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An Analytical Approach to the Hydrogen–Water Isotopic Exchange on a Stage Column

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Abstract

Hydrogen isotope separation by countercurrent hydrogen–water exchange on a stage column is studied analytically. It is assumed that the mixture is binary and that one of the components is of low concentration. The results obtained simplify the calculations and the reasoning connected with the separation process. A method to determine the optimum catalyst volume on a stage is presented.

INTRODUCTION

After a hydrophobic catalyst was invented (*1*), research activity regarding hydrogen isotope separation by hydrogen–water exchange was revitalized with a view to improve heavy water production and, especially, tritium removal from water (*2–4*). The separation process takes place on a column. This column may be of the differential type (for example, the packed column, proposed by Schindewolf et al. (*2*)) or it may be a stage column (for example, that which was used in Canada in a heavy water plant (*5*)). To describe the separation process on a stage column, a graphical procedure (*5*) or a simulation procedure using finite difference equations (*3, 6*) has been used.

In this paper an analytical treatment of the stage column is presented. It is supposed that only two isotopes are present, and one of them is of low concentration. Elementary separation factors for both water–vapor scrubbing and the vapor–hydrogen exchange step are assumed to be constant throughout the column.

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The separation process depends on a large number of parameters, so the utilization of the graphical or simulation procedure in some practical problems is difficult. The analytical treatment yields equations which can be handled easier.

THE THEORY ON THREE STREAMS

The stage column consists of a series of identical stages (Fig. 1). Each stage contains two elements, a reactor with a catalyst bed and an absorber which has the structure of a distillation column. Let A and B be any two of the three hydrogen isotopes H, D, and T, and suppose that B is of low concentration. The hydrogen gas–water vapor exchange

$$(AB)_g + (A_2O)_v \rightleftharpoons (A_2)_g + (ABO)_v$$

proceeds in the reactor, and the water vapor–liquid water exchange

$$(ABO)_v + (A_2O)_l \rightleftharpoons (A_2O)_v + (ABO)_l$$

proceeds in the absorber.

The isotope concentrations x, y, and z are small.

As is usually assumed, the exchange mole number for a volume dv of catalyst in time dt is given by

$$\tau\, dv\, dt = k_c(y - \alpha_c z)\, dv\, dt \tag{1}$$

For a steady state, this assumption, together with the material balances, leads to

$$y_s^* = \frac{V\alpha_c + G\varphi_c}{G + V\alpha_c} y_{s-1} + \alpha_c \frac{G(1 - \varphi_c)}{G + V\alpha_c} z_{s-1} \tag{2a}$$

$$z_s = \frac{V(1 - \varphi_c)}{G + V\alpha_c} y_{s-1} + \frac{G + V\alpha_c\varphi_c}{G + V\alpha_c} z_{s-1} \tag{2b}$$

where

$$\varphi_c = \exp\left[-k_c v_c\left(\frac{\alpha_c}{G} + \frac{1}{V}\right)\right] \tag{3}$$

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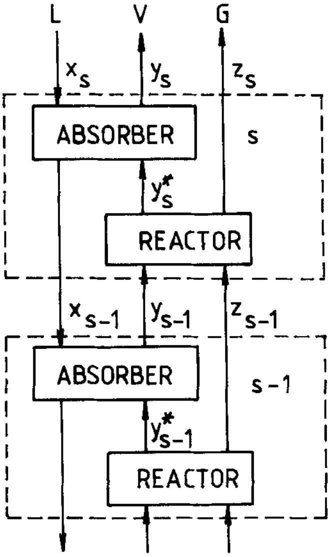

FIG. 1. Schematic structure of stage column.

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The parameter φ_c has the properties $0 < \varphi_c < 1$; if $k_c v_c \to 0$, then $\varphi_c \to 1$; and if $k_c v_c \to \infty$, then $\varphi_c \to 0$.

The exchange effect of the absorber may be described by similar relations:

$$x_s = \frac{L\alpha_d - V\varphi_d}{L\alpha_d - V} x_{s-1} - \alpha_d \frac{V(1 - \varphi_d)}{L\alpha_d - V} y_s^* \tag{4a}$$

$$y_s = \frac{L(1 - \varphi_d)}{L\alpha_d - V} x_{s-1} + \frac{L\alpha_d\varphi_d - V}{L\alpha_d - V} y_s^* \tag{4b}$$

where

$$\varphi_d = [V/(L\alpha_d)]^{N_d} \tag{5}$$

where N_d is the number of the theoretical plates in the absorber.

