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A Novel Procedure of Hydrogen Isotope Separation Based on Chemical Exchange and a Selective Permeable Membrane

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Abstract: It is shown theoretically that a novel process of hydrogen isotope separation can be obtained by combining bithermal isotopic exchange with transport through a selective permeable membrane. The theory of the process predicts that a small column with high separation and very small inventory can be realized. The method is attractive especially for small and medium scale processes, such as tritium enrichment, heavy water upgrading, and final deuterium concentration.

Keywords: Isotope separation, tritium, deuterium, chemical exchange, selective permeable membranes

INTRODUCTION

Hydrogen isotope separation is needed for many purposes and hundreds of separation methods have been proposed, but only a few of them show any real promise (1–3). The purpose of this paper is to theoretically show how a novel procedure for hydrogen isotope separation can be obtained by a combination of bithermal isotopic exchange with transport through a selective permeable membrane. It is also shown that the theoretical prediction regarding practical applicability is favorable and the author recommends this procedure for research and development.

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In the sections that follow: the separation principle; how the elementary separation can be multiplied on a countercurrent column; the theoretical background of the separation column and relations that allow evaluating the performance of the procedure; and noteworthy diagrams and examples have been described. In the last section, Discussion, the practical applicability of the procedure is discussed, and some requirements for obtaining a good efficiency are mentioned. Nomenclature is given at the end of the paper.

SEPARATION PRINCIPLE

To explain the novel separation principle we consider the device presented schematically in Fig. 1c. Two reservoirs, one cold R_c maintained at temperature T_c and one hot R_h maintained at temperature T_h, are connected by a capillary tube C in which a selective membrane M is placed. A working material, which is considered to be a mixture of hydrogen and water vapor, is introduced into reservoirs. For simplicity, it is assumed that the isotopic mixture is binary, deuterium, and protium, and that the D/H ratio is low so that the molecular species D_2O and D_2 are of negligible concentration. A catalyst CAT placed in the reservoirs makes possible the exchange reaction

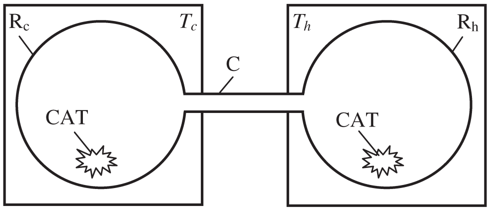
$$HD + H_2O \rightleftharpoons H_2 + HDO \tag{1}$$

The equilibrium constant of this reaction coincides with the separation factor $\alpha = (x_e/1 - x_e)/(y_e/1 - y_e)$, which for low D/H ratio is approximated as $\alpha = x_e/y_e$. According to Bardo and Wolfsberg (4),

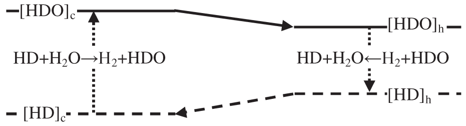
$$\ln \alpha = -0.17739 + 1.10658\left(\frac{300}{T}\right) + 0.61704\left(\frac{300}{T}\right)^2 - 0.36997\left(\frac{300}{T}\right)^3 + 0.07978\left(\frac{300}{T}\right)^4 \tag{2}$$

In order to clarify the role of the membrane we first analyze what happens in the device presented in Fig. 1a in which membrane M is absent. The higher the temperature, the more reaction (1) is displaced to the left giving rise to different concentrations of the molecular species in the reservoirs. Thus, in the absence of the membrane M, all molecular species diffuse through the capillary, and this process continues indefinitely, since the concentration differences between reservoirs are continuously maintained by reaction (1). The steady state, attained after a long time, is characterized by a dynamic equilibrium in which both deuterium and protium continuously circulate between the cold and hot reservoirs. The diagram in Fig. 1b illustrates how deuterium is carried by deuterated molecules from one reservoir to another. Because $\alpha_c > \alpha_h$, the molecular species HDO has a greater concentration in R_c than in R_h

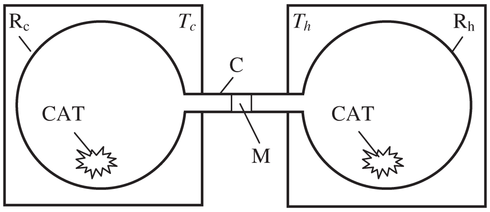
(a) Separation element without membrane



(b) Diagramp of deuterated molecules in absence of membrane



(c) Separation element with membrane



(d) Diagram of deuterated molecules in presence of membrane

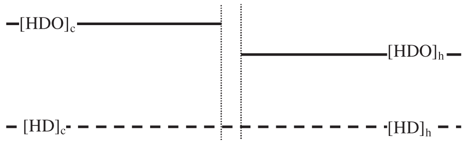


Figure 1. Schematic diagram of the separation element. R_c and R_h, cold and hot reservoirs. T_c and T_h, cold and hot temperatures. CAT, catalyst. M, selective permeable membrane.

