The Enrichment of Tritium in Hydrogen or Deuterium by Thermal Diffusion

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Tritium in H_2 or D_2, 1.7×10^{-2} Ci mol^{-1}, was enriched by means of thermal diffusion at the bottom of a 100-cm glass column with a gas reservoir on top. Four columns with different diameters (8, 20, 30, and 41 mmϕ) were used. The temperature of the wire stretched along the axis of the column was changed over a range from 200 °C to 450 °C. The maximum equilibrium separation factors in hydrogen and in deuterium were 17 and 4.5 respectively. The optimum diameters were estimated by a modification of Waldmann's equation, which can be used for the separation using the flat-type system.

The enrichment of the tritium present in the stable hydrogen isotopes is important in connection with the nuclear-fusion reaction of tritium with deuterium and with the treatment of tritium wastes. This report is concerned with the enrichment of low concentrations of tritium present in hydrogen or deuterium by means of thermal diffusion using a 100-cm glass column with a gas reservoir on top. A short column is desirable because of its ease of handling in a laboratory. The correlation between the column length and the separation factor has been reported elsewhere.[1] In this study, the diameter of the column and the temperature of the wire were changed over wide ranges, and the separation factor was obtained in each case. The possibility of an extended application of Waldmann's equation,[2,3] which can be used for a flat-type system, was examined in the hot-wire type columns, and the optimum diameter was predicted.

Experimental

The main part of the apparatus is shown in Fig. 1, where A is the separation column, constructed of Pyrex glass.

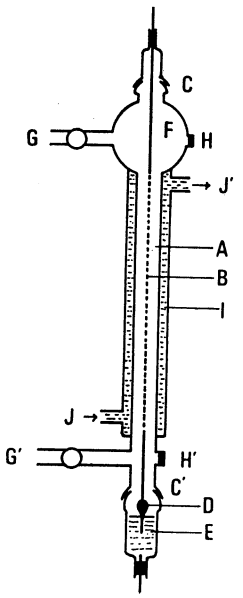

Fig. 1. Thermal diffusion column.
A: Separation column, B: nichrome wire, C and C': greaseless spherical joints, D: weight; E: mercury, F: gas reservoir, G and G': tube, H and H': sampling orifices, I: water jacket, J and J': running water.

Columns of four different diameters, 8, 20, 30, and 41 mmϕ, were used. The nichrome wire, B, stretched in the column was 0.5 mmϕ in diameter and 100 cm in length. The wire could be set along the center of the column by moving the spherical joints, C and C'. In order to stretch the wire, a small lead weight, D, was hung at the end of the wire, and it was immeresed in a mercury reservoir, E, which was connected at the end of the column. The temperature of the wire was changed over the range from 200 °C to 450 °C by means of a direct current. Each temperature was measured by means of the thermal expansion of the wire. Prior to use, the wire was heated in 100 kPa of hydrogen at 500 °C for 5 h; then the evacuation was carried out at a pressure of 10^{-3} Pa for 5 h in order to remove any active oxygen on the surface of the wire. The outside of the column was always kept at 20 °C by the use of running water. The volume of the gas reservoir, F, was 500 cm^3.

Before the study, the effect of the gas reservoir connected to the column was ascertained using the Kr–N_2 system, which had previously been tested in the same type of apparatus by Tanaka *et al.*[4] Their apparatus was devised to circulate readily the gas in the gas reservoir by the aid of a circulation tube, and they concluded that the connection of the gas reservoir with the column is quite effective for the separation. Our results were very similar to those of Tanaka *et al.*

The operating pressure of the gas was 107 kPa. The amount of sampling in each case was 30 mm^3. The concentration of tritium was measured by means of a radio-gas chromatograph.

