

Theoretical study on concentration polarization in gas separation membrane processes

Gaohong He, Yongli Mi, Po Lock Yue, Guohua Chen^{1,*}

Department of Chemical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

Received 7 April 1998; received in revised form 15 July 1998; accepted 13 August 1998

Abstract

A mathematical model was established successfully to analyze the gas separation concentration polarization which becomes an important problem due to the rapid development of membranes, especially the increase of permeation rate. The influences of membrane performance and operation parameters on concentration polarization were studied in terms of permeation fluxes of the more and the less permeable gases and separation factor. Sample calculations were presented for the two typical gas separation applications, hydrogen recovery and air separation, with shell side feed in hollow fiber module. The permeation rate was found to be a dominating factor in affecting concentration polarization, while the influences of separation factor to be significant initially and to level off gradually. Increasing feed gas velocity leads to a decrease in the concentration polarization. Operation pressures' effect is limited and the composition of feed gas shows no effect. The range in which concentration polarization is significant has been identified by studying the combined effects of the permeation rate, separation factor and feed gas velocity. Concentration polarization is important for process analysis and design when the permeation rate of the more permeable gas is larger than $1 \times 10^{-4} \text{ cm}^3 (\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ (100 GPU). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Concentration polarization; Fiber membranes; Gas separation; Hydrogen recovery; Dehumidification

1. Introduction

When a mixture is brought to a membrane surface by any driving force, there is an accumulation of the less permeable species and a depletion of the more permeable components in the boundary layer adjacent to the membrane and this causes a concentration gradient building up in the boundary layer, as shown

in Fig. 1. This phenomenon is referred to as concentration polarization. Theoretically speaking concentration polarization exists in all membrane separation processes because of the selective permeability of membrane. It has serious adverse effects in membrane separation processes. It leads to a decrease in the available driving force for the more permeable species across the membrane and an increase for the less permeable species. This reduces the overall efficiency of separation and raises the costs of capital and operation.

For liquid separation membrane processes, such as reverse osmosis and ultrafiltration, concentration

*Corresponding author. Tel.: +852-23587138; fax: +852-23580054; e-mail: kechengh@ust.hk

¹Department of Chemical Engineering, Dalian University of Technology, Dalian 116012, China.

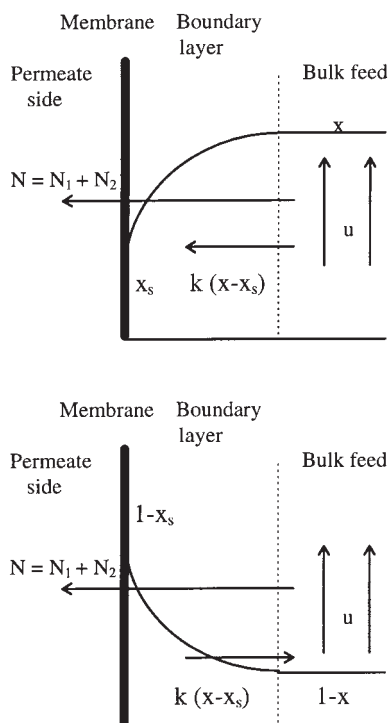


Fig. 1. Molar fraction profiles of the gases on the feed side under steady separation condition: (a) the more permeable gas; (b) the less permeable gas.

polarization is obvious. Thus its causes, consequences and controls have been studied extensively and in depth since the 1960s. Whereas for gas separation processes, due to the lower gas permeation rate and much higher diffusivity of gases, 4–5 orders of magnitude higher than that of liquid, it is generally believed that concentration polarization does not affect gas separation processes [1–3], although the membrane swollen and the gas competitive transport have shown to decrease the membrane separation efficiency. The recent technical breakthrough in the membrane separation of gases, however, has changed the scenery of membrane application seen in Prism's hydrogen recovery process in the late 1970s. Especially in the past few years, the progress in membrane materials, membrane modifications and membrane fabrication technology has substantially improved membrane separation properties. Take the permeation rate for example. Some recent research results [4–10] show more than 1 order of magnitude increase over the typical data from about 10 years ago [11]. Specifically

with acceptable separation factors, the permeation rates of H_2 , CO_2 and O_2 have reached 1.49×10^3 GPU [4], 2.33×10^3 GPU [5] and 16×10^3 GPU [6], respectively ($1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$). Membrane gas separation becomes competitive with cryogenic distillation, absorption, adsorption, etc. It opens the market of the air separation to obtain enriched nitrogen or oxygen, CO_2 recovery from natural gas, air dehumidification and organic vapor separation [12]. These high performance membranes have great potential in various gas separation applications at industrial level, and would be expected to experience the concentration polarization effect in their application.

