**Literature Cited**

1) Bello, R. C., C. W. Robinson and M. Moo-Young: *Can. J. Chem. Eng.*, **62**, 573 (1984).
2) Bohner, K. and H. Blenke: *Verfahrenstechnik*, **3**, 50 (1972).
3) Brighton, J. A. and J. B. Johnes: *J. Bas. Eng. Trans. ASME*, **86**, 835 (1964).
4) Fields, P. R. and N. K. H. Slater: *Chem. Eng. Sci.*, **38**, 647 (1983).
5) Gopal, J. S. and M. M. Sharma: *Can. J. Chem. Eng.*, **60**, 353 (1982).
6) Himmelblau, D. M.: "Process Analysis by Statistical Methods," p. 178, John Wiley & Sons, New York, p. 178 (1970).
7) Iida, Y., K. Kobayashi and S. Kumagai: *Nihon Genshiryoku Gakkaishi*, **9**, 2 (1967).
8) Jones, A. G.: *Chem. Eng. Sci.*, **40**, 449 (1985).
9) Kobayashi, K. and Y. Irino: Trans. of the 10th Japan Heat Transfer Symp., p. 41 (1973).
10) Koide, K., S. Iwamoto, Y. Takasaka, E. Takahashi, M. Kimura and H. Kubota: *J. Chem. Eng., Japan*, **17**, 611 (1984).
11) Takamatsu, T.: Master Thesis, Tokyo Institute of Technology (1969).
12) Weiland, P.: *Ger. Chem. Eng.*, **7**, 374 (1984).
13) Zuber, N. and J. A. Findlay: *Trans. ASME. J. Heat Transfer*, **87**, 453 (1965).

(Presented in part at the 17th Autumn Meeting of the Society of Chemical Engineers, Japan, at Sendai, October 1, 1983, and at the 49th Annual Meeting of The Society of Chemical Engineers, Japan, at Nagoya, April 5, 1984.)

# A MEMBRANE REACTOR USING MICROPOROUS GLASS FOR SHIFTING EQUILIBRIUM OF CYCLOHEXANE DEHYDROGENATION

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***Key Words***: Membrane Reactor, Microporous Glass Membrane, Reversible Reaction, Equilibrium Shift, Dehydrogenation of Cyclohexane

**A membrane reactor, which is a double-tubular reactor equipped with a selective membrane tube as the inner tube, was proposed. Such a reactor makes it possible to obtain a product yield of a reversible reaction beyond its equilibrium value by continuous removal of the products during reaction.**

**A microporous glass tube was employed as the selective membrane, through which gases permeate almost according to Knudsen's law. Experiments in the dehydrogenation of cyclohexane to benzene as a model reaction were carried out, using the membrane reactor under atmospheric pressure in the range of 453–493 K. It was shown experimentally and theoretically that a marked increase in conversion over that at equilibrium can be achieved.**

## Introduction

About 20 years ago, Michaels[6] pointed out that the application of membranes in reaction engineering would produce new chemical processes. According to his suggestion, it is possible to prevent a reaction mixture from attaining equilibrium composition by using a reactor containing a membrane separation unit, which is used for continuous and selective removal of products from the reaction mixture. This system, of course, will increase product yield and decrease the energy requirement for separation. We call such a reactor a "membrane reactor".

Received November 6, 1987. Correspondence concerning this article should be addressed to N. Itoh.

Such an idea has been tested by several investigators. Gryaznov[2] and Nagamoto *et al.*[7,8] studied dehydrogenation and/or hydrogenation using palladium and its alloy membranes, through which only hydrogen can diffuse. Carles *et al.*[1] attempted direct thermolysis of water vapor using a calcia-stabilized zirconia membrane, through which oxygen can be transferred in the form of $O^{2-}$ ions. In these cases, the membranes simultaneously function as catalysts. On the other hand, when the membrane itself does not have catalytic activity, a catalyst must be packed in the membrane reactor to make a reaction progress at sufficient speed. Regarding such a membrane reactor, Kameyama *et al.*[5] and Shinji *et al.*[10] succeeded in selective separation of hydrogen from a reacting

