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A Theoretical Analysis of Multicomponent Gas Separation by Means of a Membrane with Perfect Mixing

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Abstract

Numerical simulation of the separation of gas mixtures of H_2, CH_4, CO, and CO_2 through a porous glass membrane was carried out. It was found that the mole fractions of the components on the permeate side varied irregularly depending on the operating conditions., feed mole fractions, relative permeabilities, and operation factor. Theoretical analysis of membrane separation in multicomponent system was made. Some basic information were derived with respect to gas separation with a membrane for a multicomponent system.

INTRODUCTION

With the recent development of improved membranes and advances in hollow fiber technology and fabrication techniques of gas permeators, membrane separation is becoming economically competitive with other separation methods, such as distillation and adsorption. Separation of gas mixtures by permeation has been considered a standard chemical engineering unit operation.

Applications of membrane separation which have received attention include recovery of hydrogen from refinery streams and ammonia plants, sulfer dioxide removal from flue gases, hydrogen and carbon monoxide separation from synthesis gases, separation of product from reaction gases, and so on. When membrane separation is applied in such an industrial process, it is assumed to involve a multicomponent system. Most previous papers on gas separation studied binary gas mixtures. There are a few reports (*1*–*6*) about multicomponent gas separation through a membrane. However, the relationships between degree of separation and operating conditions have not been investigated.

In this paper the separation of gas mixtures of H_2, CH_4, CO, and CO_2 through a porous glass membrane is numerically simulated. It is found that the mole fraction of each component on the permeate side varies depending on operating conditions, feed mole fractions, and relative permeabilities. It is desirable that the degree of separation can be predicted theoretically from operating conditions. This paper presents a theoretical analysis of multicomponent gas separation in a single stage.

BASIC EQUATIONS

Equations for Steady-State

Figure 1 illustrates a single permeation stage of multicomponent gas separation by permeation with perfect mixing. The stage is separated into two sections by a membrane of area A and thickness δ. P_h and P_l are the pressures of the feed (high pressure) side and the permeate (low pressure) side, respectively. F_f and F_o are the inlet and outlet flow rates on the feed side, respectively, and F_p is the outlet flow rate on the permeate side. n is the number of components and Q_i is the permeability of the ith component. It is presumed that the permeabilities $Q_1, Q_2, Q_3, \ldots, Q_n$ are

$$Q_1 > Q_2 > \cdots > Q_n \tag{1}$$

x_{fi} is the mole fraction of the gas component in the feed stream at the

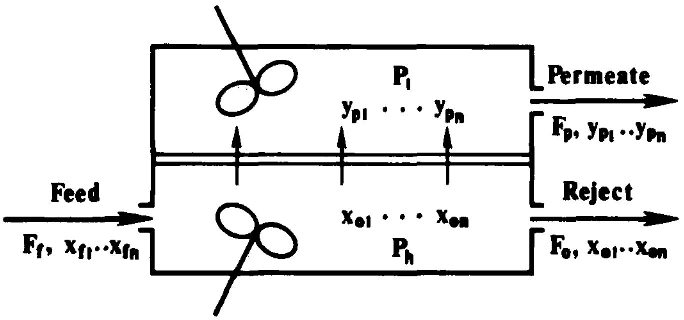

FIG. 1. Schematic diagram of single permeation stage with perfect mixing.

inlet. x_{oi} and y_{pi} are the mole fractions of the ith component on the high pressure side and the permeate side, respectively, which have the following properties:

$$\sum_{k=1}^{n} x_{fk} = 1 \tag{2}$$

$$\sum_{k=1}^{n} x_{ok} = 1 \tag{3}$$

$$\sum_{k=1}^{n} y_{pk} = 1 \tag{4}$$

The assumptions utilized in this study are as follows.

(1) Permeation obeys Fick's law.
(2) Permeability of each component is the same as that of the pure gas, and is independent of pressure.
(3) Effective membrane thickness is constant along the length of the permeator.
(4) Pressure drops of the feed and permeate gas streams are negligibly small.
(5) A perfect mixing situation exists on both sides on the membrane.

