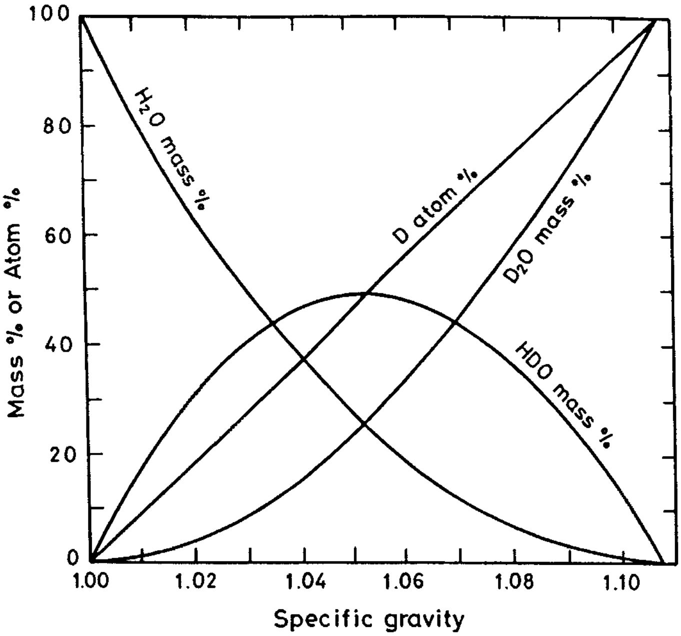

FIG. 4 Relation between specific gravity and mass% of each component in the H_2O–HDO–D_2O system at 25°C.

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TABLE 1
Experimental Results of the Enrichment of Heavy Water in a Batch-Type Vapor-Phase Thermal-Diffusion Column for 1 Hour Operation: $F = 1500$ g, $V = 300$ g, $C_F = 19\%$

	$L/F = 0.992$			$L/F = 0.984$			$L/F = 0.978$			$L/F = 0.968$			$L/F = 0.960$		
ΔT (°C)	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$
0	0.72	0	0	0.66	0	0	0.62	0	0	0.58	0	0	0.55	0	0
100	1.87	1.15	1.60	1.69	1.03	1.56	1.46	0.84	1.35	1.32	0.74	1.28	1.19	0.64	1.16
150	2.00	1.28	1.78	1.78	1.12	1.70	1.57	0.95	1.53	1.42	0.84	1.45	1.28	0.73	1.33
200	2.10	1.38	1.92	1.88	1.22	1.85	1.60	0.98	1.58	1.50	0.92	1.59	1.42	0.87	1.58
250	2.26	1.54	2.14	2.01	1.35	2.05	1.79	1.17	1.89	1.58	1.00	1.72	1.50	0.95	1.73
300	2.40	1.68	2.33	2.10	1.44	2.18	1.87	1.25	2.02	1.65	1.07	1.84	1.55	1.00	1.82

TABLE 2
Experimental Results of the Enrichment of Heavy Water in a Batch-Type Vapor-Phase Thermal-Diffusion Column for 1 Hour Operation: $F = 1500$ g, $V = 300$ g, $C_F = 33\%$

	$L/F = 0.992$			$L/F = 0.984$			$L/F = 0.978$			$L/F = 0.968$			$L/F = 0.960$		
ΔT (°C)	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$	Δ_v (%)	$\Delta_{v,t}$ (%)	$\Delta_{v,t}/\Delta_{v,0}$
0	0.88	0	0	0.81	0	0	0.75	0	0	0.72	0	0	0.67	0	0
100	2.10	1.22	1.39	1.89	1.08	1.33	1.75	1.00	1.33	1.62	0.90	1.25	1.48	0.81	1.21
150	2.27	1.39	1.58	2.04	1.23	1.52	1.87	1.12	1.49	1.73	1.01	1.40	1.56	0.89	1.33
200	2.45	1.57	1.78	2.18	1.37	1.69	1.99	1.24	1.65	1.82	1.10	1.53	1.64	0.97	1.45
250	2.65	1.77	2.01	2.38	1.57	1.94	2.03	1.28	1.71	1.97	1.25	1.74	1.71	1.04	1.55
300	2.83	1.95	2.22	2.52	1.71	2.11	2.24	1.49	1.99	2.05	1.33	1.85	1.81	1.14	1.70

of enrichment increases slightly when the evaporation rate decreases in the range studied ($300 < V < 600$ g). Since there is no thermal-diffusion effect when the temperature difference between the hot and cold walls is zero, the separation $\Delta_{v,0}$ thus obtained is merely due to distillation and partial condensation. Therefore,

$$\Delta_{v,0} = \Delta_v\big|_{\Delta T=0}$$

If we let $\Delta_{v,t}$ denotes the part of enrichment contributed by the thermal-diffusion effect in a vapor-phase thermal-diffusion column, then we may assume

$$\Delta_v = \Delta_{v,0} + \Delta_{v,t}$$

for a small degree of enrichment.