The carrier-free tritium was diluted with hydrogen or deuterium to a volume of 1.7×10^{-2} Ci mol^{-1}. Prior to use, the gas mixture was put into contact with nickel plates at 100 °C for about 50 h in order to change completely the tritium (T_2) to tritiated hydrogen (HT) or tritiated deuterium (DT), since the following catalytic reaction on nichrome wire took place during the enrichment experiment:

$$T_2 + H_2 = 2HT, \quad T_2 + D_2 = 2DT. \qquad (1)$$

Results

The tritium at the bottom of the column was rapidly concentrated soon after the temperature of the wire had been elevated; the concentrations at both ends of the column became constant within 100 min. The results on H_2–HT in various columns of different diameters are shown in Figs. 2 and 3. The results on D_2–DT are shown in Figs. 4 and 5. The change in the concentration at the bottom occured faster than that at the top, as a result of the large difference in volume between the two ends. The radioactivities of the gas

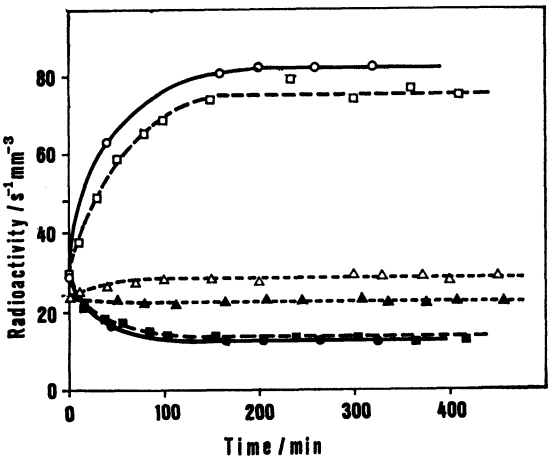

Fig. 2. Enrichment of tritium in the mixture of H_2–HT. Each specimen was taken out of the bottom (white symbols) or of the top (black symbols). The diameters of the column and the wire temperatures were: (○, ●) 20 mmϕ and 300 °C; (□, ■) 20 mmϕ and 200 °C; (△, ▲) 8 mmϕ and 450 °C.

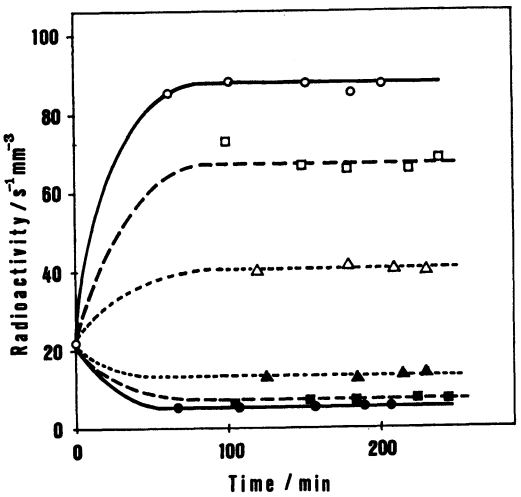

Fig. 3. Enrichment of tritium in the mixture of H_2–HT. Each specimen was taken out of the bottom (white symbols) or of the top (black symbols). The diameters of the column and the wire temperatures were: (○, ●) 30 mmϕ and 450 °C; (□, ■) 30 mmϕ and 300 °C; (△, ▲) 41 mmϕ and 300 °C.

at both ends in the equilibrium state are listed in Table 1, where c and c' are the radioactivities of the bottom and the top respectively. Since the concentration of tritium was extremely low, the equilibrium separation factor, q_e, can be written as:

$$q_e = c/c'. \quad (2)$$

The correlations between the equilibrium-separation factor and the temperature of the wire are shown in Figs. 6 and 7, together with the theoretical values, which will be explained later. In the case of H_2–HT, the separation factors of 8 mmϕ and 20 mmϕ increased initially with the elevation of the wire temperature, and then gradually decreased. However, no decrease was found on the columns of 30 mmϕ and 41 mmϕ up to