By taking total and component balances over the membrane area A, the following equations can be obtained on the basis of the above assumptions:

$$F_p = \sum_{k=1}^{n} \frac{Q_k A}{\delta} (P_h x_{ok} - P_l y_{pk}) \tag{5}$$

$$F_p y_{pi} = \frac{Q_i A}{\delta} (P_h x_{oi} - P_l y_{pi}) \qquad (i = 1, \ldots, n) \tag{6}$$

Substituting Eq. (5) into Eq. (6) and solving for y_{pi} gives

$$y_{pi} = \frac{Q_i(P_h x_{oi} - P_l y_{pi})}{\sum_{k=1}^{n} Q_k(P_h x_{ok} - P_l y_{pk})} \tag{7}$$

Solution of Simultaneous Equations

The problem is, briefly, to determine x_{oi} and y_{pi} ($i = 1, \ldots, n$), when Q_i, x_{fi} ($i = 1, \ldots, n$), P_h, P_l, and A/δ are known. On dividing Eq. (7) by the member of Eq. (7) with $i = j$, the following relation between components i and j is obtained:

$$\frac{y_{pj}}{y_{pi}} = \frac{Q_j(P_h x_{oj} - P_l y_{pj})}{Q_i(P_h x_{oi} - P_l y_{pi})} \tag{8}$$

The mass conservation yields

$$x_{fi}F_f = x_{oi}F_o + y_{pi}(F_f - F_o) \tag{9}$$

The stage cut θ is defined as

$$\theta = \frac{F_f - F_o}{F_f} \tag{10}$$

From Eqs. (9) and (10),

$$x_{fi} = x_{oi}(1 - \theta) + y_{pi}\theta \tag{11}$$

Pressure ratio γ and relative permeability q_{ij} are defined by

$$\gamma = P_h/P_l \tag{12}$$

$$q_{ij} = Q_i/Q_j \tag{13}$$

Eliminating x_{oi} and x_{oj} from Eq. (8) by the aid of Eq. (11) and solving for y_{pj} yields

$$y_{pj} = \frac{x_{fi}q_{ji}}{(x_{fi}/y_{pi}) + (q_{ji} - 1)(\gamma + \theta - \gamma\theta)} \tag{14}$$

Concentration factor β_i, operation factor ψ, and the separation factor of the ith component to the jth component α_{ij} are defined as

$$\beta_i = y_{pi}/x_{fi} \tag{15}$$

$$\psi = \gamma + \theta - \gamma\theta \tag{16}$$

SIMULATION OF MULTICOMPONENT GAS SEPARATION

Permeabilities of Gases through a Porous Glass Membrane

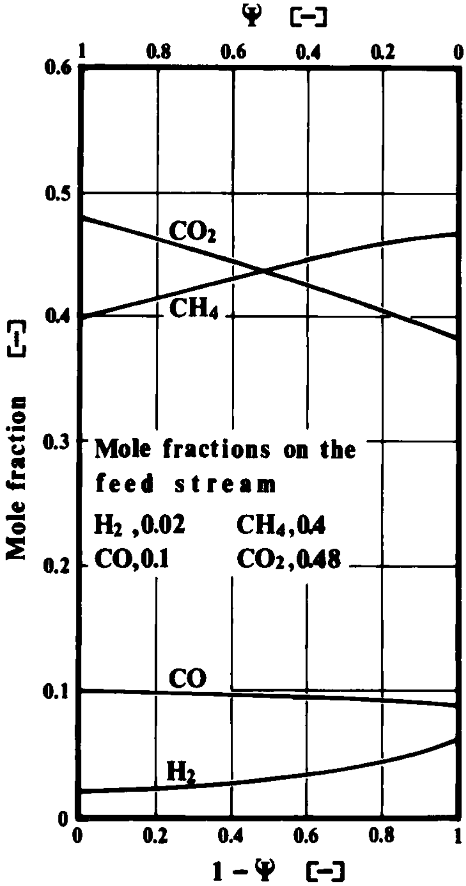

FIG. 2. Mole fractions on the permeate side as a function of $1 - \psi$.