Equations (2) and (4) constitute an algebric system of 4S equations.

The following way to approach this system is proposed here.

By eliminating y_s from Eqs. (2) and (4):

$$x_s = a_{11}x_{s-1} + a_{12}y_{s-1} + a_{13}z_{s-1} \tag{6a}$$

$$y_s = a_{21}x_{s-1} + a_{22}y_{s-1} + a_{23}z_{s-1} \tag{6b}$$

$$z_s = \qquad a_{32}y_{s-1} + a_{33}z_{s-1} \tag{6c}$$

where

$$a_{11} = \frac{L\alpha_d - V\varphi_d}{L\alpha_d - V}; \qquad a_{12} = -\frac{V\alpha_d(1-\varphi_d)}{L\alpha_d - V}\,\frac{G\varphi_c + V\alpha_c}{G + V\alpha_c};$$

$$a_{13} = -\frac{GV\alpha_c\alpha_d(1-\varphi_c)(1-\varphi_d)}{(G + V\alpha_c)(L\alpha_d - V)}; \qquad a_{21} = \frac{L(1-\varphi_d)}{L\alpha_d - V};$$

$$a_{22} = \frac{G\varphi_c + V\alpha_c}{G + V\alpha_c}\,\frac{L\alpha_d\varphi_d - V}{L\alpha_d - V}; \qquad a_{23} = \frac{G\alpha_c(1-\varphi_c)}{G + V\alpha_c}\,\frac{L\alpha_d\varphi_d - V}{L\alpha_d - V};$$

$$a_{32} = \frac{V(1-\varphi_c)}{G + V\alpha_c}; \qquad a_{33} = \frac{G + V\alpha_c\varphi_c}{G + V\alpha_c}$$

System (6) is related to a system of linear differential equations:

$$df_i/d\xi = \sum_{j=1}^{3} b_{ij}f_j, \qquad i = 1, 2, 3 \tag{7}$$

The continuous variable ξ corresponds to the discrete variable s. In order to solve System (7), a solution of the form $f_i = A_ie^{\lambda\xi}$ is tried. In a similar way, in order to solve System (6), the solution $x_s = pe^{\lambda s}$, $y_s = qe^{\lambda s}$, $z_s = e^{\lambda s}$ is tried. The general solution of System (6) is a linear combination of three solutions. There are two distinct situations.

a) If

$$L\alpha_c\alpha_d - V\alpha_c - G \neq 0 \tag{8}$$

then

$$x_s = \alpha_c\alpha_dC + C_0p_0e^{\lambda_0 s} + C_1p_1e^{\lambda_1 s} \tag{9a}$$

$$y_s = \alpha_cC + C_0q_0e^{\lambda_0 s} + C_1q_1e^{\lambda_1 s} \tag{9b}$$

$$z_s = C + C_0e^{\lambda_0 s} + C_1e^{\lambda_1 s} \tag{9c}$$

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where C, C_0, and C_1 are arbitrary constants; $\lambda_0^* = 0$; λ_0 and λ_1 with $|\lambda_0| < |\lambda_1|$ are the solutions of the characteristic equation

$$(e^{\lambda} - 1)\left\{e^{2\lambda} - \frac{LV}{(V\alpha_c + G)(L\alpha_d - V)}\left[\frac{G\alpha_d}{V}(1 + \varphi_c\varphi_d) + \frac{\varphi_c + \varphi_d}{L}(L\alpha_c\alpha_d - V\alpha_c - G)\right]e^{\lambda} + \varphi_c\varphi_d\right\} = 0 \quad (10)$$

and p_i and q_i are given by

$$p_i = \frac{G + V}{L(1 - \varphi_c)}(e^{\lambda_i} - \varphi_c); \qquad q_i = \frac{L}{V}p_i - \frac{G}{V} \quad (11)$$

b) If

$$L\alpha_c\alpha_d - V\alpha_c - G = 0 \quad (12)$$

the characteristic equation is

$$(e^{\lambda} - 1)^2(e^{\lambda} - \varphi_c\varphi_d) = 0 \quad (13)$$

with $\lambda_0^* = \lambda_0 = 0$, $\lambda_1 = \ln(\varphi_c\varphi_d)$, and the solution is