and, conversely, HD has a greater concentration in R_c than in R_h. Thus, there is a net flux of HDO through the capillary from R_c to R_h, and a net flux of HD from R_h to R_c. By means of reaction (1), deuterium passes in R_c from HD to HDO and, conversely, in R_h from HDO to HD. Protium circulates between reservoirs similarly to deuterium but in the opposite direction.

Now, let us consider the case when the membrane M is present in the capillary, Fig. 1c. The membrane is supposed to be permeable only for one of the chemical components and, to fix the ideas, consider it is permeable for hydrogen and impermeable for water vapor. The final state of this system is static; no net transfer of the molecular species takes place in the capillary. The state of the deuterated molecules is shown in Fig. 1d. Since H_2 and HD can pass freely through the capillary, their final concentrations are the same in R_c and R_h, i.e. the same deuterium concentration in hydrogen, $y_{ce} = y_{he}$. On the contrary, HDO is more concentrated in R_c than in R_h and H_2O is more concentrated in R_h than in R_c. In other words, deuterium concentration in water vapor is significantly higher in R_c than in R_h and this is an isotopic separation expressed by $x_{ce}/x_{he} = \alpha_c/\alpha_h$.

It is useful to consider the gas mixture in each reservoir as a distinct phase; let the gas mixture in the cold reservoir R_c be called the cold phase, and in the hot reservoir the hot phase.

The overall deuterium atom-fraction in the gaseous mixture is given by $\tilde{x} = \chi x + (1 - \chi)y$, where χ is the vapor fraction in the gaseous mixture. When the membrane is absent, Fig. 1a, this concentration $\tilde{x}$ has roughly the same value in R_c and R_h. When the membrane is present, Fig. 1b, $\tilde{x}$ is significantly higher in R_c than in R_h, and we introduce the separation factor between reservoirs, or between the cold and hot phases,

$$\tilde{\alpha} = \tilde{x}_{ce}/\tilde{x}_{he} = (1 - \chi_c + \alpha_c\chi_c)/(1 - \chi_h + \alpha_h\chi_h \qquad (3)$$

When $\chi_c = \chi_h = \chi$ and χ increases from 0 to 1, $\tilde{\alpha}$ increases monotonically from 1 to its maximum value α_c/α_h. However, if $\chi \rightarrow 1$ then the rate of the isotopic transfer between reservoirs tends to zero, which means that the separation power also tends to zero. The optimal χ, for which the separation power is maximal, depends on α_c and α_h but is situated around the value $\chi = 0.5$. This value will be used later in the numerical examples.

It is noteworthy that an isotopic separation effect by thermodiffusion is also present, but is relatively small, and we neglect it.

SEPARATION COLUMN

We have considered that only a capillary connects the reservoirs in Fig. 1 in order to induce the idea that the diffusion rate between reservoirs is much smaller than the rate of the reaction (1). Such a limit case is useful for some reasonings, but to increase the separative power, the diffusion rate between cold and hot phases should be as great as possible. Such a condition is well satisfied by the separation column represented schematically in Fig. 2. The column is composed of two catalytic walls, one cold CCW at temperature T_c and one hot HCW at temperature T_h. The space between the walls is divided into two compartments by the selective permeable membrane SPM. The two compartments contain the gas mixture and correspond to the two reservoirs in Fig. 1c. The cold phase is situated between the cold wall and membrane; the hot phase is situated between the hot wall and membrane.

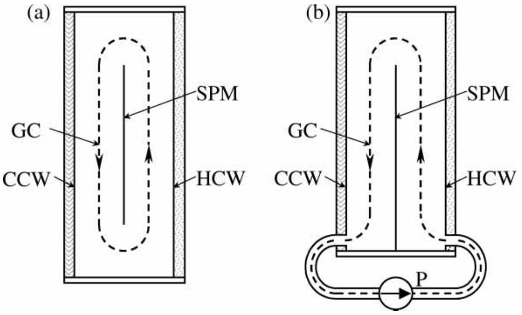


Figure 2. Schematic diagram of the separation column: (a) with free gas convection and (b) with pumped gas movement. CCW, cold catalytic wall. HCW, hot catalytic wall. SPM selective permeable membrane. GC, gas circuit. P, pump.