From Eq. (20), the function $f(\beta_i)$ is defined as

$$f(\beta_i) = \sum_{k=1}^{n} \frac{x_k q_{ki}}{1/\beta_i + (q_{ki} - 1)\psi} - 1 \tag{21}$$

Differentiating Eq. (21) by β_i, one obtains

$$\frac{df(\beta_i)}{d\beta_i} = \sum_{k=1}^{n} \frac{x_k q_{ki}}{\{1 + \beta_i(q_{ki} - 1)\psi\}^2} \tag{22}$$

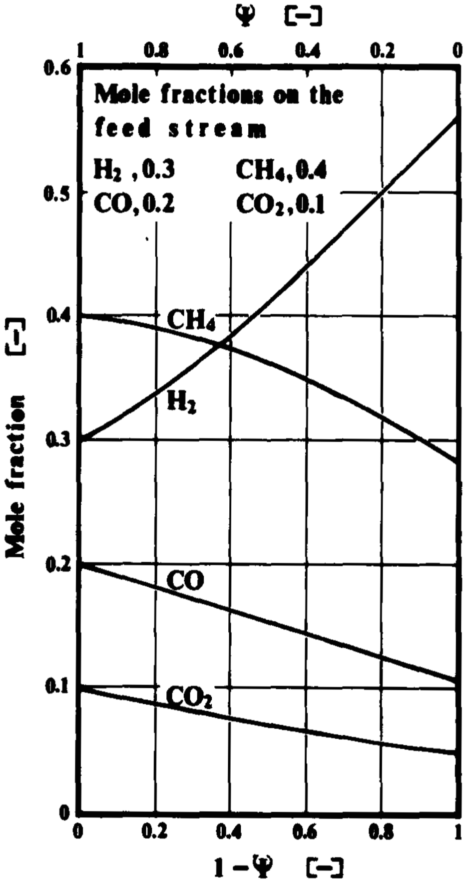

FIG. 3. Mole fractions on the permeate side as a function of 1 − ψ.

One may recognize from Eq. (22) that the function $f(\beta_i)$ is a monotoneously increasing function. The condition $\beta_i > 1$ is given as $f(1) < 0$, that is (see Appendix 3),

$$\sum_{k=1}^{n} \frac{x_k q_{ki}}{1 + (q_{ki} - 1)\psi} - 1 < 0 \tag{23}$$

Especially for the 1st component, which is always the most permeable component (see Appendix 4):

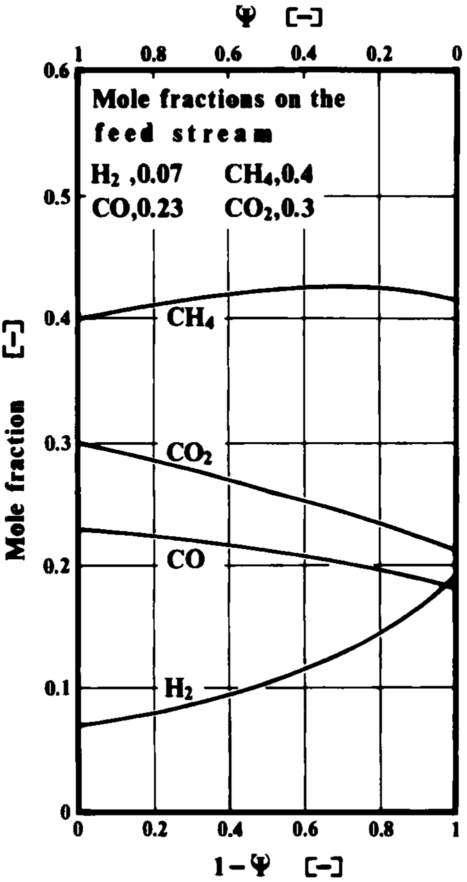

FIG. 4. Mole fractions on the permeate side as a function of $1 - \psi$.