Not surprisingly, it has been reported that the mass transfer is influenced not only by the resistance from the membrane, but also by the resistance from the flow stream in the gas separation membrane module [13]. The permeation rate of the more permeable gas was also found to decrease with the presence of the less permeable gas. Inversely the permeation rate of the less permeable gas was found to increase with the presence of the more permeable gas. These phenomena were observed with the absence of swelling and changing of the membrane [10,14]. All evidence points to the importance of concentration polarization in gas separation processes. Due to the reason mentioned in the last paragraph, concentration polarization for gas separation membrane processes has not been studied well despite the fact that the results obtained from liquid membrane system cannot be directly applied to gas system simply because of the great differences in the analysis of these two systems. Of the limited literature available, Bhattacharya et al. [15] proposed a generalized equation relating the modified Peclet number to the concentration polarization occurring in the boundary layer which is applicable to the majority of membrane separation processes including gas separations. Although they realized that in a gas–gas membrane system concentration polarization may not be negligible in the case of having a very large gas permeation rate, the exact value of this large gas permeation rate was not given in that paper. Haraya et al. [16] analyzed the effects of the selectivity of membrane and bulk composition on the concentration polarization in more details. They showed that concentration polarization is a serious problem for the system with permeation rate being 1×10^3 GPU and

selectivity being 2. Up to date there is not, however, a quantitative indication as to when concentration polarization should be considered. Moreover, concentration polarization is understood to decrease the actual separation factor. The extent of such a decrease has never been studied.

The present study is then to analyze the effects of concentration polarization on membrane performance in gas separation processes so as to identify a range within which concentration polarization is important for industrial process design and operation, and to quantify the decrease of the superficial separation factor.

2. Theory

The system studied here is membrane separation of a binary gas mixture. Under steady state, the gas molar fraction profiles in the feed side are shown in Fig. 1. The curved lines in Fig. 1(a) and (b) denote the molar fraction of the more permeable and the less permeable gases. It can be seen that the molar fraction of the more permeable gas is lower than that in the bulk, whereas the molar fraction of the less permeable gas is higher than that in the bulk – a phenomenon usually called concentration polarization. The gases' permeation fluxes are given as:

$$N_1 = J^0(P_f x_s - P_p y), \quad (1)$$

$$N_2 = J^0[P_f(1 - x_s) - P_p(1 - y)]/\alpha^0, \quad (2)$$

where N_1 and N_2 are permeation fluxes of the more and the less permeable gases, respectively, at standard temperature and pressure. J^0 is the permeation rate of the more permeable gas without concentration polarization at standard temperature and pressure. P_f and P_p are the total pressures on the feed and on the permeate sides, respectively. x_s is the molar fraction of the more permeable gas on the membrane surface on the feed side, y is the molar fraction of the more permeable gas on the permeate side. α^0 is the separation factor without concentration polarization, defined as the ratio of the permeation rate of the more permeable gas to that of the less permeable gas.

Since there is no mass accumulation in the boundary layer for steady operation condition, the mass balances of gases through the boundary layer are:

$$N_1 = k(x - x_s)\frac{P_f T_0}{P_0 T} + x(N_1 + N_2), \quad (3)$$

$$N_2 = -k(x - x_s)\frac{P_f T_0}{P_0 T} + (1 - x)(N_1 + N_2), \quad (4)$$

where k represents the mass transfer coefficient, x the molar fraction of the more permeable gas in the bulk feed, T the feed temperature, and T_0 and P_0 are the standard temperature and pressure, i.e., 273.15 K and 76 cmHg or 1.013×10^5 Pa. The first term on the right-hand side represents the mass transfer due to the diffusion and the second term quantifies the convective mass transfer that resulted from the permeation bulk flow.