$$x_s = C\alpha_c\alpha_d + C_0\alpha_c\alpha_d(a + s) + C_1p_1e^{\lambda_1 s} \quad (14a)$$

$$y_s = C\alpha_c + C_0\alpha_c(b + s) + C_1q_1e^{\lambda_1 s} \quad (14b)$$

$$z_s = C + C_0s + C_1e^{\lambda_1 s} \quad (14c)$$

where

$$a = \frac{V\alpha_c(1 - \varphi_d) + G(1 - \varphi_c\varphi_d)}{V\alpha_c(1 - \varphi_c)(1 - \varphi_d)}; \qquad b = \frac{L\alpha_d}{V(1 - \varphi_c)} \quad (15)$$

p_1 and q_1 are given by (11), and C, C_0, and C_1 are arbitrary constants.

The constants C, C_0, and C_1 may be determined from System (9) or (14) by giving, for instance, three concentrations at the two ends of the column.

Equations (9) and (14) with the characteristic Eqs. (10) and (13) represent a compact mathematical expression of the separation process. In order to solve practical problems, it is advantageous to use these equations rather than Eqs. (2) and (4).

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THE THEORY ON TWO STREAMS

Advantageous simplifications are obtained if the process is looked at as an exchange between two countercurrent streams. Suppose that the liquid water and the water vapor are taken together as a single stream with flow rate $L^* = L - V$. Its concentration x^* has to be defined in such a way that L^*x^* is the convective isotopic transfer. It follows that

$$x_s^* = (Lx_s - Vy_s)/L^* \tag{16}$$

The elementary separation factor between the two streams is given by the ratio $\alpha = x_e^*/z_e$. Taking into account that $x_e^* = (Lx_e - Vy_e)/L^*$ and $\alpha_d = x_e/y_e$, it follows that

$$\alpha = \alpha_c(L\alpha_d - V)/L^* \tag{17}$$

The stage efficiency may be characterized by the Murphree efficiency

$$E_g = (z_s - z_{s-1})/(x_{s-1}^*/\alpha - z_{s-1}) \tag{18}$$

or by the ratio

$$E = \frac{\text{number of theoretical plates}}{\text{number of stages}} \tag{19}$$

It is assumed that E_g is constant; that is, it does not depend on s. Then the usual theory of countercurrent exchange between two streams is

$$x_s^* = C'\alpha + C_0' \frac{1}{R} e^{\lambda_0 s} \tag{20a}$$

$$z_s = C' + C_0' e^{\lambda_0' s}, \qquad \text{if } \alpha R \neq 1 \tag{20b}$$

where

$$\lambda_0' = \ln\left[1 + \left(\frac{1}{\alpha R} - 1\right)E_g\right] = -E \ln(\alpha R) \tag{21}$$

and

$$x_s = C'\alpha + C_0'\alpha\left(\frac{1}{E} + s\right) \tag{22a}$$

$$z_s = C' + C_0' s, \qquad \text{if } \alpha R = 1 \tag{22b}$$

The condition $\alpha R = 1$ is equivalent to Eq. (12).

Relative to the two-stream theory, it is necessary to solve two problems: a) determination of the relationship between the efficiency E_g (or E) and the stage parameters, and b) evaluation of the error made by this simplified theory.

If x_s and y_s as given by Eqs. (9a) and (9b) are substituted in Eq. (16), then

$$x_s^* = C\alpha + C_0 \frac{1}{R} e^{\lambda_0 s} + C_1 \frac{1}{R} e^{\lambda_1 s} \tag{23a}$$

$$z_s = C + C_0 e^{\lambda_0 s} + C_1 e^{\lambda_1 s}, \qquad \alpha R \neq 1 \tag{23b}$$

Comparison of the Systems (20) and (23) shows that the two-stream theory gives the same results as the three-stream theory only if the last exponential term in Eqs. (23) is negligible and if

$$\lambda_0' = \lambda_0, \qquad R \neq 1 \tag{24}$$

A consequence of the overall theory (7) is that the term containing $e^{\lambda_1 s}$ describes the end effect and differs from zero only at the bottom of the column. The end effect consists of a small supplementary exchange which may be evaluated and which represents the error made by the two-stream theory.