$$\sum_{k=1}^{n} \frac{x_k q_{k1}}{1 + (q_{k1} - 1)\psi} - 1 < 0 \tag{24}$$

For the nth component, which is always the least permeable component, (see Appendix 4):

$$\sum_{k=1}^{n} \frac{x_k q_{kn}}{1 + (q_{kn} - 1)\psi} - 1 > 0 \tag{25}$$

Therefore if Eq. (23) is satisfied, the ith component is concentrated after

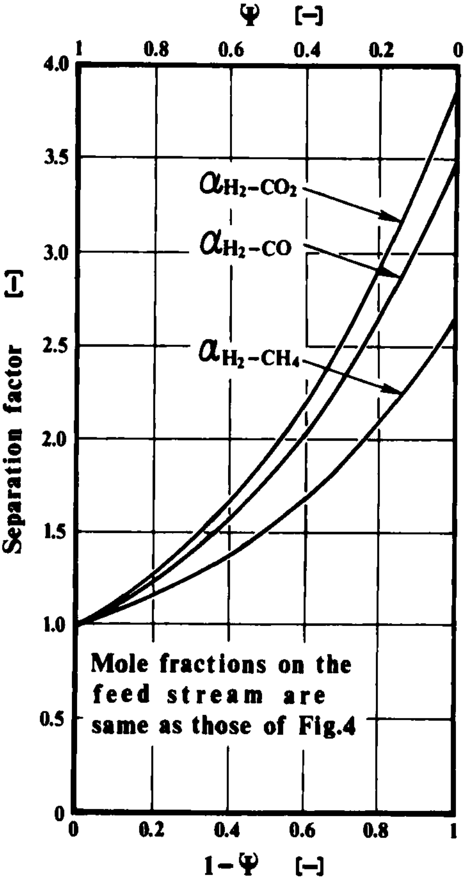

FIG. 5. Separation factors of hydrogen to the other gases as a function of 1 − ψ.

permeation. The most permeable component is always concentrated, and the least permeable component is always diluted.

Relationship between Concentration Factor and Operation Factor

Differentiating Eq. (20) by ψ gives

$$\frac{d\beta_i}{d\psi} = \sum_{k=1}^{n} \frac{x_k q_{ki}(q_{ki} - 1)}{\{1/\beta_i + (q_{ki} - 1)\psi\}^2} \bigg/ \sum_{k=1}^{n} \frac{x_k q_{ki}}{\{1 + \beta_i^2(q_{ki} - 1)\psi\}^2} \qquad (26)$$

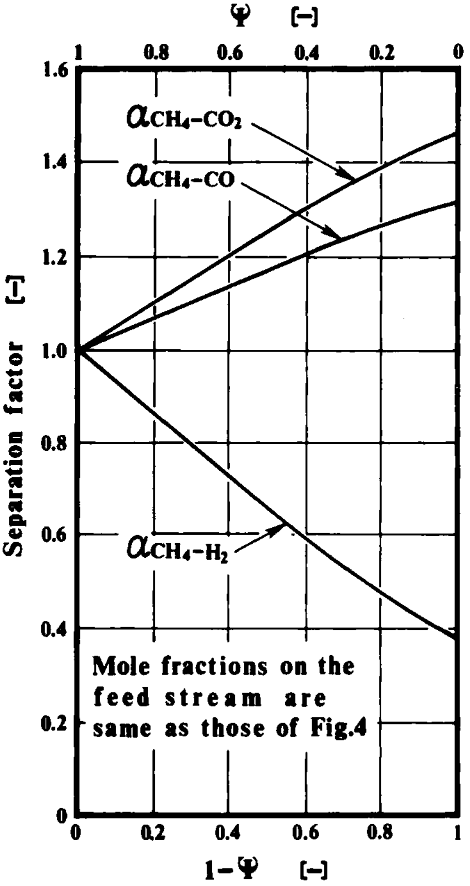

FIG. 6. Separation factors of methane to the other gases as a function of 1 – ψ.