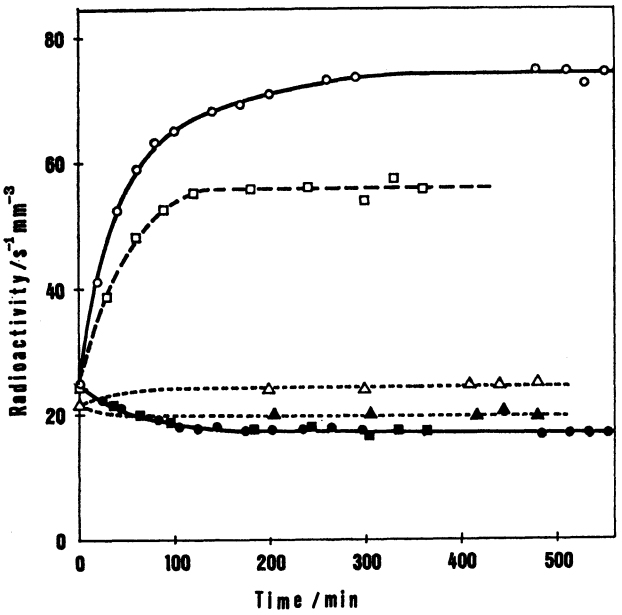

Fig. 4. Enrichment of tritium in the mixture of D_2–DT. Each specimen was taken out of the bottom (white symbols) or of the top (black symbols). The diameters of the column and the wire temperatures were: (○, ●) 20 mmϕ and 450 °C; (□, ■) 20 mmϕ and 200 °C; (△, ▲) 8 mmϕ and 200 °C.

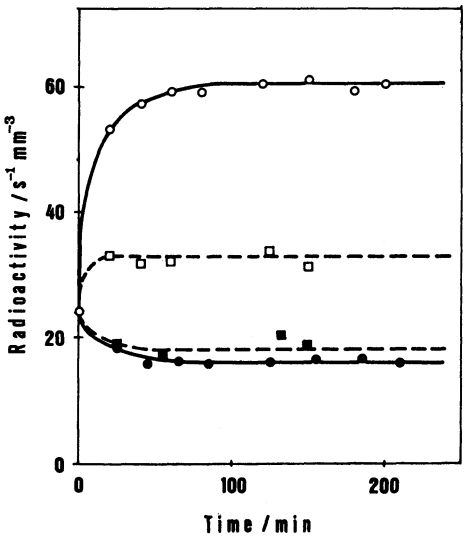

Fig. 5. Enrichment of tritium in the mixture of D_2–DT. Each specimen was taken out of the bottom (white symbols) or of the top (black symbols). The diameters of the column and the wire temperatures were: (○, ●) 30 mmϕ and 450 °C; (□, ■) 30 mmϕ and 200 °C.

450 °C. In the case of D_2–DT, all the separation factors were smaller than those of H_2–HT. It is noticeable that the separation factor of 20 mmϕ in this case became larger than that of 30 mmϕ at all temperature regions investigated.

Discussion

The optimum diameter for the enrichment in a wire-type column may be obtained simply by making

TABLE 1. RADIOACTIVITIES OF TRITIUM AT THE BOTTOM AND THE TOP OF THE COLUMN IN THE EQUILIBRIUM STATE

Mixtures	Column diameter (mmϕ)		Radioactivities/s^{-1} mm^{-3} Temperature of the wire/°C					
			200	250	300	350	400	450
H_2–HT	8(bottom)	c	30.34	32.98	31.74	40.02	33.74	29.02
	(top)	c'	25.09	23.18	22.16	27.51	23.97	21.77
	20(bottom)	c	75.26	84.07	88.68	85.33	87.56	87.46
	(top)	c'	13.62	12.72	12.04	9.44	9.45	9.76
	30(bottom)	c	47.92	—	56.24	59.92	85.62	88.16
	(top)	c'	7.13	—	5.74	5.17	5.93	5.21
	41(bottom)	c	31.55	—	39.72	—	53.55	59.43
	(top)	c'	14.80	—	13.05	—	10.04	8.95
D_2–DT	8(bottom)	c	24.87	—	24.47	28.44	—	28.68
	(top)	c'	20.16	—	19.57	23.13	—	23.08
	20(bottom)	c	56.52	62.10	66.87	—	70.92	70.51
	(top)	c'	17.72	16.03	16.01	—	15.46	15.56
	30(bottom)	c	32.13	39.67	47.29	—	55.05	60.09
	(top)	c'	18.26	19.65	20.63	—	17.77	16.33