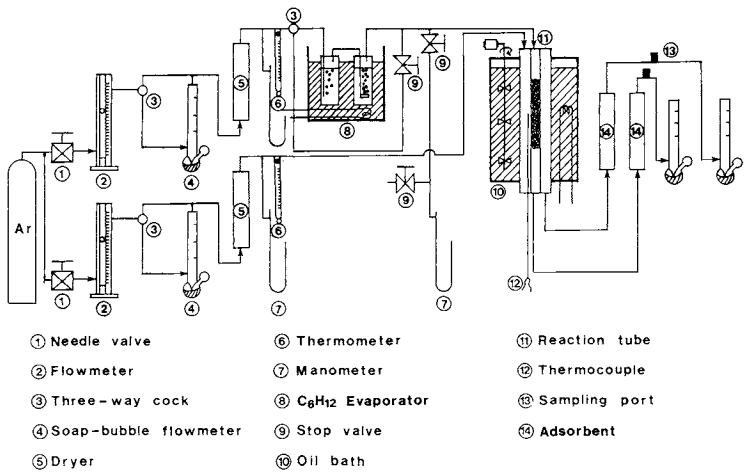


**Fig. 1.** Schematic illustration of the experimental apparatus

mixture using a microporous glass membrane. As a result, they obtained a higher conversion than that at equilibrium.

We made a computer simulation of the latter type and showed in the previous paper[3] that its reactor performance would be much improved over that of a conventional catalyst-packed reactor. However, the quantitative analysis of this type of reactor is incomplete from the standpoint of chemical reaction engineering. It is neccessary to verify the principle experimentally and to establish a reactor design procedure. Therefore, we have tried to clarify such subjects using the dehydrogenation of cyclohexane to benzene with a microporous membrane as a model.

For the dehydrogenation of cyclohexane to benzene over a Pt-$Al_2O_3$ catalyst, the rate equation has already been determined.[4] While the permeation rates of inorganic gases such as He, Ar, $H_2$, $N_2$ and $O_2$ through the microporous glass membrane have been measured,[9] there are no data available for benzene and cyclohexane. Accordingly, in the present study the permeation rates of benzene and cyclohexane were first measured at temperatures from 344 to 464 K under atmospheric pressure; their permeabilities were determined by analyzing the results. Then, it was shown both experimentally and theoretically that a remarkable increase in conversion over that at equilibrium can be obtained using this membrane reactor.

## 1. Experimental

### 1.1 Apparatus

**Figure 1** shows the experimental apparatus. The membrane reactor is set in an oil bath to ensure a constant temperature. Its details are shown in **Fig. 2**. The cylindrical microporous glass membrane used as the inner tube has the physical properties shown in **Table 1**. For measurement of the permeation rates, glass beads of 1.4 mm average diameter were packed

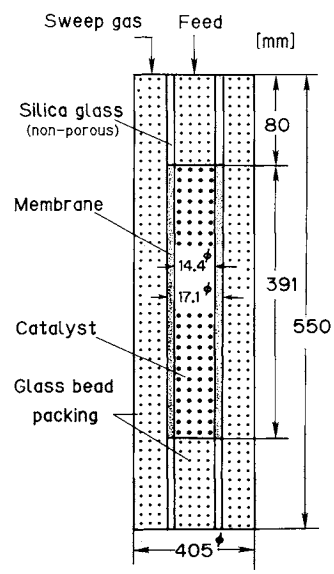


**Fig. 2.** Details of the membrane reactor

**Table 1.** Physical properties and geometries of tubular microporous glass membrane

| | |
|---|---|
| Mean pore diameter | 4.0 nm |
| Void fraction | 0.28 |
| Outside diameter | 17.1 mm |
| Inside diameter | 14.4 mm |
| Axial length | 391 mm |

in both sides of the double-tubular reactor instead of catalyst pellets, which were packed inside the tubular membrane for dehydrogenation experiments. The catalyst used was 0.5 wt% platinum supported on cylindrical alumina (3.3 mm in diameter and 3.6 mm high).

### 1.2 Method

Each permeation rate of the two gaseous species (benzene and cyclohexane) in the temperature range 344–464 K was determined by applying a continuous and co-current flow method for binary systems as

described below. The feed gas of benzene or cyclohexane was generated as a saturated vapor by flowing argon through an evaporator, and it was sent to the inner side of the reactor. To the outer side, argon was introduced as a sweep gas. The flow rates of benzene or cyclohexane at the outlets were determined by adsorbing them for 0.3–1.0 h with two activated carbon (1–1.4 mm$^{\Phi}$) columns (16$^{\Phi}$ × 200 mm) in an ice-cold water bath and then measuring the weight of adsorption. Within the adsorption time, which was dependent on the flow rate of benzene or cyclohexane, it was confirmed experimentally that no benzene (or cyclohexane) was included in the gas mixture flowing from the columns.