For the 1st component, $d\beta_i/d\psi < 0$ because $q_{k1} \leqslant 1$ ($k = 1, \ldots, n$). For the nth component, $d\beta_i/d\psi > 0$, because $q_{kn} \geqslant 1$ ($k = 1, \ldots, n$). Therefore, the concentration factor of the most permeable component increases with a decrease of the operation factor, and that of the least permeable component decreases with a decrease of the operation factor. For the other component, the concentration factor varies and has a maximum value against the operation factor. At the maximum point, β_i and ψ satisfy $d\beta_i/d\psi = 0$, that is,

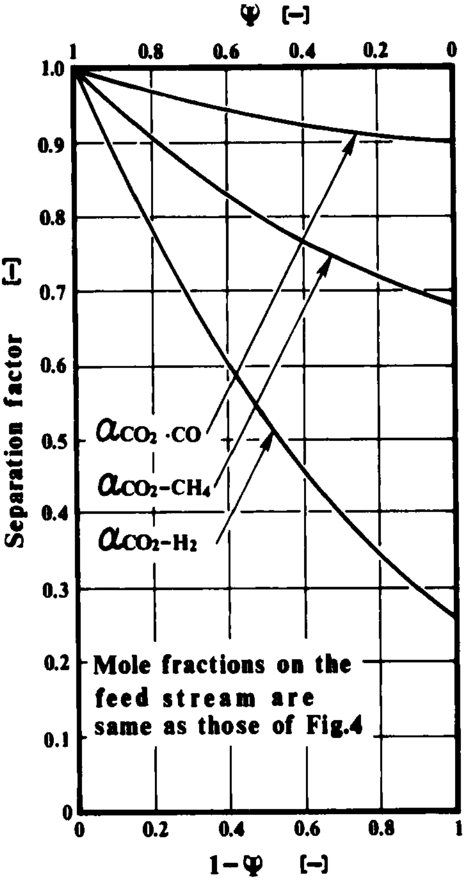

FIG. 7. Separation factors of carbon dioxide to the other gases as a function of 1 − ψ.

$$\sum_{k=1}^{n} \frac{x_k q_{ki}(q_{ki} - 1)}{\{1/\beta_i + (q_{ki} - 1)\psi\}^2} = 0 \tag{27}$$

Limiting Concentration Factor

The concentration factor β_i at $\psi = 0$ is defined as the limiting concentration factor β_i^*. From Eq. (20), β_i^* is given as

$$\beta_i^* = \frac{1}{\sum_{k=1}^{n} x_k q_{ki}} \tag{28}$$

$$= \frac{Q_i}{\sum_{k=1}^{n} x_k Q_k} \tag{29}$$

Considering the results in the previous section, we conclude that for the most permeable component, the limiting concentration factor is at its maximum value. For the least permeable component, the limiting concentration factor is at its minimum value.

Relation between the Separation Factor and the Relative Permeability and Operation Factor

Inserting Eq. (19) into Eq. (17) yields

$$\alpha_{ij} = q_{ij} + (1 - q_{ij})\beta_i\psi \tag{30}$$

$$= (q_{ij} - 1)(1 - \beta_i\psi) + 1 \tag{31}$$

Since $y_{pi} > 0$, we obtain the following relation from Eqs. (7) and (11):

$$1 - \beta_i\psi > 0 \tag{32}$$

Differentiating Eq. (31) by ψ gives

$$\frac{d\alpha_{ij}}{d\psi} = \beta_i(1 - q_{ij}) \tag{33}$$

From Eqs. (31), (32), and (33), we conclude that if $Q_i > Q_j$, the separation factor α_{ij} is larger than 1, and increases with decreasing ψ. If $Q_i < Q_j$, the separation factor α_{ij} is smaller than 1, and decreases with decreasing ψ.

Limiting Separation Factor

The separation factor α_{ij} at $\psi = 0$ is defined as the limiting separation factor α_{ij}^*. From Eqs. (18) and (29):

$$\alpha_{ij}^{*} = \frac{\sum_{k=1}^{n} x_k q_{kj}}{\sum_{k=1}^{n} x_k q_{ki}} \tag{34}$$

$$= Q_j/Q_i \tag{35}$$

Considering the results of the previous section, it is concluded that the limiting separation factor is at its maximum if $Q_i > Q_j$ and at its minimum if $Q_i < Q_j$.

CONCLUSIONS

Several elementary facts with respect to multicomponent gas separation with a membrane were derived as follows.