In the space between the walls, the temperature increases steadily from T_c to T_h. However, at equilibrium, the concentrations of the molecular species are determined by the temperature at which the exchange reaction (1) takes place. The equilibrium distribution of the molecular concentrations in the cold phase is determined by T_c and in the hot phase by T_h. Consequently, if in the column, Fig. 2, the gas phases do not move and the system is at steady state then the cold phase has the same composition as in reservoir R_c, Fig. 1c, and the hot phase has the same composition as in reservoir R_h. The isotopic separation between phases is given by the same Eq. (3).

The elementary separation process can be multiplied by countercurrent movement of the two phases as shown in Fig. 2.

The gas movement can be realized by free convection, Fig. 2(a), for which the column preferably has an upright position. Because of a density difference, the cold phase moves downward and the hot phase upward. At the ends of the column the membrane is interrupted, such that the gas mixture turns from one compartment to the other.

The gas movement can be driven by pumping, Fig. 2(b). In this case the gas flow rate can be better controlled and, on the other hand, a long column can be made compact by folding or coiling. However, the pressure difference introduced by pumping should be low, otherwise hydrogen and vapor have a tendency of separating along the column.

THEORETICAL BACKGROUND OF THE SEPARATION COLUMN

Flat Plate Geometry and the Height of the Theoretical Plate

Using the theory of some countercurrent processes developed previously (5–8), an advanced mathematical description of the separation column could be carried out. However, only a simplified version is given here, which is sufficient for an initial performance evaluation of the separation process. Moreover, the long deductions are omitted, and only the basic relationships and the assumptions in which they are established are given.

At the column ends, the velocity, temperature, and concentration fields have particular features and their mathematical description would necessitate laborious treatment. These end effects were studied for similar countercurrent processes and it was found that their contribution to the separation is less than 1/2 the theoretical plate (6). Thus we neglect here the end effects and consider only the central zone of the column where the fields are completely developed.

At low D/H ratio, there is a case in which the isotopic concentration varies linearly along the column, and the height of the equivalent theoretical plate *h* has the simplest expression (5–8). This case occurs when

$$G/L = \tilde{\alpha} \tag{4}$$

For G/L ratio taking values in a domain of practical interest, the function $h(G/L)$ has a relatively small slope. Thus the approximation $h(G/L) \simeq h(\tilde{\alpha})$ can be done, for which h has the form

$$h = A_{\mathrm{s}}L + A_{\mathrm{d}}/L \tag{5}$$

A_s and A_d are parameters whose expressions for flat plate geometry are given by

$$A_s = \frac{1}{b(1-\chi_c+\chi_c\alpha_c)}\left[\frac{\tilde{\alpha}^2\alpha_h\chi_h^2}{K_h} + \frac{(1-\chi_c+\chi_c\alpha_c)^2}{K_{ch}} + \frac{\alpha_c\chi_c^2}{K_c}\right] \tag{5a}$$

$$\begin{aligned} A_d = {} & \frac{b}{1-\chi_c+\chi_c\alpha_c}(\xi_m-\xi_{hw})n^{(\xi 2)}[(1-\chi_h)D_{\mathrm{HD}}^{(\xi 2)} + \chi_h D_{\mathrm{HDO}}^{(\xi 2)}\alpha_h] \\ & + (\xi_{cw}-\xi_m)n^{(\xi 5)}[(1-\chi_c)D_{\mathrm{HD}}^{(\xi 5)} + \chi_c D_{\mathrm{HDO}}^{(\xi 5)}\alpha_c] \end{aligned} \tag{5b}$$

K_h, K_{ch}, and K_c are rate constants given by

$$\frac{1}{K_h} = \frac{\xi_2-\xi_{hw}}{n^{(\xi 1)}}\left[\frac{\alpha_h}{(1-\chi_h)D_{\mathrm{HD}}^{(\xi 1)}} + \frac{1}{\chi_h D_{\mathrm{HDO}}^{(\xi 1)}}\right] + \frac{1}{K_{hw}} \tag{6a}$$

$$\frac{1}{K_{ch}} = \frac{\xi_m-\xi_2}{n^{(\xi 3)}(1-\chi_h)D_{\mathrm{HD}}^{(\xi 3)}} + \frac{1}{K_m} + \frac{\xi_5-\xi_m}{n^{(\xi 4)}(1-\chi_c)D_{\mathrm{HD}}^{(\xi 4)}} \tag{6b}$$

$$\frac{b}{K_c} = \frac{\xi_{cw}-\xi_5}{n^{(\xi 6)}}\left[\frac{\alpha_c}{(1-\chi_c)D_{\mathrm{HD}}^{(\xi 6)}} + \frac{1}{\chi_c D_{\mathrm{HDO}}^{(\xi 6)}}\right] + \frac{1}{K_{cw}} \tag{6c}$$

Now, let us explain the notations and the assumptions used to establish the expressions (5a–6c). Consider Fig. 3, in which ξ is the coordinate axis perpendicular to the hot and cold walls.

