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A STUDY OF A NEW HYDROGEN ISOTOPE SEPARATION SYSTEM USING A SIMULATED MOVING BED

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ABSTRACT

A new hydrogen isotope separation system has been experimentally studied to concentrate deuterium from natural hydrogen. The present system comprises four columns packed with Pd particles and is operated in such a way that Pd particles and a hydrogen isotope gas flow simulated countercurrently. Deuterium is concentrated at the top end of the column at room temperature and atmospheric pressure. The deuterium concentration increases with an increase in the number of passages through the columns. When a 0.00996 in molar fraction $D_2 + 0.994\ H_2$ mixture or natural hydrogen with 0.00015 D in atomic molar fraction was passed through 16 columns, the maximum atomic molar fraction of deuterium at the column top end were 0.728 or 0.0508, respectively.

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INTRODUCTION

Several studies of the hydrogen isotope separation using beds packed with hydrogen-absorbing metal particles have been carried out by chromatographic processes (1–3), pressure swing absorption (PSA) (4), and temperature swing absorption (TSA) (5). The chromatographic process can attain high enrichment with once-through operation. However, it is a batch process and a long column is needed in order to attain high enrichment. Although PSA and TSA are a semicontinuous system, they cannot attain high enrichment regardless of complicated operation at a high-pressure condition. We proposed an alternately countercurrently moving bed process (6–7), which can attain high enrichment by semicontinuous operation.

Here, we study a hydrogen isotope separation system using simulated moving-bed technique. The hydrogen isotope separation by simulated moving-bed process has been carried out by Andreev et al. (8). Although Andreev's apparatus used a special rotary valve, the present system used a conventional 5-way valve and 3-way valves. This system is composed of four columns packed with Pd particles. A gas mixture of hydrogen isotopes and Pd particles in the bed move in a simulated countercurrent way by opening and closing valves. The conventional simulated moving-bed system is continuous operation, but the present system is semicontinuous operation, where an isotopic gas mixture is fed continuously but the product flow is withdrawn for a specific time interval. The advantage of the system is that the enrichment process is obtained by opening and closing the valves, which is similar to a chromatographic process for a long column. The highly enriched deuterium is obtained at the top end of the column. We call it a 4-column simulated moving-bed system. The present system can be applied to hydrogen isotope separation in a fuel cycle of a fusion reactor, in hydrogen isotope-handling laboratories, or in industrial separation of deuterium from natural hydrogen.

OPERATION OF 4-COLUMN SIMULATED MOVING-BED SYSTEM

Figure 1 shows a schematic diagram of the deuterium concentration process by the 4-column moving-bed system. The whole system is comprised of four columns packed with Pd particles. Three columns (C2, C3, C4) in the figure are at the conditions of absorption and isotope exchange of hydrogen isotopes. The rest (C1) is at the condition of desorption of hydrogen isotopes by heating. The former three columns are at bottom, middle, and top positions. Hydrogen isotope gas mixture flows from C2 at the bottom position to C4 at the top position. C1 is at a standby position. Hydrogen isotope gas is introduced into C2 and is absorbed

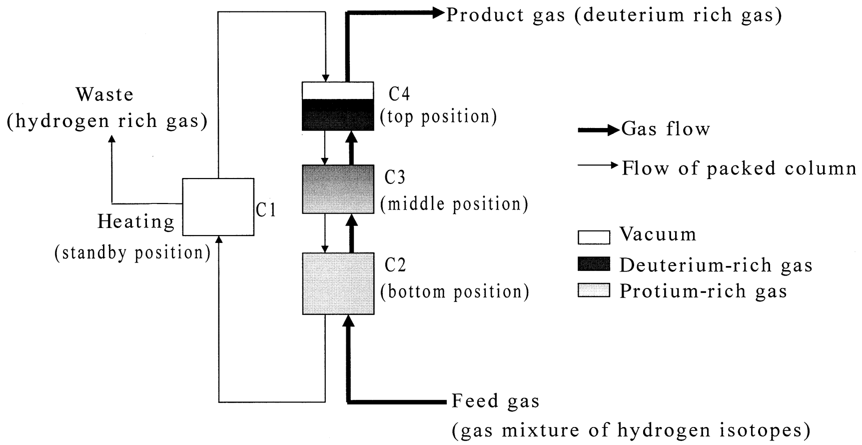

Figure 1. A schematic diagram of deuterium concentration process by 4-column moving bed.