(1) When Eq. (23) is satisfied, the ith component is concentrated after permeation. The most permeable component is always concentrated. The least permeable component is always diluted.

(2) The concentration factor of the most permeable component increases with a decrease of the operation factor ψ. The concentration factor of the least permeable component decreases with a decrease of the operation factor. For the other component, its concentration factor has a maximum value in the region $0 < \psi < 1$. Then the concentration factor and the operation factor satisfy Eqs. (20) and (27).

(3) When $Q_i > Q_j$, the separation factor α_{ij} is always larger than 1. It increases with a decrease of the operation factor. When $Q_i < Q_j$, the separation factor α_{ij} is always smaller than 1. It decreases with a decrease of the operation factor.

APPENDIX 1

Figure A-1 shows a general profile of the function $f(\beta_i)$. With the condition that $y_{pi}(i = 1, \ldots, n)$ is always positive, one obtains the following condition from Eq. (19):

$$\frac{q_{ji}}{1/\beta_i + (q_{ji} - 1)\psi} > 0 \tag{A-1}$$

This condition can be rewritten as

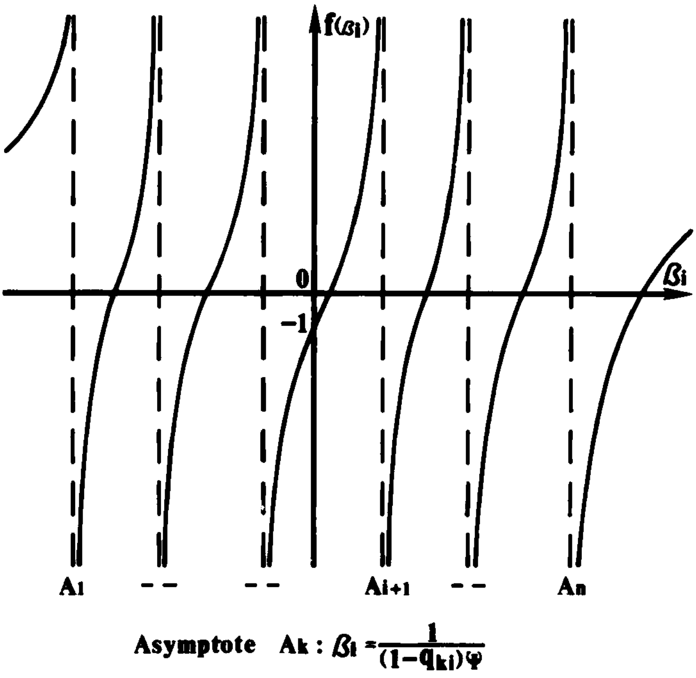

FIG. A-1. Profile of the function $f(\beta_i)$.

$$0 < \beta_i < \frac{1}{(1 - q_{i+1,i})\psi} \qquad (i = 1, \ldots, n - 1) \tag{A-2}$$

$$0 < \beta_n \tag{A-3}$$

Equation (20) has *n* solutions, as shown in Fig. A-1. However, there is only one solution which satisfies the above condition.

APPENDIX 2

$$1 - \psi = (1 - \gamma)(1 - \theta) \tag{A-4}$$

$$= \frac{P_h - P_l}{P_h} \frac{F_f - F_p}{F_f} \tag{A-5}$$

Therefore, $1 - \psi$ is the product of the ratio of the pressure difference $P_h - P_l$ to P_h and the ratio of F_o ($= F_f - F_p$) to F_f.

APPENDIX 3

As shown in Fig. A-2, the line $\beta_i = 1$ exists in the region expressed by Eq. (A-2) or Eq. (A-3). The function $f(\beta_i)$ monotonously increases in this range, and therefore Eq. (23) is obtained.