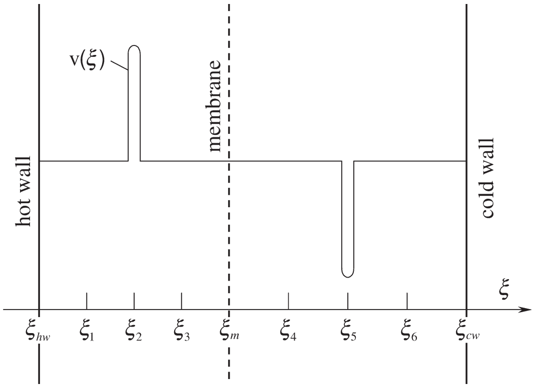


Figure 3. Assumed gas velocity profile $v(\xi)$ and coordinate points ξ_i used in the mathematical description.

The thickness of the membrane is assumed negligible and the membrane coordinate is denoted by ξ_m. By ξ_{hw} and ξ_{cw} are denoted the hot and cold wall-coordinates, $\xi_{hw} < \xi_m < \xi_{cw}$.

The diffusion coefficients D_{HD} and D_{HDO}, and the total molar density n are assumed as stepwise functions for which the following intermediary points are used:

$$\xi_1 = \xi_{hw} + 0.25(\xi_m - \xi_{hw}), \quad \xi_2 = \xi_{hw} + 0.5(\xi_m - \xi_{hw}), \quad \xi_3 = \xi_{hw} + 0.75(\xi_m - \xi_{hw}) \tag{7a}$$

$$\xi_4 = \xi_m + 0.25(\xi_{cw} - \xi_m), \quad \xi_5 = \xi_m + 0.5(\xi_{cw} - \xi_m), \quad \xi_6 = \xi_m + 0.75(\xi_{cw} - \xi_m) \tag{7b}$$

Thus the superior indices (ξ1) ... (ξ6) at D_{HD}, D_{HDO}, and n show that these quantities have the values that correspond to the temperatures that are present at the coordinates $\xi_1 \ldots \xi_6$.

Gas velocity v(ξ) is assumed to be zero overall except at some small intervals, around ξ_2 in the hot zone, and around ξ_5 in the cold zone, where the whole mixture flow is concentrated, as suggested in Fig. 3. This assumption simplifies the results and, although unnatural, does not produce essential deviations of the results.

K_{hv} and K_{cw} are the rate constants of the catalytic hot and cold walls, the deuterium transport on a unit-surface of wall being defined by

$$\tau_{hw} = K_{hw}(x_{hw} - \alpha_h y_{hw}), \quad \tau_{cw} = K_{cw}(\alpha_c y_{cw} - x_{cw}) \tag{8}$$

Similarly, K_m is the rate constant of the deuterium transport through a unit-surface of membrane

$$\tau_m = K_m(y_{hm} - y_{cm}) \tag{9}$$

where indices *hm* and *cm* mean the h̲ot and c̲old m̲embrane faces.

Cylindrical Geometry and the Height of the Theoretical Plate

For the cylindrical geometry, Eq. (5) is valid but the coefficients A_s and A_d are given by

$$A_s = \frac{1}{1-\chi_c+\chi_c\alpha_c}\frac{1}{2\pi}\left[\frac{\tilde{\alpha}^2\alpha_h\chi_h^2}{k_h}+\frac{(1-\chi_c+\chi_c\alpha_c)^2}{k_{ch}}+\frac{\alpha_c\chi_c^2}{k_c}\right] \tag{10a}$$

$$A_d = \frac{\pi}{1-\chi_c+\chi_c\alpha_c}\Big\{(r_m^2-r_{hw}^2)n^{(r2)}[(1-\chi_h)D_{\mathrm{HD}}^{(r2)}+\chi_h D_{\mathrm{HDO}}^{(r2)}\alpha_h]$$

$$+(r_{cw}^2-r_m^2)n^{(r5)}[(1-\chi_c)D_{\mathrm{HD}}^{(r5)}+\chi_c D_{\mathrm{HDO}}^{(r5)}\alpha_c]\Big\} \tag{10b}$$