In the reaction experiments, a vapor saturated with cyclohexane was fed inside the membrane tube, and simultaneously argon as a sweep gas was introduced into the outer annular space co-currently. Both the product (benzene) and the unreacted cyclohexane from the outlets of both sides were analyzed by means of a gas chromatograph (Shimadzu 4C, 3 mm$^{\Phi}$ × 1 m column of Durapak) and their total flow rates on each side were measured in the same manner as that mentioned above. The material balance was within ± 5%. Considering a mass balance of cyclohexane on both the inner and outer sides, the conversion $X$ [—] can be calculated by

$$X=\frac{u_C^0-(u_C+v_C)}{u_C^0} \tag{1}$$

where $u_C^0$ [mol·s$^{-1}$] is the flow rate of cyclohexane at the inlet and $u_C$ and $v_C$ [mol·s$^{-1}$] are those at any axial position on the inner and outer sides of the reactor tube, respectively. Experiments were carried out under atmospheric pressure and within a temperature range of 453–493 K.

## 2. Analysis

### 2.1 Assumptions

The following assumptions were made so as to develop basic equations for analysis.

(1) Attainment of isothermal condition.

(2) Plug flow and negligible pressure drop in the axial direction exist on both the inner and outer sides.

(3) Absence of axial or radial diffusion.

(4) Permeability of each gas is independent of its concentration.

### 2.2 Equations for determining the permeabilities

**Figure 3** shows a schematic diagram of the membrane reactor. In a steady state, the driving force of the permeation of each gas component through the microporous membrane is its partial pressure difference between the inner and outer sides. This leads to change in the molar flow rate of components $i$ and $j$ in both the inner and outer sides. In Fig. 3, $u_i$ and $v_i$ [mol·s$^{-1}$] show the molar flow rate of component $i$ (argon) in the inner and outer sides, respectively; similarly, $u_j$ and $v_j$ for component $j$ (benzene or cyclohexane). Therefore, taking a mass balance of each gas component across a longitudinal length $dl$ [m] of the inner and outer sides of the membrane reactor, two simultaneous ordinary differential equations are obtained; they are represented in dimensionless form as

$$\frac{dU_i}{dL}=\frac{2\pi\bar{P}_iP_sl_0}{(u_i^0+v_i^0)\ln(r_{out}/r_{in})}\left(\frac{P_{out}}{P_s}\frac{1-U_i}{1+\beta-U_i-\beta U_j}-\frac{P_{in}}{P_s}\frac{U_i}{U_i+\beta U_j}\right) \tag{2}$$

$$\frac{dU_j}{dL}=\frac{2\pi\bar{P}_jP_sl_0}{u_j^0\ln(r_{out}/r_{in})}\left(\frac{P_{out}}{P_s}\frac{1-U_j}{1+1/\beta-U_j-U_i/\beta}-\frac{P_{in}}{P_s}\frac{U_j}{U_j+U_i/\beta}\right) \tag{3}$$

where

$$U_i=\frac{u_i}{u_i^0+v_i^0},\quad U_j=\frac{u_j}{u_j^0},\quad L=\frac{l}{l_0}\quad [—]$$

$$\beta=\frac{u_j^0}{u_i^0+v_i^0}\quad [—]$$

Also, the following relations in terms of mass balance are valid.

$$V_i=1-U_i \tag{4}$$

$$V_j=1-U_j \tag{5}$$

where $\bar{P}_i$ and $\bar{P}_j$ [mol·m$^{-1}$·s$^{-1}$·Pa$^{-1}$] are the permeabilities of components $i$ and $j$, respectively. $P_s$ [Pa]