APPENDIX 4

$$\sum_{k=1}^{n} \frac{x_k q_{k1}}{1 + (q_{k1} - 1)\psi} = \sum_{k=1}^{n} \frac{x_k}{(q_{1k} - 1)(1 - \psi) + 1} \qquad \text{(A-6)}$$

$$< \sum_{k=1}^{n} x_k \quad (= 1) \qquad \text{(A-7)}$$

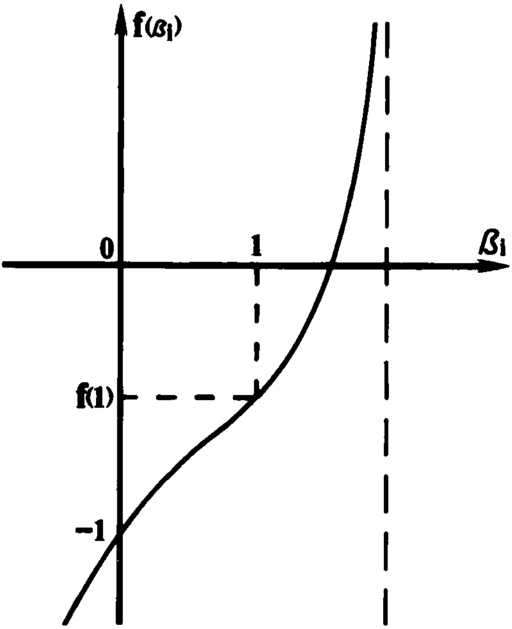

FIG. A-2. Illustration of the function $f(\beta_i)$ near $\beta_i = 1$.

because $q_{1k} > 1$ and $0 < \psi < 1$.

$$\sum_{k=1}^{n} \frac{x_k q_{kn}}{1 + (q_{kn} - 1)\psi} = \sum_{k=1}^{n} \frac{x_k}{(q_{nk} - 1)(1 - \psi) + 1} \tag{A-8}$$

$$> \sum_{k=1}^{n} x_k \quad (= 1) \tag{A-9}$$

because $q_{nk} < 1$. Therefore, we obtain Eqs. (24) and (25).

SYMBOLS

$f(\beta_i)$	function defined by Eq. (21) (-)
n	number of components (-)
P_h	total pressure on the high pressure side (Pa)
P_l	total pressure on the permeate side (Pa)
Q_i	permeability of the ith component (mol/s · m · Pa)
q_{ij}	relative permeability, Q_i/Q_j (-)
x_{fi}	mole fraction of the ith component on the feed stream at the inlet (-)
x_{oi}	mole fraction of the ith component on the high pressure side (-)
y_{pi}	mole fraction of the ith component on the permeate side (-)
α_{ij}	separation factor defined by Eq. (17) (-)
α_{ij}^*	limiting separation factor, Q_i/Q_j (-)
β_i	concentration factor of the ith component, y_{pi}/x_{fi} (-)
β_i^*	limiting concentration factor defined by Eq. (28) (-)
γ	pressure ratio, P_l/P_h (-)
θ	stage cut defined by Eq. (10) (-)
ψ	operation factor defined by Eq. (16) (-)

Subscripts

$1, n$	most and least permeable components
i, j, k	i, j, and kth components
H_2, CH_4, CO, CO_2	hydrogen, methane, carbon monoxide, and carbon dioxide gases

REFERENCES

1. A. De La Gartza, G. A. Garrett, and J. E. Murphy, *Chem. Eng. Sci.*, *15,* 188 (1961).
2. S. T. Hwang and K. Kammermeyer, *Membranes in Separations,* Wiley, New York, 1975.
3. S. A. Stern, T. F. Sinclair, P. J. Gareis, N. P. Vahldieck, and P. H. Mohr, *Ind. Eng. Chem.*, *57,* 49 (1965).
4. Y. Shindo, T. Hakuta, H. Yoshitome, and H. Inoue, *Sep. Sci. Technol.*, *20,* 445 (1985).
5. C. Y. Pan and H. W. Habgood, *Ind. Eng. Chem., Fundam.*, *13,* 323 (1974).
6. C. Y. Pan and H. W. Habgood, *Can. J. Chem. Eng.*, *56,* 197 (1978).
7. M. Knudsen, *Ann. Phys.*, *28,* 75 (1908).
8. M. Smoluchowski, *Ibid.*, *33,* 1559 (1910).
9. Y. Shindo, T. Hakuta, H. Yoshitome, and H. Inoue, *J. Chem. Eng. Jpn.*, *16,* 120 (1983).

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