The expressions for k_h, k_{ch}, and k_c are

$$\frac{1}{k_h} = \frac{\ln(r_2/r_{hw})}{n^{(r1)}}\left[\frac{\alpha_h}{(1-\chi_h)D_{\mathrm{HD}}^{(r1)}}+\frac{1}{\chi_h D_{\mathrm{HDO}}^{(r1)}}\right]+\frac{1}{r_{hw}K_{hw}} \tag{11a}$$

$$\frac{1}{k_{ch}} = \frac{\ln(r_m/r_2)}{n^{(r3)}(1-\chi_h)D_{\mathrm{HD}}^{(r3)}}+\frac{1}{r_m K_m}+\frac{\ln(r_5/r_m)}{n^{(r4)}(1-\chi_c)D_{\mathrm{HD}}^{(r4)}} \tag{11b}$$

$$\frac{1}{k_c} = \frac{\ln(r_{cw}/r_5)}{n^{(r6)}}\left[\frac{\alpha_c}{(1-\chi_c)D_{\mathrm{HD}}^{(r6)}}+\frac{1}{\chi_c D_{\mathrm{HDO}}^{(r6)}}\right]+\frac{1}{r_{cw}K_{cw}} \tag{11c}$$

Instead of the axial coordinate ξ, the radial coordinate r is used. The relative positions of the hot wall, membrane, and cold wall coordinates are $r_{hw} < r_m < r_{cw}$. The intermediate points are given by

$$r_1 = r_{hw}+0.25(r_m-r_{hw}), \quad r_2 = r_{hw}+0.5(r_m-r_{hw}),$$

$$r_3 = r_{hw}+0.75(r_m-r_{hw}) \tag{12a}$$

$$r_4 = r_m+0.25(r_{cw}-r_m), \quad r_5 = r_m+0.5(r_{cw}-r_m),$$

$$r_6 = r_m+0.75(r_{cw}-r_m) \tag{12b}$$

Gas flow is concentrated around r_2 in the hot zone and around r_5 in the cold zone. K_{hw} and K_{cw} have the same meaning as for the flat plate geometry.

PERFORMANCE PARAMETERS

The most important parameters used to evaluate the performance of a separation process are the density of separative power, specific energy consumption, and the characteristic time.

The density of separative power is the separative work produced by a unit length of column in a unit of time. Cohen showed how to determine the separative work for countercurrent elements (9). If an element of column is operated in optimal conditions, the density of the separative power is found to be

$$\rho_{sp} = (\sqrt{\tilde{\alpha}} - 1)^2 \frac{L}{h} \tag{13}$$

The specific energy consumption, that is the heat necessary to obtain a unit of separative work, is

$$\rho_q = Q/\rho_{sp} \tag{14}$$

where Q is the heat transported from the hot to cold walls per unit time and per unit column length.

The relaxation or equilibrium time of the column is directly proportional to the characteristic time defined by

$$\theta = N/\rho_{sp} \tag{15}$$

where N is the total mole number (of hydrogen and water vapor) per unit column length.

The first term in Eq. (5) refers to transversal transport that produces separative work. The second term is due to longitudinal diffusion that destroys separative work. Function h has a minimum value given by

$$h_{\min} = 2\sqrt{A_s A_d} \qquad \text{for} \qquad L = L_{h-\min} = \sqrt{A_d/A_s} \tag{16}$$

Eq. (13) can be written

$$\rho_{sp} = \rho_{sp0}/[1 + (L_{h-\min}/L)^2] \quad \text{where} \quad \rho_{sp0} = (\sqrt{\tilde{\alpha}} - 1)^2/A_s \tag{17}$$

Note that ρ_{sp} increases monotonically with L and attains its maximum ρ_{sp0} when $L \rightarrow \infty$.

Work with $L_{h-\min}$ is useful when one wishes to obtain a large separation on a small column. Usually, we are interested in large separative power density ρ_{sp}, and for this purpose a too large L is not necessary. For instance, if $L = 4L_{h-\min}$ then $\rho_{sp} = 0.94\rho_{_{\mathrm{sp}}}0$, and if $L = 10L_{h-\min}$ then $\rho_{sp} = 0.99\rho_{sp0}$.