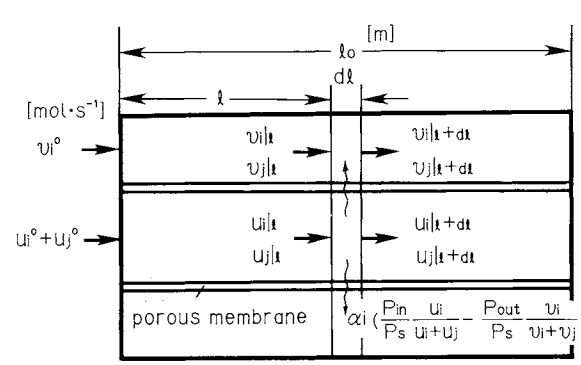


**Fig. 3.** Flow model inside the double-tube reactor using a membrane as the inner tube

**Table 2.** Parameters in Eq. (7)

| | $H_2$ | Ar |
|---|---|---|
| $K\times10^{11}$ [(mol·kg·K)$^{1/2}$/(m·s·Pa)] | 4.01 | 4.12 |
| $\varepsilon^*/k$ [K] | 142 | 249 |
| $\alpha^*$ [—] | 0.246 | 0.246 |
| $\beta^*$ [—] | 0.606 | 0.606 |

is a reference pressure for obtaining dimensionless form and was $1.013\times10^5$ Pa (1 atm). $P_{out}$ and $P_{in}$ [Pa] are the total pressures in the outer and inner sides, respectively. Equations (2)–(5) were solved numerically under the initial condition that

$$L=0:\ U_i=\frac{u_i^0}{u_i^0+v_i^0},\quad U_j=1 \tag{6}$$

All values except $\bar{P}_i$ and $\bar{P}_j$ are known from the experimental conditions; thus two parameters remain unknown. However, $\bar{P}_A$ for the permeability of argon can be estimated by using a correlation by Shindo *et al.*,[9] according to which the permeabilities of some inorganic gases such as argon and hydrogen at a temperature of $T$ [K] are represented by

$$\bar{P}_i=\frac{K}{\sqrt{M_iT}}\left[\frac{1}{1+\beta^*\varepsilon^*/kT}+\alpha^*(\exp(\varepsilon^*/kT)-1)\right] \tag{7}$$

where $M_i$ is the molecular weight of component $i$. The parameters used in Eq. (7) are given in **Table 2**. Thus, the number of unknown parameters is reduced to one. Finally, $\bar{P}_j$ ($\bar{P}_B$ or $\bar{P}_C$) was determined by comparing the experimentally obtained flow rates of component $j$ at the outlet with those calculated by Eqs. (2)–(5) and by obtaining good agreement between the two rates by trial and error. The model equations above were numerically solved by the Runge-Kutta-Gill method.

### 2.3 Equations for evaluating membrane reactor performance

The basic differential equations describing the changes occurring in the flow of each component accompanying the reaction in the membrane reactor were presented in the previous study.[3] The disappearance rate of cyclohexane, $r_C$ [mol·m$^{-3}$·s$^{-1}$], can be expressed by[4]

$$r_C=-\frac{k_C(K_Pp_C/p_H^3-p_B)}{1+K_BK_Pp_C/p_H^3} \tag{8}$$

$$k_C=0.221\exp(-4270/T)\quad[\text{mol}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}]$$

$$K_B=2.03\times10^{-10}\exp(6270/T)\quad[\text{Pa}^{-1}]$$

$$K_P=4.89\times10^{35}\exp(-26490/T)\quad[\text{Pa}^3]$$

where $p_i$ [Pa] is the partial pressure of component $i$.

Using the $\bar{P}_i$ determined above and the rate equation by Eq. (8) the basic equations can be numerically solved by the Runge-Kutta-Gill method.

## 3. Results and Discussion

### 3.1 Permeabilities of $C_6H_6$ and $C_6H_{12}$

Experimental points indicated by some of the symbols in **Fig. 4** show a change in the flow rate of cyclohexane at the outlet when the flow rate of the sweep gas (argon) increases in the order: ■ < ▲ < ●. Values of $\bar{P}_C$, which was used as a parameter in calculations, were obtained by fitting the calculated value of $U_C$ at the outlet to the experimental point as indicated in Fig. 4. By taking the average of the values thus obtained, the permeability was determined. It is clear from the calculated curves that the dimensionless flow rate of cyclohexane in the inner side, $U_C$, gradually decreases due to its permeation from the inner to outer side.