in C2, C3, and C4. Just when C4 is sufficiently filled with hydrogen isotopes, C2 is cut off. C2 is moved to the standby position, and C1 is moved to the top position. The hydrogen in C2 is desorbed by heating. C3 and C4 are moved to the middle and bottom positions, respectively. With repetitions of these steps, the hydrogen gas mixture and the Pd particles are moved in a countercurrent way. It does not mean to move the columns in an actual countercurrent way. In the present system, the gas mixture and Pd particles are moved in a simulated countercurrent way by opening and closing valves.

The concentration operation by the 4-column simulated moving-bed system is shown in Fig. 2. The operation was comprised of the following four steps.

a) Pretreatment step; hydrogen or other impurities in four columns packed with Pd particles are completely desorbed by heating.
b) Gas feed step; the three columns (C1, C2, C3) are connected through valves. Both end valves of C4 are closed. C1 at the bottom position is fed with a gas mixture of hydrogen isotopes. The top end valve of C3 is closed.
c) Concentration step; the concentration step is composed of the following four stages:
   –In stage 1, just when the pressure of C3 at the top position reaches the feed gas pressure, C1 is cut off and C4 is connected to C3 through valves. The gas inlet is switched from the bottom of C1 to that of C2, and the gas mixture is fed to C2, so that the gas mixture flows in a way

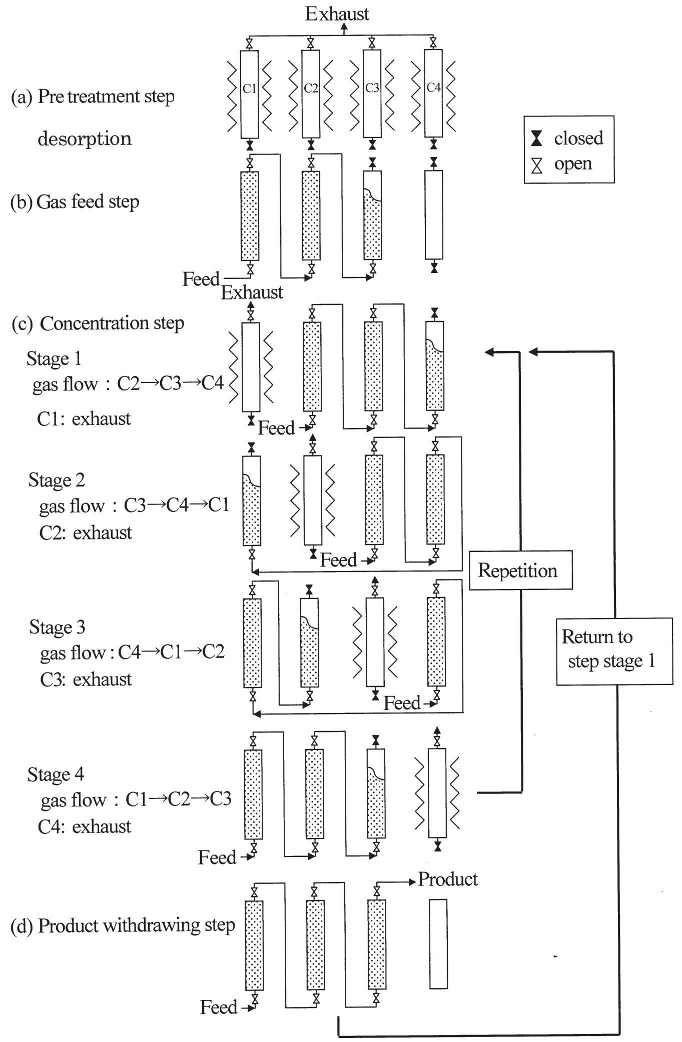

Figure 2. Diagram of the concentration operation by 4-column system.

of C2→C3→C4. Hydrogen isotopes in C1 are exhausted as a waste by heating. Deuterium is highly enriched at a frontal region of the top position column.

–In stage 2, the gas mixture flows C3→C4→C1 in a similar way to stage 1.

–In stage 3, the gas mixture flows C4→C1→C2.
–In stage 4, the gas mixture flows C1→C2→C3.