NOTEWORTHY EXAMPLES

In order to shed light upon the applicability of the separation procedure, some noteworthy examples were calculated. For this purpose, the diffusion coefficients D_{HD} and D_{HDO}, of HD and HDO in a gas mixture, and the thermal conductivity λ of the hydrogen-vapor mixture were necessary. For low D/H ratio, $\mathrm{D_{HD}}$ and D_{HDO} are expressed by binary diffusion coefficients (6),

$$\frac{1}{D_{\mathrm{HD}}} = \frac{\chi}{D_{\mathrm{HD-H_2O}}} + \frac{1-\chi}{D_{\mathrm{HD-H_2}}}, \quad \frac{1}{D_{\mathrm{HDO}}} = \frac{\chi}{D_{\mathrm{HDO-H_2O}}} + \frac{1-\chi}{D_{\mathrm{HDO-H_2}}} \tag{18}$$

The binary coefficients $D_{\mathrm{HD-H_2}}$, $D_{\mathrm{HD-H_2}}$O, and $D_{\mathrm{HDO-H_2}}$ were derived from "Molecular Theory of Gases and Liquids" by Hirschfelder et al. (10). For $D_{\mathrm{HDO\ -\ H_2}}$O, Eq. (8.2–44) in Ref. 7 combined with experimental data from Landolt-Börnstein (11) were used. Thus the following relations were established:

$$pD_{\mathrm{HD-H_2}} = -6.223 + 4.576\,(T/100) + 0.5812\,(T/100)^2 \tag{18a}$$

$$pD_{\mathrm{HD-H_2O}} = -5.159 + 2.994\,(T/100) + 0.3631\,(T/100)^2 \tag{18b}$$

$$pD_{\mathrm{HDO-H_2}} = -6.15 + 3.569\,(T/100) + 0.4328\,(T/100)^2 \tag{18c}$$

$$pD_{\mathrm{HDO-H_2O}} = -2.741 + 1.374\,(T/100) + 0.2001(T/100)^2 \tag{18d}$$

For the thermal conductivity of the gas mixture, the interpolation equation

$$\lambda = \lambda_h + (\lambda_h - \lambda_v)[\chi - 0.98\chi(1-\chi)] \tag{19}$$

was used, where λ_h and λ_v are thermal conductivities of hydrogen and water vapor given by $\lambda_h = 0.079 + 0.000364T$, $\lambda_v = -0.00746 + 0.0000832T$.

In all examples, the catalytic walls and membrane are considered ideal, that is $K_{cw} = K_{hw} = K_m = \infty$.

Firstly, we consider atmospheric pressure ($p = 101325$ Pa) at which, to avoid water vapor condensation, the cold temperature cannot be lower than about 82°C.

Figure 4 illustrates the dependence of h and ρ_{sp}/b on the specific flow rate L/b. Such diagrams allow choosing the working value for L/b. In most practical cases, a sufficiently large L/b ratio is convenient, such that the contribution of the longitudinal diffusion is negligible and ρ_{sp}/b can be approximated by its superior limit ρ_{sp0}/b.

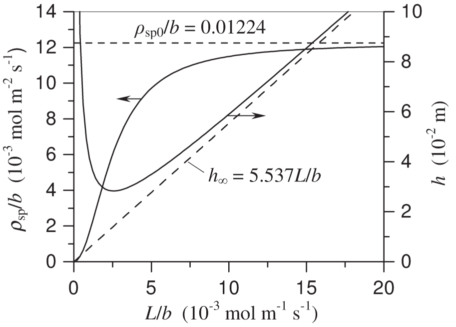


Figure 4. Density of the separative power ρ_{sp}/b and equivalent height of the theoretical plate h versus specific flow rate L/b for planar geometry, $t_c = 82$°C, $t_h = 500$°C, $p = 101325$ Pa, $d_c = d_h = 0.005$ m, $\chi_c = \chi_h = 0.5$, $K_{cw} = K_{hw} = K_m = \infty$.

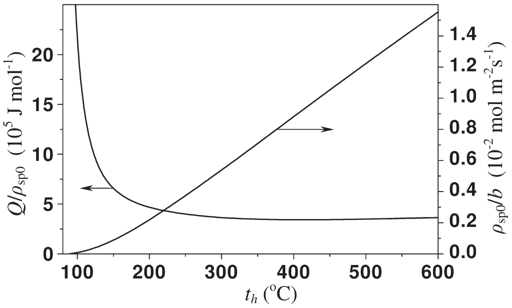


Figure 5. Density of the separative power ρ_{sp0}/b and energy consumption per unit of separative power Q/ρ_{sp0} versus hot wall temperature t_h for planar geometry, $t_c = 82°C$, $p = 101325$ Pa, $d_c = d_h = 0.005$, $\chi_c = \chi_h = 0.5$, and $K_{cw} = K_{hw} = K_m = \infty$.