Rearranging Eq. (1), one gets

$$N_1 = J^0 \cdot P_f \cdot \left[x_s - (y - x_s) \cdot \frac{P_p}{P_f} - x_s \frac{P_p}{P_f} \right] \quad (5)$$

In many industrial gas membrane separation processes, $(y - x_s)P_p/P_f$ is negligible compared with $(1 - P_p/P_f)x_s$. Then Eq. (5) can be simplified into

$$N_1 = P_f \left(1 - \frac{P_p}{P_f} \right) J^0 x_s. \quad (6)$$

Similarly, Eq. (2) becomes

$$N_2 = P_f \frac{J^0}{\alpha^0} \left(1 - \frac{P_p}{P_f} \right) (1 - x_s). \quad (7)$$

It should be pointed out here, however, that the omission of $(y - x_s)P_p/P_f$ may cause up to 10% error in N_1 calculation for cases such as the nitrogen enrichment process. For the present study the error will be smaller because the ratio of N_1 to N_1^0 (or N_2 to N_2^0) will be used in our analysis as will be seen subsequently. From Eqs. (3), (6) and (7), the following expression for x_s can be obtained:

$$x_s = \frac{x(k + J^0 F \beta)}{k + J^0 F [1 - x(1 - \beta)]} \quad (8)$$

with

$$F = P_0 \frac{T}{T_0} \left(1 - \frac{P_p}{P_f} \right), \quad (9)$$

$$\beta = \frac{1}{\alpha^0}. \quad (10)$$

When $\alpha^0 = 1$ or $k \rightarrow \infty$, there is no concentration polarization. From Eq. (8) one obtains, as expected,

that

$$x_s = x. \quad (11)$$

Thus the permeation fluxes of the more and the less permeable gases in this case can be calculated according to Eqs. (6) and (7) as:

$$N_1^0 = P_f \left(\frac{1 - P_p}{P_f} \right) J^0 x, \quad (12)$$

$$N_2^0 = P_f \frac{J^0}{\alpha^0} \left(1 - \frac{P_p}{P_f} \right) (1 - x), \quad (13)$$

where N_1^0 and N_2^0 represent permeation fluxes of the more and the less permeable gases without concentration polarization.

When there is concentration polarization, a superficial permeation rate of the more permeable gas, J , and a superficial separation factor, α , can be defined as:

$$N_1 = P_f \left(1 - \frac{P_p}{P_f} \right) Jx, \quad (14)$$

$$N_2 = P_f \frac{J}{\alpha} \left(1 - \frac{P_p}{P_f} \right) (1 - x). \quad (15)$$

The effects of concentration polarization on the change of the permeation fluxes of the more and the less permeable gases can be described by the following ratios:

$$CP_1 = \frac{N_1}{N_1^0}, \quad (16)$$

$$CP_2 = \frac{N_2}{N_2^0}. \quad (17)$$

From Eqs. (6)–(8) and (13), the following expressions can be obtained:

$$CP_1 = \frac{N_1}{N_1^0} = \frac{x_s}{x} = \frac{k + J^0 F \beta}{k + J^0 F [1 - x(1 - \beta)]}, \quad (18)$$

$$\begin{aligned} CP_2 &= \frac{N_2}{N_2^0} = \frac{1 - x_s}{1 - x} = \frac{1}{1 - x} - \frac{x}{1 - x} \frac{N_1}{N_1^0} \\ &= \frac{1}{1 - x} - \frac{x}{1 - x} CP_1. \end{aligned} \quad (19)$$

The overall concentration polarization degree, CP, which describes the effect of concentration polarization on the change of the separation factor can be expressed as:

$$CP = \frac{\alpha}{\alpha^0}. \quad (20)$$

From Eqs. (12)–(15) and (19), the following expression can be derived:

$$CP = \frac{\alpha}{\alpha^0} = \frac{N_1}{N_1^0} \frac{N_2^0}{N_2} = \frac{CP_1}{CP_2} = \frac{CP_1(1 - x)}{1 - x CP_1} \quad (21)$$

Eqs. (18), (19) and (21) provide the fundamental formula for the analysis of concentration polarization for gas separation membrane processes as seen subsequently.