The concentration step is repeated until the required concentration at the top position column is completed.

d) Product withdrawing step; the product including enriched deuterium is withdrawn through the end valve of the top position column. The concentration operation ((C) + (D)) is continued by returning to stage 1 of the concentration step.

A highly enriched deuterium product is obtained at the product withdrawing step, and a deuterium-depleted waste is obtained as the exhaust gas at the respective stages in the concentration step.

EXPERIMENTAL APPARATUS AND PROCEDURES

Figure 3 shows a schematic diagram of the experimental apparatus. The apparatus is composed of four columns, 3-way and 5-way valves, C-A thermocouples, a temperature controller, a mass-flow controller, and a pressure strain gauge. The separation column is 700 mm long and 3.0 mm in inner diameter and

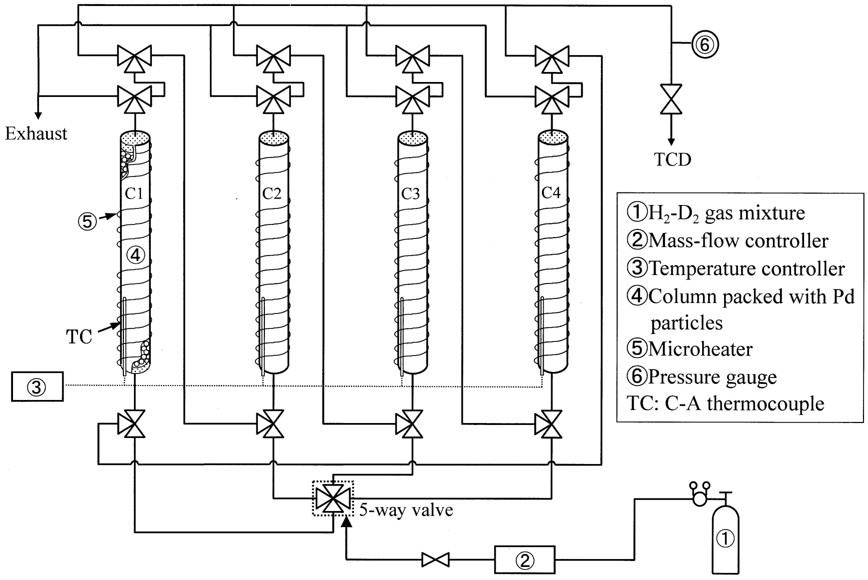

Figure 3. A schematic diagram of the experimental apparatus.

is packed with 10 g of Pd particles of 350 μm in a mean diameter. The stated purity of Pd is 99.99 wt% with the following impurities: 40 ppm Pt, 2 ppm Ru, 7 ppm Cu, 4 ppm Fe, 2 ppm Pb, 4 ppm Si, 10 ppm Ti, 4 ppm As, and 2 ppm B. The columns were heated by a microheater, and their temperatures were regulated by a temperature controller. The gas flow rate was regulated by the mass-flow controller. As a preliminary experiment, the effects of the gas flow rate and the column temperature on concentration behavior were investigated. The gas flow rate was set to be 4.2×10^{-5} mol/s (56 ml(NTP)/min) throughout the present experiment, and the column temperature was set to 303 K.

The experiment was carried out by operating the valves and switching on or off the heater shown in Fig. 2. The columns were heated up to 493 K under atmospheric pressure to desorb any gases from Pd particles. The columns were supplied with any of the two hydrogen–deuterium gas mixtures in atomic molar fraction D_2(0.00996)-H_2(0.990) and natural hydrogen produced by water-vapor reforming of methanol, which includes the deuterium atomic molar fraction of 0.00015. The D_2(0.00996)-H_2(0.990) mixture was prepared by mixing pure hydrogen (6 nines purity) and deuterium containing atomic molar fraction of 0.997. No further purification of the gases was made. The absorbed hydrogen in the standby position column was desorbed by heating it up to 493 K under atmospheric pressure. The number of columns where the gas mixture was passed through varied from 1 to 16. A product flow was drawn from the top of the series columns after the gas mixture passed through a required number of columns. A thermal conductivity detector (TCD, YANACO, Model G-1880T) was used to measure the atomic molar fraction of deuterium in the product flow. The TCD has two flow cells, and the reference gas used is pure natural hydrogen. The TCD generates a voltage that is in proportion to the deuterium atomic molar fraction. The TCD was calibrated almost in the range from 0.00996 to 0.997 deuterium molar fraction. Data acquisition system (YOKOGAWA, Model WE-7000) was used to collect data on pressure, temperature, the flow rate, and the gas composition continuously. The resolution of the WE-7000 is 0.1 K or 10 μV.