Figure 5 shows that if the hot wall temperature increases over 500°C, ρ_{sp0} continues to increase, although the value of α_h changes only slightly. This behavior is due to the increase of the diffusion coefficients with temperature.

The specific energy consumption Q/ρ_{sp0} is almost constant over 300°C. However, a heat source of higher temperature is more expensive, and for this reason the examples that follow are made for a hot temperature of 500°C.

Example 1 (Atmospheric Pressure)

Given Data

Flat plate geometry; $d_c = d_h = 0.005$ m; $p = 101325$ Pa; $\chi_c = \chi_h = 0.5$; $t_c = 82°C$; $t_h = 500°C$; $K_{cw} = K_{hw} = K_m = \infty$.

Computed Data

$\alpha_c = 2.803$; $\alpha_h = 1.3940$; $\tilde{\alpha} = 1.5885$; $A_s b = 5.537$ m^2 s mol^{-1}; $A_d/b = 3.615 \cdot 10^{-5}$ mol s^{-1}; $\rho_{sp0}/b = 0.01224$ mol m^{-2}S^{-1}; $Q/\rho_{sp0} = 3.468 \cdot 10^5$ *J*, $\theta = 18.47$ s

a. To separate 1 kg heavy water in one year to 99.8% D, from a natural source with 0.015% D, the following are necessary:
   Separative work = 327177 mol/kg(D_2O)
   Energy consumption = 31519 kWh/kg(D_2O)
   Column surface (lengths times breadth) = 0.9278 m^{2}year/kg(D_2O)

b. To separate 1 kg heavy water in one year to 99.8%D, from a pre-enriched water of 5% D, the following are necessary:
   Separative work = 1209 mol/kg(D_2O)
   Energy consumption = 116.5 kWh/kg(D_2O)
   Column surface (lengths times breadth) = 0.003429 m^2year/kg(D_2O)

Example 2 (Low Pressure)

Given Data

Flat plate geometry; $d_c = d_h = 0.005$ m; $p = 0.2467 \cdot 10^5$ Pa; $\chi_c = \chi_h = 0.5$; $t_c = 50°C$; $t_h = 500°C$; $K_{cw} = K_{hw} = K_m = \infty$.

Computed Data

$\alpha_c = 3.196$; $\alpha_h = 1.3840$; $\tilde{\alpha} = 1.7527$; $A_s b = 1.526$ m^2 s mol^{-1}; $A_d/b = 13.80 \cdot 10^{-5}$ mol s^{-1}; $\rho_{sp0}/b = 0.06873$ mol m^{-2} s^{-1}; $Q/\rho_{sp0} = 64892$ J; $\theta = 0.4085$ s

a. To separate 1 kg heavy water in one year to 99.8%D, from a natural source with 0.015%D, the following are necessary:
   Separative work = 327177 mol/kg(D_2O)
   Energy consumption = 5907 kWh/kg(D_2O)
   Column surface (lengths times breadth) = 0.1653 m^2year/kg(D_2O)

b. To separate 1 kg heavy water in one year to 99.8% D, from a pre-enriched water of 5%D, the following are necessary:
   Separative work = 1209 mol/kg(D_2O)
   Energy consumption = 21.83 kWh/kg(D_2O)
   Column surface (lengths times breadth) = 0.0006109 m^2year/kg(D_2O)

DISCUSSION

Based on the described procedure one can conceive separation columns of small dimensions, high separation, and very small inventory. According to Fig. 4, for a specific flow rate of $L/b = 0.0159$ mol m^{-1} s^{-1} mol m^{-1} s^{-1}, a theoretical plate height $h = 0.09$ m is obtained. As the elementary separation factor is $\tilde{\alpha} = 1.5885$, it follows that a column of 3 m length can give a huge separation of $\tilde{\alpha}^{3/\mathrm{h}} = 5 \cdot 10^6$. A greater specific flow rate L/b can be also used, but then the theoretical plate height becomes greater according to the asymptotic equation $h_\infty = 5.537\,L/b$. The column inventory is very low, it is four orders of magnitude smaller than that in an equivalent water distillation column packed with Dickson rings.

These properties make the procedure appropriate for small-scale separation. The procedure seems to be very attractive for tritium separation, where a relatively small installation with small inventory is required. The procedure could also be preferred in nuclear reactors for heavy water reconcentration and in heavy water plants for final concentration.

The procedure is less attractive for the primary concentration of deuterium, because the specific energy consumption is too high and because too much column surface is necessary. However, in many industrial processes, heat is transferred from a hot source to a less hot receptor. Such a heat transfer could be made through a separation column and thus the isotope separation cost would be relieved of the energy cost.