(1) Effects of Distillation and Condensation

Under operation with no thermal-diffusion effect, $\Delta T = 0$ and $\Delta_v = \Delta_{v,0}$ (or $\Delta_{v,t} = 0$), and the enrichment is carried out merely by distillation coupled with partial condensation. As expected, Tables 1 and 2 show that the degree of enrichment ($\Delta_{v,0} = \Delta_v - \Delta_{v,t}$) is enhanced as the L/F ratio (the ratio of the mass remaining in the boiler after 1 hour of operation to that at time zero) increases. Moreover, enrichment for a higher feed concentration ($C_F = 33\%$) is better than that of a lower feed concentration ($C_F = 19\%$).

(2) Effect of Vapor-Phase Thermal Diffusion

Tables 1 and 2 show that the degree of enrichment $\Delta_{v,t}$ contributed by the vapor-phase thermal-diffusion effect alone is enhanced when the temperature difference, the value of L/F, or the feed concentration increases. This is the essential feature of thermal diffusion, even in liquid-phase operation.

(3) Comparison of the Effects of Vapor-Phase Thermal Diffusion and Liquid-Phase Thermal Diffusion

A liquid-phase thermal-diffusion column was also employed in this study. The diffusion section is 57 in. long and the annular space is 0.016 in. During operation, the temperatures of the hot and cold walls were kept at 47 and 14°C, respectively. The experimental equipment and procedure are exactly the same as those in previous work (3). The experimental results are presented in Table 3.

TABLE 3
Experimental Results of the Enrichment of Heavy Water in a Liquid-Phase Thermal-Diffusion Column for 1 Hour Operation: $L/F = 0.5$, $\Delta T = 33°C$, $C_F = 33\%$

L (g)	$\Delta_{l,t}$ (%)
5.36	0.255
4.53	0.255
3.67	0.283
2.83	0.312

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The effect of vapor-phase thermal diffusion may be compared with that of liquid-phase thermal diffusion in Tables 1, 2, and 3. The effects of thermal diffusion on both the degree of enrichment ($\Delta_{v,t}$) and the amount of product (L) obtained in the vapor-phase column are much larger than those (L, $\Delta_{l,t}$) obtained in the liquid-phase column. Moreover, in addition to the effect of thermal diffusion, the vapor-phase thermal-diffusion column also produces the effects of distillation and condensation. Consequently, it is believed that enrichment of heavy water in vapor-phase thermal-diffusion columns would be technically feasible.

CONCLUSION

The material possessing a larger molecular weight (say D_2O in the H_2O–HDO–D_2O system) generally has a lower volatility and a lower concentration in the vapor phase than in the liquid phase from which the vapor is produced. In addition, for molecules in which the interaction force between the molecules varies as an inverse power of the distance between the molecules, the direction of thermal diffusion for a power greater than 5 (say H_2O and D_2O as well as HDO and D_2O) is such that the heavier molecules (say D_2O) in general move toward the cold part of the solution. Furthermore, heavier molecules have lower volatility and preferably condense on the cold wall and return to the boiler. Accordingly, with the combination of the effects of thermal diffusion, distillation, and partial condensation, separation of such a liquid mixture (e.g., the D_2O–HDO–H_2O system) in a vapor-phase thermal-diffusion column will result in largely enhancing the separation obtained merely by either distillation or thermal diffusion in the liquid phase. It is also shown by the experimental results that even the part of enrichment contributed by the vapor-phase thermal-diffusion effect is much more effective than liquid-phase thermal diffusion.

SYMBOLS

C	mass fraction of heavy water
C_F	C in the boiler of batch-type vapor-phase column (VPC) at the initial time, or in the feed stream of continuous-type liquid-phase column (LPC)
C_l	C in the bottom product stream of LPC
C_v	C in the boiler of VPC after 1-hour operation
F	mass of liquid mixture in the boiler of VPC at the initial time, or in the feed stream of LPC after 1-hour operation (g)
L	mass of liquid mixture in the boiler of VPC after 1-hour opera-

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	tion, or in the bottom product stream of LPC after 1-hour operation (g)
V	evaporation rate of liquid mixture in the boiler of VPC (g/h)
Δ	degree of enrichment, $C_v - C_F$ or $C_l - C_F$
$\Delta_{l,t}$	Δ obtained in liquid-phase column (LPC) due to thermal diffusion
Δ_v	Δ obtained in vapor-phase column (VPC)
$\Delta_{v,0}$	part of Δ_v obtained due to distillation and condensation ($\Delta T = 0$, without thermal-diffusion effect)
$\Delta_{v,t}$	part of Δ_v obtained due to thermal-diffusion effect alone
ΔT	temperature difference between hot and cold surfaces (K)

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