Under the experimental conditions, the time needed to switch from one column to another column was 18 min (the heating time was 5 min and the cooling time was 13 min) and the gas feed time was 15 min.

RESULTS AND DISCUSSION

It was also found from preliminary experiments that the isotopic equilibrium among H_2, HD, and D_2 after passing through a single column packed with Pd particles is always established. In addition, the presence of HD in the feed gas doesn't affect the deuterium atom fraction in the product flow. Therefore, atomic molar fraction of deuterium is used as a unit of the deuterium concentration in the present paper.

Deuterium Concentration Curve

Figures 4 and 5 show the deuterium concentration curves after passing through a specified number of columns for the feed condition of the D_2(0.00996)-H_2(0.990) mixture and natural hydrogen. The time 0 on the horizontal axis in Figs. 4 and 5 is defined as time when the product gas starts to break through. As seen in the figures, the maximum deuterium atomic molar fraction and the width of the elution curves increase with an increase in the number of the columns where the gas mixture passed through. Hereafter, the number of passed columns is noted as n. With repetitions of the concentration step, highly enriched deuterium and a wide elution curve are obtained. The wider elution curve can lead to an easier way to obtain a product. When the gas mixtures were passed through 16 columns, the maximum deuterium atomic molar fraction, $(x_{D,out})_{\max}$, was 0.728 and 0.0508 for their respective feed gas. The concentration ratio was defined as the ratio of the deuterium concentration in product to that in feed gas, $x_{D,out}/x_{D,in}$. The maximum concentration ratio, $(x_{D,out})_{\max}/x_{D,in}$, was 73 for the D_2(0.00996)-H_2(0.990) mix-

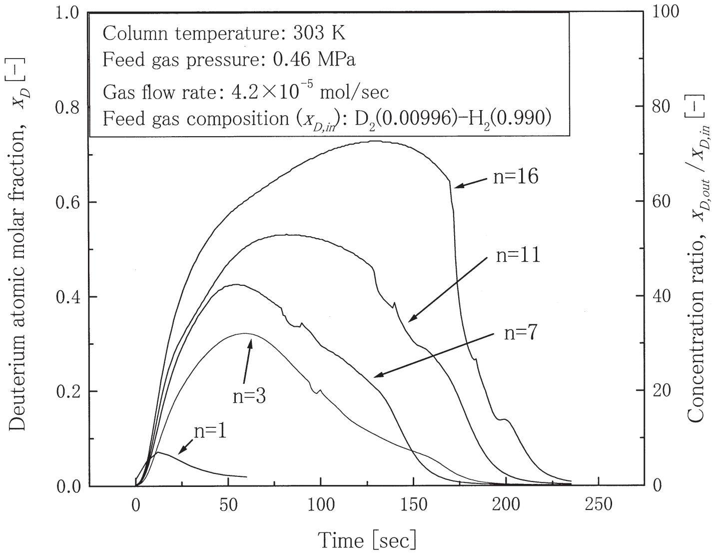

Figure 4. Variations of elution curves with the number of passed columns for D_2(0.00996)-H_2(0.990) feed.