3. Selection of basic parameters

The hollow fiber membrane module with shell side feed, which is more popular and competitive in gas separation membrane processes, is chosen as model module for the following analysis. The mean mass transfer coefficient on the feed side is determined by the following correlation:

$$k = \frac{0.0732 d_e^{0.6} D^{0.67} u^{0.6}}{d_o^{0.4} \nu^{0.27}}, \quad (22)$$

where d_e is the hydraulic diameter, D the diffusion coefficient of the feed gas, u the velocity of the feed gas along the hollow fiber, d_o the fiber outside diameter, and ν is the kinematic viscosity of the feed gas. Eq. (22) was obtained from heat transfer on the shell side of an unbaffled heat exchanger [17] and verified experimentally by Wang et al. [13] for quantifying mass transfer coefficient in hollow fiber gas membrane separation. This equation is not perfect in that it is not a dimensionless equation with the proportional coefficient having a dimension of $\text{cm}^{-0.6}$ in order for k to be in cm s^{-1} . In addition, this equation does not show the effect of permeate flow explicitly but lumps this effect with other factors. While we do not have a better correlation to use for the time being and Eq. (22) has been recently verified experimentally, we adopt it for the present analysis with care. Although neither of the two references [13,17] has explicitly indicated the valid ranges of Reynolds and Schmidt number for Eq. (22), we understood that the experimental study [13] was conducted at laminar flow condition with typical Sc number at 0.65. Thus our selection of parameters was made not much beyond the experimentally tested range. The ratio of the permeate mass

flow to that of the cross mass flow was below 0.12%. Thus the N_1+N_2 effect on k may be negligible.

Presently the main commercial application of gas permeation is hydrogen recovery. The other gas separation membrane process that is becoming increasingly important is the separation of air into nitrogen- and oxygen-enriched streams. Thus the typical data of these two processes are used as reference in selecting parameters for the calculation of concentration polarization. Physical properties of the mixture such as viscosity, diffusion coefficient, and density at standard temperature and pressure are fixed at some typical values for the sake of simplicity. The hydraulic diameter $d_e=0.068$ cm was calculated using the given d_o and the typical filling density of hollow fiber membrane in the module, 40%. The detailed data chosen for the present analysis are listed in Table 1.

4. Results and discussion

From Eqs. (18), (19) and (21), one can see that the concentration polarization would depend on the permeation rate, separation factor, mass transfer coefficient that is a function of gas velocity for a given system, operation pressures (F and k), and possibly gas composition. The effects of each parameter are analyzed as follows. It is useful to emphasize here that when a particular parameter is discussed, all other parameters are assumed to be fixed at values given in Table 1.

Table 1
Data used in the model calculations

Parameter	System I (Hydrogen recovery)	System II (Air separation)
D_0 (cm ² s ⁻¹)	0.674	0.181
ρ_0 (g cm ⁻³)	0.09×10^{-3}	1.29×10^{-3}
α^0	50	4
J^0 (GPU ^a)	100 or 1000	100
P_p (cmHg)	1140	76
P_f (cmHg)	4560	760
T (K)	320	300
μ (g cm ⁻¹ s ⁻¹)	1.72×10^{-4}	1.72×10^{-4}
d_o (cm)	0.045	0.045
d_e (cm)	0.068	0.068
u (cm s ⁻¹)	50	50

^a 1 GPU = 1×10^{-6} cm³(STP) cm⁻² s⁻¹ cmHg⁻¹.

4.1. Effect of permeation rate

The permeation rate of the more permeable gas, J^0 , is the most important factor influencing the concentration polarization degree. We begin our analysis with the two extreme cases, i.e., $J^0=0$ and $J^0 \rightarrow \infty$. According to Eqs. (18), (19) and (21), for the former case, as expected, $CP_1=CP_2=CP=1$. It verifies the common belief that the concentration polarization is negligible when permeate rate is small. For the later case, it is easy to obtain the following expressions:

$$\lim_{J^0 \rightarrow \infty} CP_1 = \frac{\beta}{1 - x(1 - \beta)}, \quad (23)$$

$$\lim_{J^0 \rightarrow \infty} CP_2 = \frac{1}{1 - x(1 - \beta)}, \quad (24)$$

$$\lim_{J^0 \rightarrow \infty} CP = \beta. \quad (25)$$

For this limiting case, the concentration polarization is independent of the mass transfer coefficient k . This is a reasonable result because the diffusion effect is negligible in comparison with the permeation bulk flow. Eqs. (25) and (20) give an interesting result:

$$\lim_{J^0 \rightarrow \infty} \alpha = 1. \quad (26)$$

It states that in this extreme case, the gas mixture cannot be separated by membrane because of the serious concentration polarization effect.