In the above examples, both catalytic walls and selective permeable membrane were considered ideal, with $K_{cw} = K_{hw} = K_m = \infty$, because it is important to know the superior limit of the separation performance. On the other hand it seams possible that very good components can be realized.

A hot catalytic wall with large K_{hw} is easy to realize as the catalytic activity increases rapidly with temperature.

The separation performance improves strongly when the temperature of the cold wall decreases. Thus a very active catalyst is required for the cold wall. However, there are very good platinum catalysts, hydrophobic or hydrophilic, with which a high value for K_{cw} could be obtained.

The membrane should be characterized by a large K_m and, at the same time, should have a catalytic activity for reaction (1) as low as possible. One can show that if the membrane has a high catalytic activity then its presence is almost useless. A research to elaborate the required membrane can start from a literature survey on membrane separation processes as that by Ritter and Ebner (12).

If the membrane is removed, the system still produces separation, because diffusivity of hydrogen is higher than that of water molecules. In other words, the gas mixture is like a membrane that is more permeable to hydrogen than to water vapor. Without the membrane the separation power diminishes about ten times because $\tilde{\alpha}$ diminishes. Moreover, the isotope separation is reduced because hydrogen and vapor separate from each other along the column due to thermodiffusion.

NOMENCLATURE

A_d	coefficient in Eq. (5) (m mol/s)
A_s	coefficient in Eq. (5) (m s/mol)
b	breadth of planar column (m)

D_{HDc}, D_{HDh}, D_{HDOc}, D_{HDOh}	coefficients of diffusion of HD and HDO in gas mixture, in cold and hot zones (m^2/s)
d_c	$\xi_{cw} - \xi_m$, thickness of cold zone (m)
d_h	$\xi_m - \xi_{hw}$, thickness of hot zone (m)
G	flow rate of the ascendant gas mixture (mol/s)
h	height of the equivalent theoretical plate (m)
k_c, k_h, k_{ch}	rate constants, Eqs. (11a–c) (mol/m s)
K_c, K_h, K_{ch}	rate constants, Eqs. (6a–c) (mol/m s)
K_{hw}, K_{cw}, K_m	rate constants, Eqs. 8, 9 (mol/m s)
L	flow rate of the descendent gas mixture (mol/s)
$L_{h-\min}$	L for which h is minim (mol/s)
n_c, n_h	molar densities of the gas mixture in cold and hot zones ($\mathrm{mol}/\mathrm{m}^3$)
p	pressure (Pa)
Q	heat transport, Eq. (14) (J/m s)
r, $r_1, \ldots$	radial coordinates, Eq. (12a–b) (m)
S_c, S_h	cold, hot cross areas of cold and hot zones (m^2)
t_c, t_h	temperature cold, hot (C)
T_c, T_h	temperature cold, hot (K)
x, y	D-atom fraction in water vapor and hydrogen gas ($-$)
x_e, y_e	x and y at equilibrium ($-$)
$\tilde{x}$	$\chi x + (1 - \chi)y$, overall D-atom fraction in gaseous mixture ($-$)
x_e, y_e	x and y at equilibrium ($-$)
$\tilde{x}$	$\chi x + (1 - \chi)y$, overall D-atom fraction in gaseous mixture ($-$)
$\tilde{x}_c$, $\tilde{x}_h$	$\tilde{x}$ in cold and hot zones ($-$)
$\tilde{x}_{ce}$, $\tilde{x}_{he}$	$\tilde{x}_c$, $\tilde{x}_h$ at equilibrium ($-$)
χ	water vapor fraction in gaseous mixture ($-$)
χ_c, χ_h	χ in cold and hot zones ($-$)
α	x_e/y_e, deuterium separation factor between water vapor and hydrogen ($-$)
α_c, α_h	α for T_c, T_h ($-$)
$\tilde{\alpha}$	$\tilde{x}_{ce}/\tilde{x}_{he}$, deuterium separation factors between cold and hot zones ($-$)
λ, λ_h, λ_v	thermal conductivity for mixture, hydrogen, and vapor (J/m K)
ξ_{hw}, $\xi_1, \ldots$	coordinate, Fig. 3, Eqs. (7a–b) (m)
ρ_{sp}	density of separative power, Eq. (13) (mol/m s)
ρ_{sp0}	maximum of ρ_{sp}, when $L \to \infty$ (mol/m s)
θ	characteristic time, Eq. (15) (s)
ρ_q	specific energy consumption, Eqs. (8–9) (J/mol)
τ_{hw}, τ_{cw}, τ_m	transports, Eqs. (8–9) (mol/m s)

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