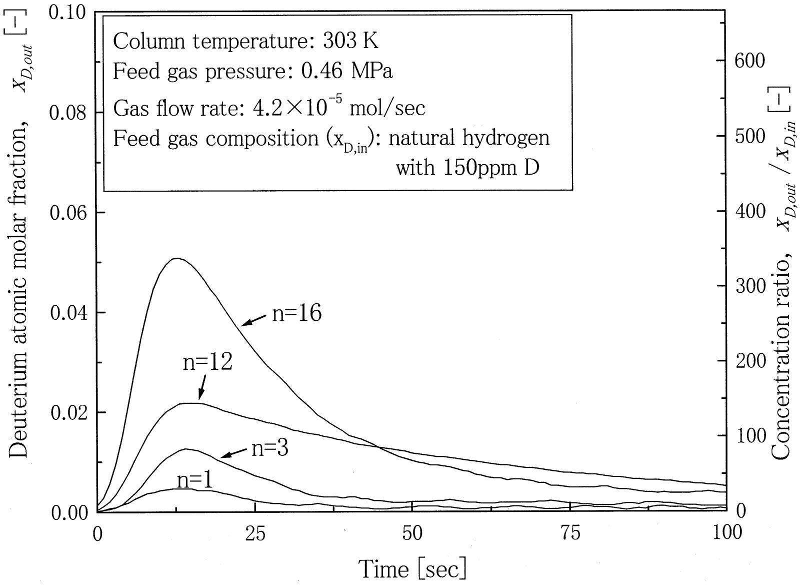

Figure 5. Variations of elution curves with the number of passed columns for natural hydrogen feed.

ture and 367 for natural hydrogen. The width of the elution curve was about 3 min for the D_2(0.00996)-H_2(0.990) mixture and 30 s for natural hydrogen. Thus highly enriched deuterium can be obtained from the top end of the columns by the present system. Energy is necessary to heat columns for desorption.

Recovery Ratio

Figures 6 and 7 show the recovered deuterium amount versus the number of passed columns for the D_2(0.00996)-H_2(0.990) mixture and natural hydrogen, respectively. The recovered deuterium amount was calculated from the integration area of the deuterium concentration curve when $(x_{D,out} - x_{D,in})/(x_{D,out})_{\max} > 0.05$. The recovered deuterium amount was found to be proportional to n. The linearity means a constant recovery ratio because the feed amount is also in proportion to n. The recovery ratio is defined as the ratio of the recovered deuterium amount to the feed deuterium amount. The recovery ratio ranged from 0.419 to 0.458 for the D_2(0.00996)-H_2(0.990) mixture and 0.481 to 0.629 for natural hydrogen. The mean value for the recovery ratio is 0.44 ± 0.02 for the D_2(0.00996)-H_2(0.990) mixture and 0.51 ± 0.04 for natural hydrogen except for n = 1. The recovery

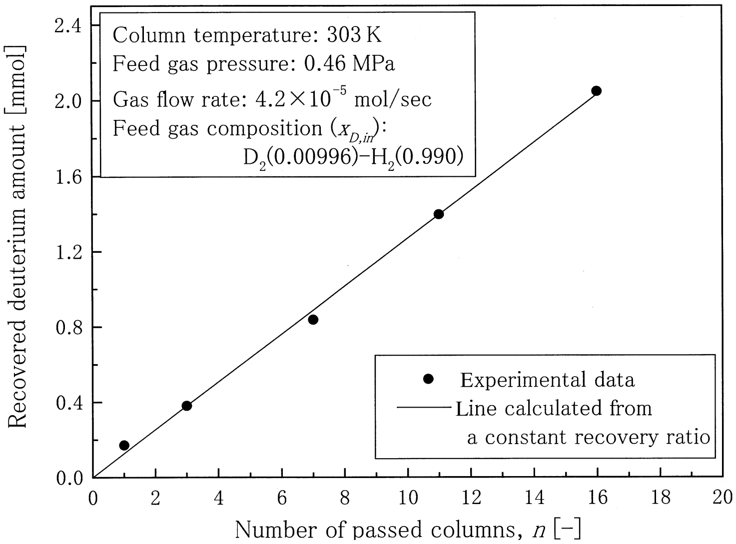

Figure 6. Recovered deuterium amount for D_2(0.00996)-H_2(0.990) versus the number of passed columns.