In the current normal separation operations, the value of J^0 is usually between 10×10^3 and 1×10^3 GPU, instead of near zero or infinity. For the convenience of analysis, Eqs. (18) and (19) are rearranged so as:

$$CP_1 = \frac{\beta}{1 - x(1 - \beta)} + \frac{k(1 - \beta)(1 - x)}{1 - x(1 - \beta)} \times \frac{1}{k + J^0 F[1 - x(1 - \beta)]}, \quad (27)$$

$$CP_2 = \frac{1}{1 - x(1 - \beta)} + \frac{kx(1 - \beta)}{1 - x(1 - \beta)} \times \frac{1}{k + J^0 F[1 - x(1 - \beta)]}. \quad (28)$$

Eqs. (27) and (28) show the linear relations between CP_1 and CP_2 with $(1/(k + J^0 F[1 - \beta]))$. With the increase of J^0 , CP_1 decreases and CP_2 increases, thus CP decreases. A decrease in CP means that concen-

tration polarization becomes more serious. According to the sample calculation of Systems I and II as shown in Fig. 2, when $J^0 > 200$ GPU, CP is almost less than 0.9, concentration polarization affects separation processes obviously. When J^0 reaches 1000 GPU, CP can be 0.56 in System I and 0.72 in System II. The current value of J^0 for hydrogen separation can reach

1490 GPU [4], CP would then reduce to 0.2 according to Fig. 2(a). It means that the actual separation factor α is only 20% of the intrinsic separation factor α^0 . For air separation, the highest reported J^0 is 1.6×10^4 GPU [6]. In this case, CP would be lower than 0.3. Of course the overall effect of J^0 on CP depends on the separation factor α^0 , as seen in Section 4.2.