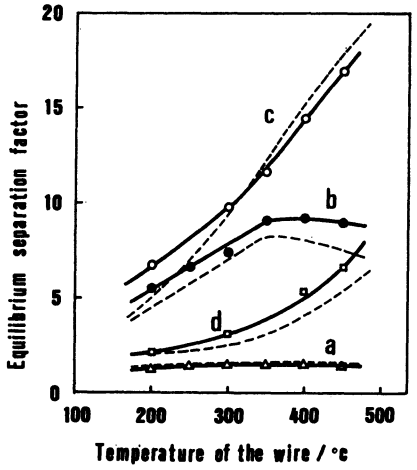

Fig. 6. The temperature dependence of experimental q_e (——) and theoretical q_e (------) in H_2–HT.
(a): 8, (b): 20, (c): 30, (d): 41 mmϕ.

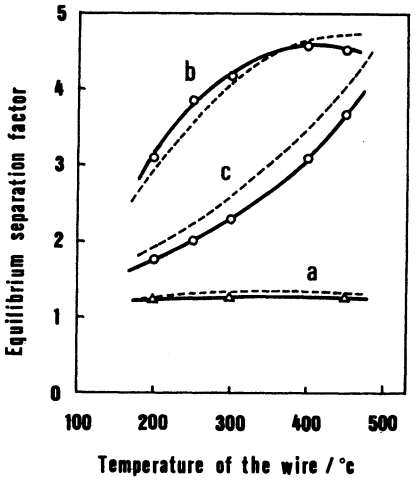

Fig. 7. The temperature dependence of experimental q_e (——) and theoretical q_e (------) in D_2–DT.
(a): 8, (b): 20, (c): 30 mmϕ.

small modifications of Waldmann's method, developed for flat-type systems. Waldmann's equation is written as Eq. 3[4] when the concentration of one component is very low:

$$\ln A'/A = -h/H^*, \tag{3}$$

where A and A' are the concentrations at both ends of the flat-type system and where h is the effective length of the system. H^* is given as follows:

$$H^* = \frac{T_0}{\Delta T}\frac{1+\alpha\left(\frac{d}{d^*}\right)^6}{\beta\left(\frac{d}{d^*}\right)^3}d, \tag{4}$$

where d is the distance between two walls, where T_0 is the average temperature of two walls: $(T_1+T_2)/2$ and

$$\Delta T = T_1 - T_2, \tag{5}$$

where α is the constant which depends on the intermolecular potential of the gas, and where β is the constant which depends not only on the intermolecular potential, but also on the ordinary diffusion coefficient and the thermal-diffusion coefficient. The optimum distance between the two walls, d^*, is given by:

$$d^* = \sqrt[3]{610\frac{R}{\mu g P}\frac{T_0^2}{\Delta T}D\eta}, \tag{6}$$

where R is the gas constant, g is the gravitational acceleration, P is the pressure of the gas, D is the ordinary diffusion coefficient, η is the viscosity of the gas, and

$$\mu = M_1X_1 + M_2(1-X_1), \tag{7}$$

where M_1 and M_2 are the molecular weights of the two components of the mixture and X_1 is the mole fraction of M_1.

When these equations are applied to wire-type columns, α and β must be modified, and the distance between the two walls, d, is replaced by the radius of the column. The optimum radius of the wire-type column can be simply calculated from d^* by multiplying it by the constant corresponding to α. The constants, α and β, for the column used are evaluated by fitting

the calculated q_e value to the experimental q_e value. The calculated results are shown by dotted lines in Figs. 6 and 7. In the case of H_2–HT, α and β were given as 1.8 and 0.14 respectively, while in the case of D_2–DT, α and β were given as 1.8 and 7.0×10^{-2} respectively. In this calculation, the concentration of tritium was rewritten in terms of radioactivity:

$$\ln c/c' = -h/H^*, \tag{8}$$

and the theoretical separation factor, q_e, was obtained from Eqs. 2 and 8 as follows:

$$q_e = \exp(h/H^*). \tag{9}$$

The viscosity of hydrogen at T_0 was available from the literature.[5] The viscosity of deuterium at T_0 was obtained by postulating that the isotope effect is 1.39[6] at all the temperatures used. The diffusion coefficient of H_2–HT was available from the literature,[7,8] but that of D_2–DT was not. The diffusion coefficient of D_2–DT used was the average of D_2–HT[7] and D_2–T_2.[7] In these cases, the coefficient of each system at T_0 was obtained from the linear relation between $\log D$ and $\log T$. Figs. 6 and 7 show two cases where each calculated q_e value comes closest to the experimental q_e value. Accordingly, it can be said that α and β are independent of the wire temperature. Figures 6 and 7 can be rewritten as Figs. 8 and 9, where the dependence of q_e on d/d^* at various temperatures is shown. These figures indicate that q_e is greatly affected by d/d^* and that the maximum q_e is given at 0.80 on the d/d^* abscissa in both cases, irrespective of the temperature of the wire.

The following results were obtained from this study:

1. The separation factors of tritium in H_2–HT and D_2–DT (1.7×10^{-2} Ci mol^{-1}) systems for thermal-diffusion columns 100 cm in length could be obtained by changing the diameter of the column and the wire temperature.
2. It was found that a modified application of Waldmann's equation to the hot-wire-type column was possible by introducing two parameters. These parameters were independent of the wire temperature.
3. The optimum radius of the column for the enrichment was given as 80% of the optimum distance of a flat-type apparatus.

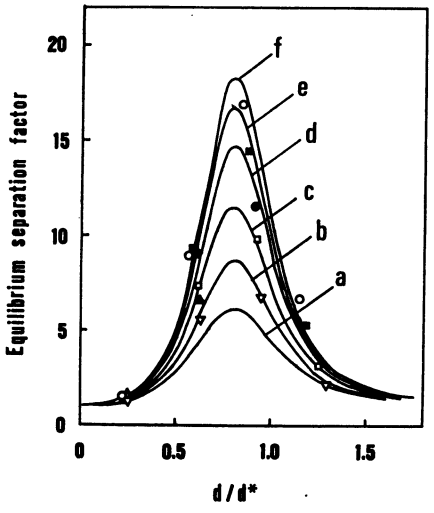

Fig. 8. Dependence of theoretical q_e and experimental q_e on d/d^* in H_2–HT.
The wire temperatures were in the case of theoretical q_e: (a) 200; (b) 250; (c) 300; (d) 350; (e) 400; (f) 450 °C; in the case of experimental q_e: (▽) 200; (▲) 250; (□) 300; (●) 350; (■) 400; (○) 450 °C.

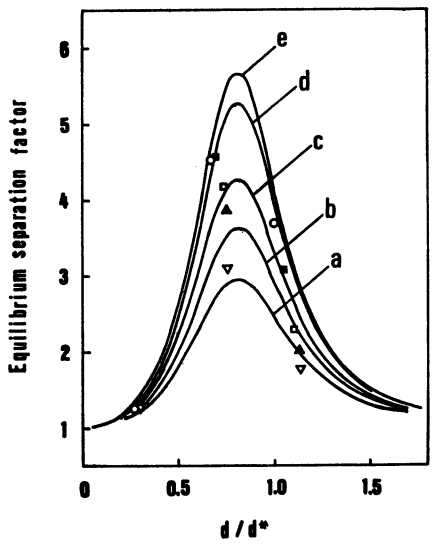

Fig. 9. Dependence of theoretical q_e and experimental q_e on d/d^* in D_2–DT.
The wire temperatures were in the case of theoretical q_e: (a) 200; (b) 250; (c); 300; (d) 400; (e) 450 °C; in the case of experimental q_e: (▽) 200; (▲) 250; (□) 300; (■) 400; (○) 450 °C;.

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