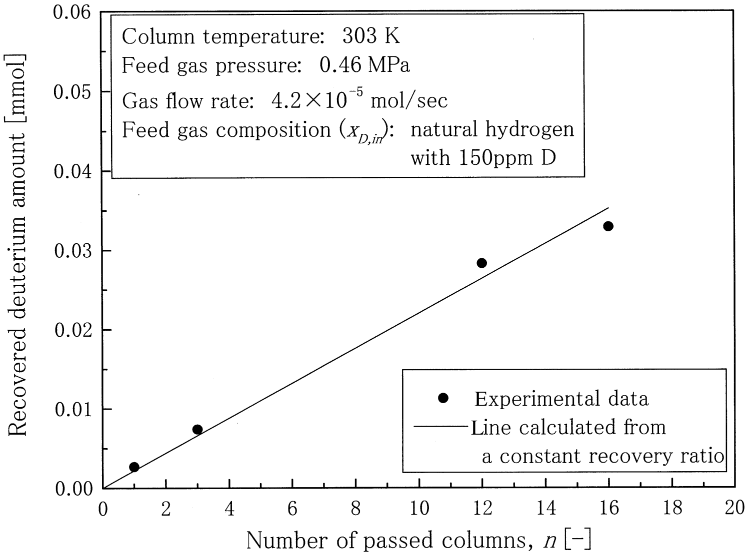

Figure 7. Recovered deuterium amount for natural hydrogen versus the number of passed columns.

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ratio of natural hydrogen for $n = 1$ was large because the concentration ratio is low and the deuterium concentration is close to the background of TCD, and for that reason its was excluded from the mean value. When $n = 16$, 1.09 mL (NPT) of deuterium was recovered from 11.4 L of natural hydrogen. The rest was exhausted as the waste. The waste gas with depleted deuterium is used as natural hydrogen in chemical processes.

Here, we evaluate an ideal deuterium recovery ratio for the frontal chromatography based on the equilibrium theory (1). When a hydrogen–deuterium mixture with a deuterium atomic molar fraction x_D is supplied to a Pd bed with a constant molar flow rate V for a certain time Δt, the hydrogen-absorbing zone in the bed comprising two bands emerges. The first band is in equilibrium with the feed gas, and the less-absorbing species (D in this case) is absorbed in the second band. Two equations can be derived based on the overall material balance as follows:

$$Vx_D\,\Delta t = q_I\,y_D + q_{II} \tag{1}$$

$$V(1 - x_D)\,\Delta t = q_I\,(1 - y_D) \tag{2}$$

Here, q_I and q_{II} are the total absorption molar amounts in the first band and the second band, respectively, and y_D is the D/(H + D) ratio in the solid phase. When deuterium only in the second band is recovered as a product, the recovery ratio R is defined as follows;

$$R = \frac{q_{II}}{q_I\,y_D + q_{II}} \tag{3}$$

The isotope separation factor $\alpha_{\text{H-D}}$ between hydrogen and deuterium is defined as follows:

$$\alpha_{\text{H-D}} = \frac{x_D(1 - y_D)}{y_D\,(1 - x_D)} \tag{4}$$

From Eqs. (1) to (4), one can derive the recovery ratio as follows;

$$R = \frac{\alpha_{\text{H-D}} - 1}{\alpha_{\text{H-D}}} \tag{5}$$

The $\alpha_{\text{H-D}}$ value is 1.88 at 303K from our previous study (9). Accordingly, R is 0.47. This theoretical R comparatively agrees with the experimental result for the D_2(0.00996)-H_2(0.990) mixture and natural hydrogen.

CONCLUSIONS

Hydrogen isotopes were efficiently separated by the 4-column simulated moving-bed system. Deuterium was concentrated at the top end of the series column, and the waste was exhausted by the desorption. When the gas mixtures were passed through 16 columns, the maximum deuterium atomic molar fraction was 0.728 for the D_2(0.00996)-H_2(0.990) mixture and 0.0508 for natural hydrogen. The recovered deuterium amount was found to be proportional to the number of passed columns. The recovery ratio of deuterium was 0.44 ± 0.02 for the D_2(0.00996)-H_2(0.990) mixture and 0.49 ± 0.02 for natural hydrogen. This recovery ratio agreed with that obtained by the local equilibrium model. The energy is added only for heating in the exhaustion. Therefore, the industrial separation of deuterium from natural hydrogen is possible by the present system.

NOMENCLATURE

x_D	deuterium atomic molar fraction (−)
n	number of passed columns (−)
Δt	time interval (sec)
V	molar flow rate (mol/sec)
q	total absorption molar amounts (mol)
y_D	D/(H + D) ratio in the solid phase (−)
R	recovery ratio (−)
$\alpha_{\text{H-D}}$	isotope separation factor between hydrogen and deuterium (−)

Subscripts

in	inlet
out	outlet
max	maximum
I	first band
II	second band

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