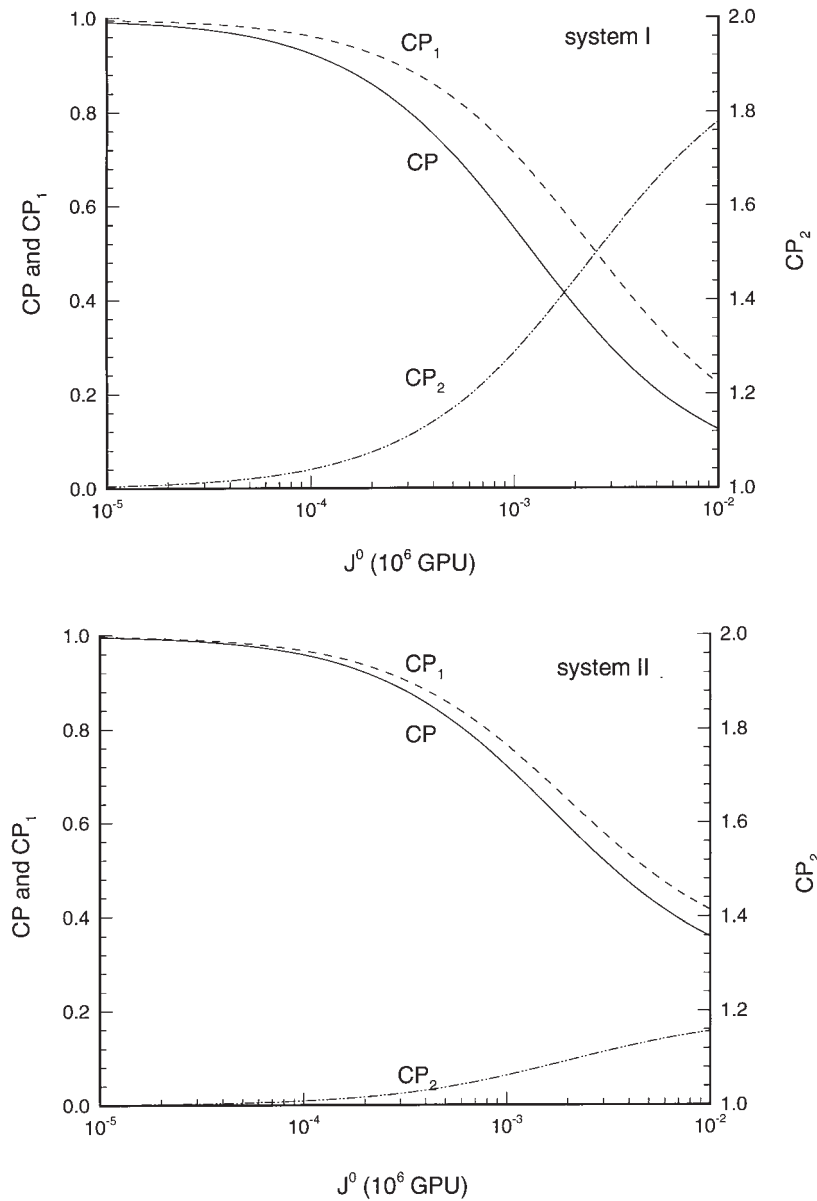


Fig. 2. Effect of permeation rate J^0 on concentration polarization: (a) System I; (b) System II.

4.2. Effect of the separation factor

The separation factor α^0 , which is the ratio of permeation rate of the more permeable gas to that of the less permeable gas and which affects the relative accumulation or depletion of gases on the membrane surface, is another important factor influencing the concentration polarization. When $\alpha^0=1$ there is no separation and hence no concentration polarization, $CP=CP_1=CP_2=1$ is obtained from Eqs. (18), (19) and (21) as expected. In order to have a clear picture of how separation factor affects the concentration polarization for normal separation system, it is necessary to rearrange Eqs. (18) and (19) to have a linear relationship of CP_1 and CP_2 with $(1/(k+J^0F(1-x)+J^0Fx\beta))$.

$$CP_1 = \frac{1}{x} - \frac{(1-x)(k+J^0F)}{x[k+J^0F(1-x)+J^0Fx\beta]}, \quad (29)$$

$$CP_2 = \frac{k+J^0F}{k+J^0F(1-x)+J^0Fx\beta}. \quad (30)$$

Now, it is easy to know that with α^0 increasing or β decreasing, CP_1 decreases and CP_2 increases, hence CP decreases. In other words, concentration polarization becomes more serious for larger α^0 . But when α^0 is high enough, the value of $J^0Fx\beta$ becomes insignificant compared with $k+J^0F(1-x)$. Then further increase of α^0 will not change CP_1 , CP_2 or CP appreciably. This finding is not a surprise because in such a case there is very little of the more permeable gas in the boundary layer due to the high separation factor, thus the concentration polarization is mainly controlled by the depletion rate of the pure less permeable gas in the boundary. When α^0 approaches infinity, CP_1 , CP_2 and CP would approach constant values as:

$$\lim_{\alpha^0 \rightarrow \infty} CP_1 = \frac{k}{k+J^0F(1-x)}, \quad (31)$$

$$\lim_{\alpha^0 \rightarrow \infty} CP_2 = \frac{k+J^0F}{k+J^0F(1-x)}, \quad (32)$$

$$\lim_{\alpha^0 \rightarrow \infty} CP = \frac{k}{k+J^0F}. \quad (33)$$

Eqs. (31)–(33) are useful in estimating the extent of concentration polarization, the actual permeation fluxes and the real separation results for systems with high separation factor, such as air drying where α^0 is

usually larger than 1000. Actually, as will be seen from the subsequent analysis, these equations can also be used as an approximate estimation for other systems with much smaller α^0 such as most of the hydrogen and helium recovery, some of the CO_2 separation, and other membrane gas separation processes in which the separation factor is larger than 20.

The sample calculation shown in Fig. 3 illustrates the analysis. In both Fig. 3(a) and (b), the concentration polarization degree (CP) decreases significantly. That is to say that concentration polarization becomes more serious with the increase of the separation factor until α^0 is about 20 for Fig. 3(a) and 10 for Fig. 3(b). Further increase in α^0 shows no appreciable effects on concentration polarization degree. Although sample calculations were made for hydrogen recovery (System I) and air separation (System II), the results for other gas separation systems would be similar because the changes of the physical properties for the different gas systems are very limited.

From Eqs. (29) and (30), one can find that the effects of α^0 on CP_1 and CP_2 are coupled with J^0 . Such a phenomenon is also clearly demonstrated in the sample calculation shown in Fig. 3. The effects of α^0 on CP_1 and CP_2 are limited by the permeation rate. For a higher permeation rate, a larger range of α^0 can significantly affect the concentration polarization and the limit value of CP is smaller.