Suppose a large value of s is introduced in Eq. (9c) so that the last exponential term is negligible. A larger value, $s + \Delta s$, is introduced into Eq. (20b) to obtain the identity

$$C + C_0 e^{\lambda_0 s} \equiv C' + C_0' e^{\lambda_0 \Delta s} e^{\lambda_0 s}$$

This identity is satisfied for every large s if and only if $C = C'$ and $\Delta s = \lambda_0^{-1} \ln (C_0/C_0')$. Δs represents the error made by the two-stream theory. It may be expressed in theoretical plate units:

$$\Delta N = E \Delta s = \frac{E \ln (C_0/C_0')}{\lambda_0}, \qquad \alpha R \neq 1 \tag{25}$$

The efficiency E_g (or E) may be expressed from Eqs. (21) and (24) in terms of λ_0 which is a root of Eqs. (11). In this way the efficiency may be calculated from the stage parameters.

If $\alpha R = 1$, it is obtained in a similar way with $C_0 = C_0'$ and

$$E = E_g = \frac{V}{\alpha_d L} \frac{(1 - \varphi_c)(1 - \varphi_d)}{1 - \varphi_c \varphi_d}, \qquad R = 1 \tag{26}$$

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$$\Delta N \approx E(C - C')/C'_0, \qquad \alpha R = 1 \tag{27}$$

As can be seen, the error ΔN depends on the integral constants; that is, it depends on the boundary condition. If the boundary conditions are operative and not too unbalanced, then ΔN is only a fraction of a theoretical plate. Consider, for example, that x_0 and z_0 are given and $y_0 = x_0/\alpha_d$. By applying these conditions, C_0 and C'_0 are determined from Systems (9) and (20), respectively, and then substituted into Eq. (25). By using λ_0 from Eqs. (21) and (24):

$$\Delta N = -\left\{\ln\left[\frac{(\alpha_d L - V)p_1 - \alpha_d G}{(p_1 - p_0)(\alpha_d L - V)}\right]\right\}[\ln(\alpha R)]^{-1}, \qquad \alpha R \neq 1 \tag{28}$$

Applying the same conditions, System (14) gives C and System (22) gives C' and C'_0. These constants and E, as given by Eq. (26), are introduced into Eq. (27) to give

$$\Delta N = \frac{V}{\alpha_d L}\,\frac{\varphi_d(1 - \varphi_c)^2}{(1 - \varphi_c\varphi_d)^2}, \qquad \alpha R = 1 \tag{29}$$

Each of the two factors in this expression is less than 1.

Some characteristics calculated with Eqs. (28) and (29) are given in Fig. 2. Figure 2 shows that it is not expected for ΔN to be greater than 0.25. Moreover, to reduce the stage number of the column, small values for the parameters φ_c and φ_d are preferred, in which case ΔN is smaller. Thus, if the two-stream theory is applied to a column of, say, five theoretical plates, then an error of about 2% is made.

Since ΔN does not depend on the total number of theoretical plates N, the relative error $\Delta N/N$ decreases as N increases. By tritium extraction from heavy water, α is smaller, N is larger, and the error $\Delta N/N$ is smaller.

THE STAGE CATALYST VOLUME

If for a total number of N theoretical plates an error of 0.1–0.2 theoretical plates may be accepted, then the two-stream theory may be applied and all calculations and the reasoning are simplified. To illustrate these simplifications, consider the dependence on φ_c of the number of stages S^* and of the catalyst volume V^* necessary to give a theoretical plate. The parameters S^* and V^* are useful because they are proportional to the number of stages and the catalyst inventory,