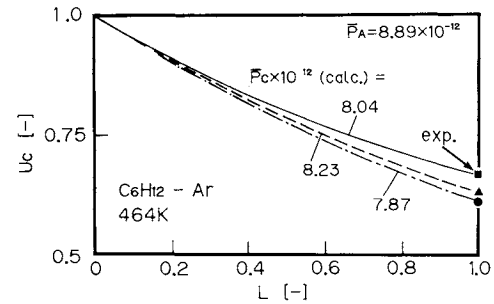


**Fig. 4.** Calculated lines in good agreement with experimental points for $C_6H_{12}$–Ar system

**Table 3.** Permeability for benzene

| $T$ [K] | $\bar{P}_B\times10^{11}$ [mol/(m·s·Pa)] | $\bar{P}_A\times10^{11}$ [mol/(m·s·Pa)] | Deviation [—] |
|---|---|---|---|
| 344 | 5.49 | 1.06 | 7.24 |
| 404 | 1.95 | 0.961 | 2.84 |
| 463 | 1.26 | 0.890 | 1.97 |

**Table 4.** Permeability for cyclohexane

| $T$ [K] | $\bar{P}_C\times10^{11}$ [mol/(m·s·Pa)] | $\bar{P}_A\times10^{11}$ [mol/(m·s·Pa)] | Deviation [—] |
|---|---|---|---|
| 347 | 2.12 | 1.04 | 2.90 |
| 406 | 1.15 | 0.959 | 1.74 |
| 463 | 0.804 | 0.889 | 1.31 |

The permeabilities of benzene and cyclohexane at various temperatures are summarized in **Tables 3** and **4**. The deviation factors in these tables were introduced to show clearly the extent to which the flow behavior deviates from the so-called Knudsen flow. They are defined as:

$$\text{Deviation factor}=\frac{\bar{P}_B/\bar{P}_A}{\sqrt{M_A/M_B}}\quad\text{or}\quad\frac{\bar{P}_C/\bar{P}_A}{\sqrt{M_A/M_C}} \tag{9}$$

The permeation of argon is quite close to Knudsen's flow. When the factor becomes 1, it can be said that the permeation of benzene or cyclohexane occurs by Knudsen's flow. Practically, the deviation of the factor from 1 increases with decrease in temperature in both cases.

The temperature dependency of $\bar{P}_H$, $\bar{P}_A$, $\bar{P}_B$ and $\bar{P}_C$ is shown in **Fig. 5**. Since the flow of hydrogen and argon closely obeys Knudsen's flow, linear relations can be found between the permeabilities ($\bar{P}_H$, $\bar{P}_A$) and

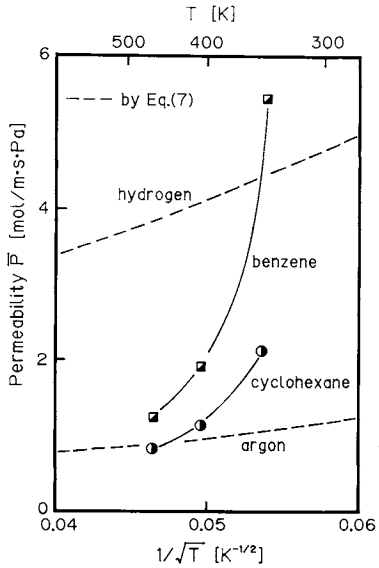


**Fig. 5.** Correlation of permeabilities *versus* $1/\sqrt{T}$

the inverse of the square root of temperature ($1/\sqrt{T}$). Such relations are not valid for $\bar{P}_B$ and $\bar{P}_C$, especially in a lower temperature range. Marked increases in $\bar{P}_B$ and $\bar{P}_C$ are considered to be mainly due to the so-called surface diffusion flow.

### 3.2 Comparison between experimental and calculated results for the membrane reactor

In **Figs. 6–8**, experimental and calculated results are shown as plots of conversion vs. flow rate of the sweep gas $v_A^0$ [mol·s$^{-1}$]. In the calculations, the permeabilities of benzene and cyclohexane at the reaction temperatures were estimated by extrapolation or interpolation based on the values in Tables 3 and 4. In the case of $v_A^0=0$, since it is the same situation as that occurring with a conventional catalytic reactor, the attainable maximum conversion is an equilibrium one determined thermodynamically and can never exceed this value. However, it is possible by using the membrane reactor to obtain a conversion greater than that at equilibrium through selective and continuous removal of the products. This is confirmed by all the experimental data. The conversion increases and exceeds that at equilibrium with increasing flow rate of the sweep gas $v_A^0$ and with decreasing feed rate of cyclohexane $v_C^0$. The former is because the flux of the products removal is increased by increasing the sweep gas and thus increasing the differences in their pressures between the inner and outer tubes to provide the driving force of permeation. Such an effect is also enhanced by decreasing the feed rate of cyclohexane; this is the reason for the latter.