If $CP=90\%$ is selected as the acceptable limit for concentration polarization, the combined effects of permeation rate and separation factor can be analyzed as shown in Fig. 4. Each curve divides the plane into two parts, the part above the curve gives $CP<90\%$, whereas the part below the curve gives $CP>90\%$. It is straightforward that the concentration polarization is tolerable only if the point of (α^0, J^0) is located below the $CP=90\%$ curve. Specifically, when $J^0<100$ GPU, the concentration polarization is acceptable. When $J^0>200$ GPU and $\alpha^0>10$ or when $J^0>300$ GPU and $\alpha^0>3$, concentration polarization must be serious. Whereas for $100<J^0<200$ GPU and $\alpha^0>10$, concentration polarization is possible with its exact extent depending on the operation parameter – feed gas velocity whose effect on CPs is analyzed in Section 4.3. By now the membrane performance points (α^0, J^0) are above the curve in Fig. 4 for all air dehydration, some of the hydrogen and helium

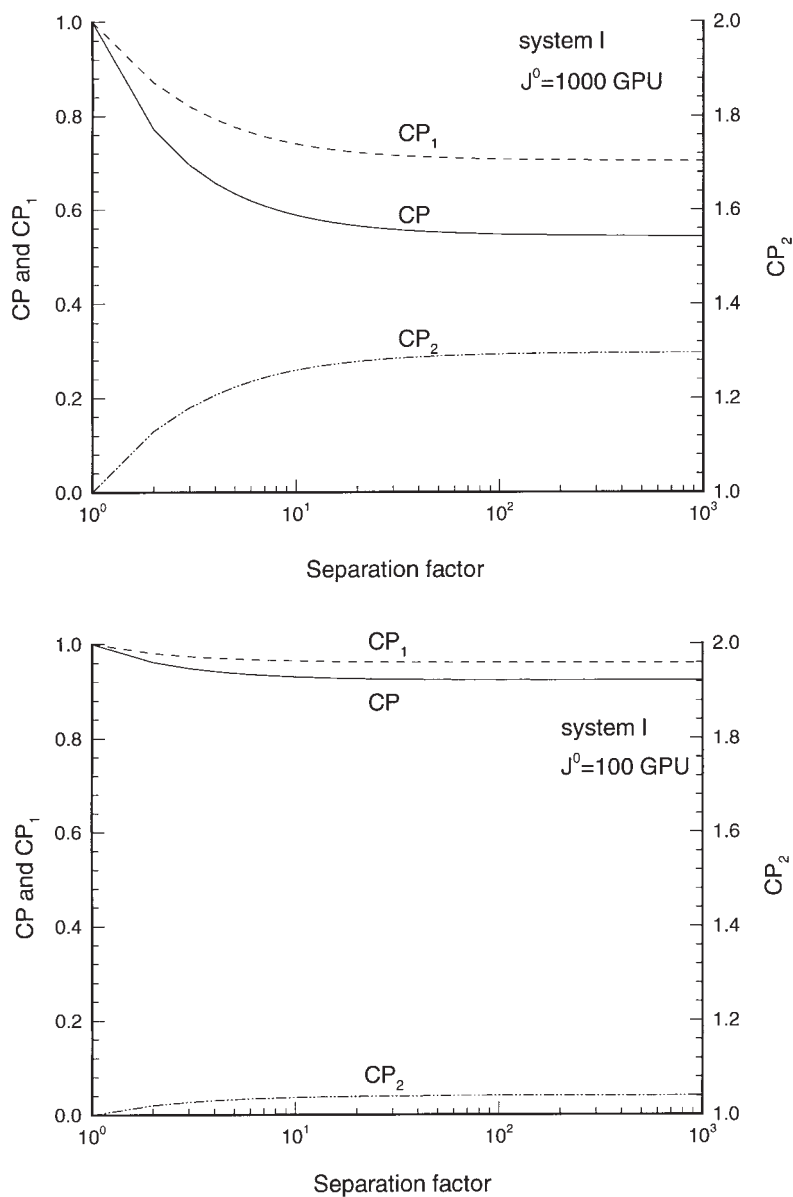


Fig. 3. Effect of separation factor α^0 on concentration polarization: (a) System I with $J^0 = 1000$ GPU; (b) System I with $J^0 = 100$ GPU.

recovery, and a few of CO_2 separation processes. For example, one kind of Ubes polyimide hollow fiber membrane which allows gas permeating from the shell to the bore side has $J^0 = 500$ GPU and $\alpha^0 = 83$ in hydrogen and nitrogen systems [18]. Hence these processes must suffer from the concentration polarization problems.