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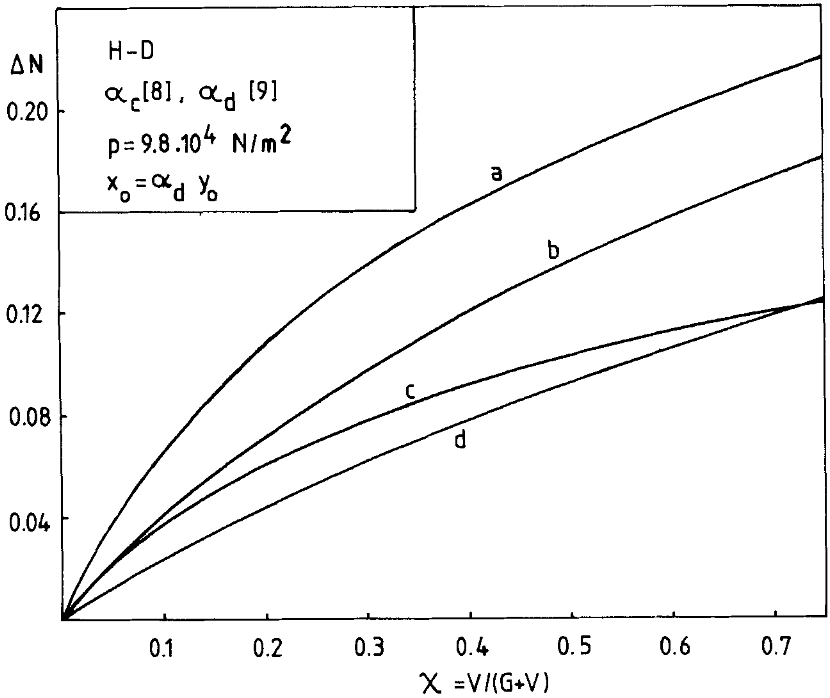

FIG. 2. Examples of characteristics regarding the error ΔN made in theory on two streams: a) $\alpha R = 1$, $\varphi_c = \varphi_d = 0.8$; b) $R = 1$, $\varphi_c = \varphi_d = 0.8$; c) $\alpha R = 1$, $\varphi_c = \varphi_d = 0.2$; d) $R = 1$, $\varphi_c = \varphi_d = 0.2$.

respectively, of the separation column. Thus, choosing a value for φ_c is a problem of investment optimization.

By removing v_c from Eq. (3) and E from Eq. (21) or (26):

$$S^* = 1/E = \begin{cases} -\lambda_0^{-1} \ln(\alpha R), & \alpha R \neq 1 \\ \dfrac{\alpha_d L}{V} \dfrac{1 - \varphi_c \varphi_d}{(1 - \varphi_c)(1 - \varphi_d)}, & \alpha R = 1 \end{cases} \tag{30}$$

$$V^* = v_c S^* = \begin{cases} \dfrac{G}{\alpha_c k_c} \dfrac{\ln \varphi_c \ln(\alpha R)}{\lambda_0[1 + G/(V\alpha_c)]}, & \alpha R \neq 1 \\ -\dfrac{G}{\alpha_c k_c} \dfrac{(1 - \varphi_c \varphi_d) \ln \varphi_c}{(1 - \varphi_c)(1 - \varphi_d)}, & \alpha R = 1 \end{cases} \tag{31}$$

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If $\varphi_c = 0$, then S^* has the minimum value S^*_m and $V^* = \infty$; if $\varphi_c = 1$, then $S^* = \infty$ and V^* has the minimum value V^*_m. The minimum values are given by

$$S^*_m = \begin{cases} -\ln(\alpha R)/\ln \dfrac{L\alpha_d/V + \varphi_d(\alpha R - 1)}{\alpha R[1 + G/(V\alpha_c)]}, & \alpha R \neq 1 \\ \dfrac{L\alpha_d}{V}\dfrac{1}{1 - \varphi_d}, & \alpha R = 1 \end{cases} \tag{32}$$

$$V^*_m = \begin{cases} \dfrac{G}{\alpha_c k_c}\dfrac{\alpha R \ln(\alpha R)}{\alpha R - 1}, & \alpha R \neq 1 \\ \dfrac{G}{\alpha_c k_c}, & \alpha R = 1 \end{cases} \tag{33}$$

Examples of Functions (30) and (31) are illustrated graphically in Fig. 3.

To choose a value for the parameter φ_c, the catalyst price and stage cost have to be known. Let C_{st} be the stage cost without the catalyst cost, and let C_{cat} be the price of a unit volume of catalyst. Then the cost of a theoretical plate is

$$C_{tp} = C_{st}S^* + C_{cat}V^* \tag{34}$$

The optimum φ_c is that for which C_{tp} is minimum.

In case accurate data are not available so that Eq. (34) cannot be applied, then a diagram such as that presented in Fig. 3 may be used to choose a reasonable φ_c.