Although it is possible to obtain a higher conversion than that at equilibrium with the membrane reactor, the reaction cannot be completed owing to the permeation of cyclohexane itself to the outer side.

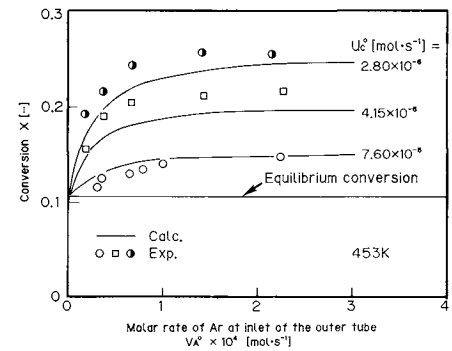


**Fig. 6.** Results of reaction experiments and the corresponding predicted curves

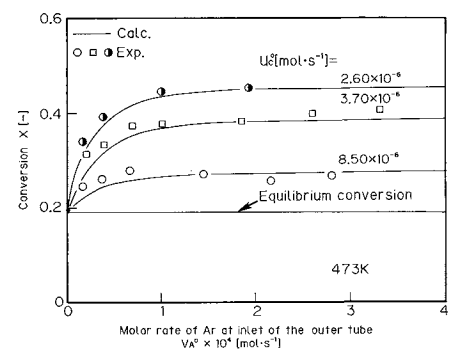


**Fig. 7.** Results of reaction experiments and the corresponding predicted curves

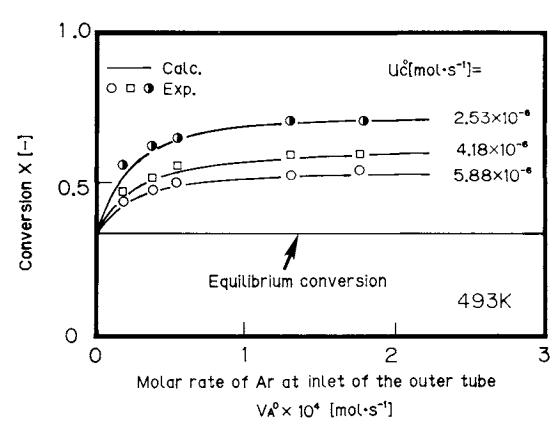


**Fig. 8.** Results of reaction experiments and the corresponding predicted curves

The rates of permeation of gaseous species through the porous membrane are approximately proportional to the reciprocal of the root of the molecular weight, so that even the reactant, i.e., cyclohexane, passes through the membrane tube: this leads to some loss in conversion as can be easily understood from Eq. (1). If a membrane having a higher selectivity for products is used, reactor performance will be improved.

In Figs. 6–8, the calculated curves corresponding to the experimental data are also shown. Since the results obtained by solving the basic equations are approximately consistent with the data, the simple

model proposed seems reliable with regard to membrane reactor design.

## Conclusion

We proposed a membrane reactor of the double-tubular type using a microporous glass membrane as the inner tube to improve the yield of a reversible reaction by selectively removing the products through the membrane. Dehydrogenation of cyclohexane to benzene was taken as a model reaction.

First, the permeation rates of benzene and cyclohexane through the membrane were measured in a temperature range of 344–464 K under atmospheric pressure. Experiments for binary systems, i.e. $C_6H_6$–Ar and $C_6H_{12}$–Ar, were conducted by a co-current flow method. Model equations for analyzing changes in flow rates of two gaseous species and determining their permeabilities were derived assuming isothermal and plug flow conditions within the reactor. The permeabilities ($\bar{P}_B$ and $\bar{P}_C$) were obtained by using them as unknown parameters in the calculations and through greater agreement between the calculated results and experimental data. A marked increase in both $\bar{P}_B$ and $\bar{P}_C$ was observed, especially in a low temperature range.

Dehydrogenation experiments were carried out under atmospheric pressure in the range of 453–493 K. The conversions obtained were increased beyond those attainable at the equilibrium condition with an increase in flow rate of the sweep gas, that is, in the separation speed of the products, especially hydrogen. A simple model presented in the previous study could describe the experimental results.

### Nomenclature

| | | | |
|---|---|---|---|
| $K$ | = | constant in Eq. (7) | $[(\mathrm{mol\cdot kg\cdot K})^{1/2}\cdot(\mathrm{mol\cdot s\cdot Pa})^{-1}]$ |
| $K_B$ | = | adsorption equilibrium constant of benzene | $[\mathrm{Pa}^{-1}]$ |
| $K_P$ | = | equilibrium constant | $[\mathrm{Pa}^3]$ |
| $k$ | = | Boltzmann constant | $[\mathrm{J\cdot K^{-1}}]$ |
| $k_C$ | = | apparent rate constant in Eq. (8) | $[\mathrm{mol\cdot m^{-3}\cdot Pa^{-1}\cdot s^{-1}}]$ |
| $L$ | = | $l/l_0$ | [—] |
| $l$ | = | reactor length | [m] |
| $l_0$ | = | total reactor length | [m] |
| $M_i$ | = | molecular weight of component $i$ | $[\mathrm{kg\cdot mol^{-1}}]$ |
| $\bar{P}_i$ | = | permeability of component $i$ | $[\mathrm{mol\cdot m^{-1}\cdot s^{-1}\cdot Pa^{-1}}]$ |
| $P_{in}$ | = | total pressure on the inner side | [Pa] |
| $P_{out}$ | = | total pressure on the outer side | [Pa] |
| $P_s$ | = | reference pressure ($=1.013\times10^5$ Pa) | [Pa] |
| $p_i$ | = | partial pressure of component $i$ | [Pa] |
| $r_C$ | = | dehydrogenation rate of cyclohexane | $[\mathrm{mol\cdot m^{-3}\cdot s^{-1}}]$ |
| $r_{in}$ | = | inner radius of membrane tube | [mm] |
| $r_{out}$ | = | outer radius of membrane tube | [mm] |
| $T$ | = | absolute temperature | [K] |
| $U_i$ | = | dimensionless flow rate | [—] |
| $u_A^0$ | = | flow rate of argon at inlet of the inner side | $[\mathrm{mol\cdot s^{-1}}]$ |
| $u_C^0$ | = | flow rate of cyclohexane at inlet of the inner side | $[\mathrm{mol\cdot s^{-1}}]$ |
| $u_i$ | = | flow rate of component $i$ in the inner side | $[\mathrm{mol\cdot s^{-1}}]$ |
| $v_A^0$ | = | flow rate of argon at inlet of the outer side | $[\mathrm{mol\cdot s^{-1}}]$ |
| $V_i$ | = | dimensionless flow rate | [—] |
| $v_i$ | = | flow rate of component $i$ in the outer side | $[\mathrm{mol\cdot s^{-1}}]$ |
| $X$ | = | conversion | [—] |
| $\alpha^*$ | = | constant in Eq. (7) | [—] |
| $\beta$ | = | $u_j^0/(u_i^0+v_j^0)$ | [—] |
| $\beta^*$ | = | constant in Eq. (7) | [—] |
| $\varepsilon^*$ | = | constant in Eq. (7) | [J] |

⟨Subscripts⟩

| | | |
|---|---|---|
| A | = | argon |
| B | = | benzene |
| C | = | cyclohexane |
| H | = | hydrogen |
| $i,j$ | = | components $i,j$ |

### Literature Cited


1) Carles, B. and J. F. Baumard: *High Temperatures-High Pressures*, **14**, 681 (1982).
2) Gryaznov, V. M.: *Kinetics and Catalysis*, **12**, 640 (1970).
3) Itoh, N., Y. Shindo, K. Haraya, K. Obata, T. Hakuta and H. Yoshitome: *Kagaku Kogaku Ronbunshu*, **9**, 572 (1983).
4) Itoh, N., H. Tanabe, Y. Shindo and T. Hakuta: *Sekiyu Gakkaishi*, **28**, 323 (1985).
5) Kameyama, T., M. Dokiya, M. Fujishige, H. Yokokawa and K. Fukuda: *Ind. Eng. Chem. Fund.*, **20**, 97 (1981).
6) Michaels, A. S.: *Chem. Eng. Prog.*, **64**, 31 (1968).
7) Nagamoto, H. and H. Inoue: *Chem. Eng. Commun.*, **34**, 315 (1985).
8) Nagamoto, H. and H. Inoue: *J. Chem. Eng. Japan*, **14**, 377 (1981).
9) Shindo, Y., T. Hakuta, H. Yoshitome and H. Inoue: *J. Chem. Eng. Japan*, **16**, 521 (1983).
10) Shinji, O., M. Misono and Y. Yoneda: *Bull. Chem. Soc. Jpn.*, **55**, 2760 (1982).