CONCLUSIONS

Hydrogen–water isotope exchange on a stage column is treated analytically. It is assumed that only two isotopes are present and that one of them is of low concentrations. Two methods of treatment are presented: the three-stream theory and two-stream theory.

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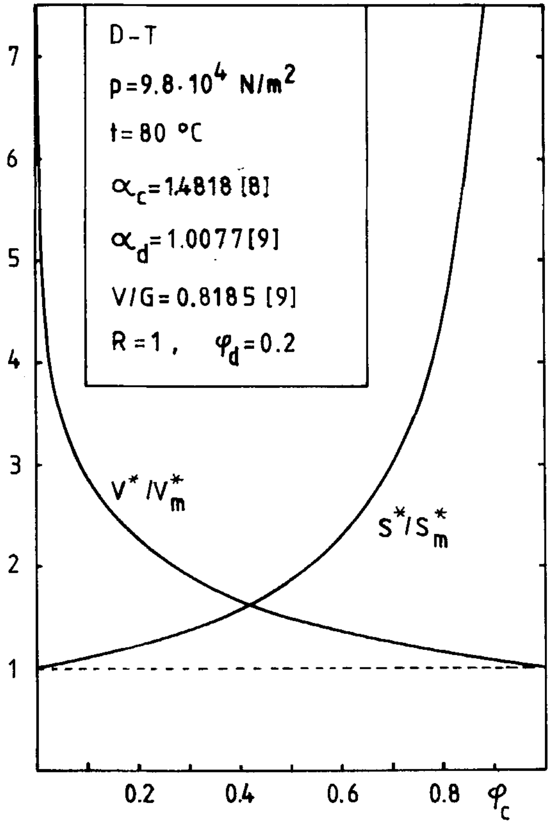

FIG. 3. Dependence on φ_c of the relative number of plates S^*/S^*_m and of the relative catalyst inventory V^*/V^*_m.

Three-stream theory takes into consideration the exchange between liquid water, water vapor, and hydrogen gas. The main result is the analytical expressions of isotope concentration given by Eqs. (9) or (14) which compactly incorporate the separation process on the multistage column.

In the two-stream theory the liquid water and the water vapor are considered to be a single stream. Thus, the process is an exchange between two countercurrent streams. This simplified theory introduces an absolute error equivalent to a part of a column of about 0.1–0.2

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theoretical plates. The two-stream theory has the advantage that all exchange calculations are simpler and the usual concepts of theoretical plate and Murphree efficiency may be used.

SYMBOLS

C, C_0, C_1	integrating constants in theory on three streams
C', C_0'	integrating constants in theory on two streams
C_{tp}	cost of a theoretical plate
E	efficiency defined by Eq. (19)
E_g	Murphree efficiency defined by Eq. (18)
G	flow rate of hydrogen gas (mol/T, where T is a time unit that may be seconds, minutes, hours, etc.)
k_c	rate constant for isotopic exchange (mol $L^{-3}T^{-1}$)
L	flow rate of liquid water (mol/T)
L^*	difference $L - V$ (mol/T)
N	total number of theoretical plates on column
ΔN	error made by the theory on two streams expressed in theoretical plates
R	slope of operating line, the ratio L^*/G
s	stage number
S	total number of stages in column
S^*	number of stages per theoretical plate
S_m^*	minimum of S^*
V	flow rate of water vapor (mol/T)
V^*	catalyst volume per theoretical plate (L^3)
V_m^*	minimum of V^*
x, y, z	isotope concentration of liquid water, water vapor, and hydrogen gas, respectively
x^*	mean isotope concentration defined by Eq. (16)
y^*	isotope concentration of water vapor at the top of a catalyst bed

Greek Symbols

$\alpha, \alpha_c, \alpha_d$	elementary separation factors given by the ratios x_e^*/z_e, y_e/z_e, and x_e/y_e, respectively
φ_c	parameter of catalyst bed defined by Eq. (3)

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φ_d	parameter of absorber defined by Eq. (5)
$\lambda_0^*, \lambda_0, \lambda_1, \lambda'$	characteristic values, $\lambda_0^* = 0$, $\lambda' = \lambda_0$, and $\lvert\lambda_d\rvert < \lvert\lambda_1\rvert$

Subscripts

e	equilibrium
m	minimum
s	stage index

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