4.3. Effect of feed gas velocity

The velocity of feed gas u which influences the mass transfer coefficient k is the most important operation parameter that determines the concentration polarization degree. As a matter of fact, increasing feed velocity is one of the most often employed technique

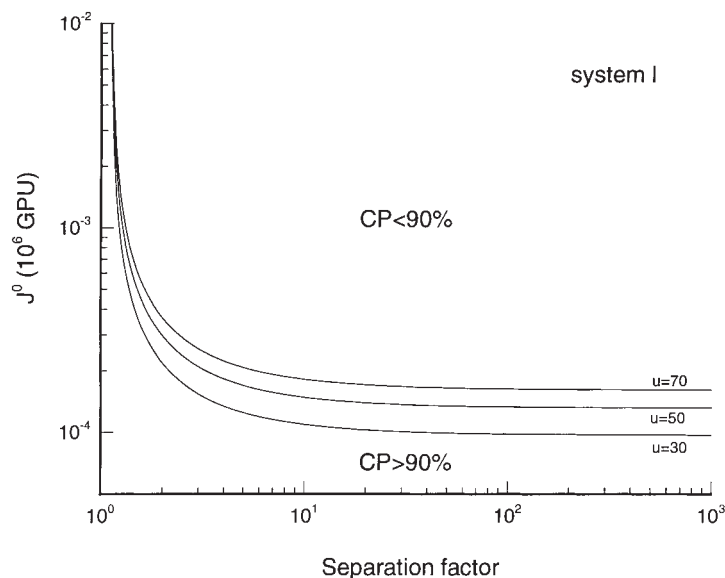


Fig. 4. Combined effect of permeation rate and separation factor on concentration polarization (System I).

to reduce concentration polarization in liquid separation. Similar to the analysis with regard to J^0 and α^0 , Eqs. (18) and (19) are rearranged to obtain:

$$CP_1 = 1 - \frac{J^0 F(1-x)(1-\beta)}{k + J^0 F[1-x(1-\beta)]}, \quad (34)$$

$$CP_2 = 1 + \frac{J^0 Fx(1-\beta)}{k + J^0 F[1-x(1-\beta)]}. \quad (35)$$

While $k \propto u^{0.6}$, it is obvious from the above two equations that CP_1 increases and CP_2 decreases with the increase of u . Thus CP increases and the concentration polarization is reduced by increasing feed velocity. Exactly what the magnitude of u effect on CP is can be seen from Fig. 5. When J^0 is small, as shown in Fig. 5(a) and (b), the increase of CP is almost linearly proportional to the feed velocity initially ($u < 1 \text{ cm s}^{-1}$). As the feed velocity increases, its effect on the concentration polarization gradually decreases because the boundary layer is thin enough. For the larger J^0 , the effect of the cross flow velocity u is smaller compared with that for smaller J^0 , particularly for $u < 1 \text{ cm s}^{-1}$. The effect of u against the large J^0 starts to show only after u is sufficiently large, as shown in Fig. 5(c). Since feed velocity is usually limited by the power of gas compressor, membrane strength, gas recovery, etc., the controlling factor for

the concentration polarization is again the permeate rate. By increasing the values of J^0 from 100 to 1000 GPU, CP drops from about 0.23 to slightly higher than 0.05 at $u = 0.1 \text{ cm s}^{-1}$ as seen in Fig. 5(b) and (c). By increasing velocity to 100 cm s^{-1} , CP becomes more than 0.9 for the low J^0 case while $CP < 0.65$ for the high J^0 one. The velocity of the feed gas alone cannot eliminate concentration polarization.

4.4. Effect of operation pressure

The operation pressures are other operation parameters that can influence the concentration polarization, although they can only be selected in a limited range because of the energy cost and membrane or module strength. Nevertheless, the following analysis gives an indication of CP_1 , CP_2 and CP change with P_f and P_p . For a fixed permeate side pressure P_p , the increase of the feed side pressure P_f results in an increase of driving force for the gas permeation, which is dominant compared to other changed parameters, such as k . The increased permeation fluxes mean more serious concentration polarization, which is similar to the analysis in Section 4.1. When the total pressure difference across the membrane is constant, the increase of the pressures would lead to the increase

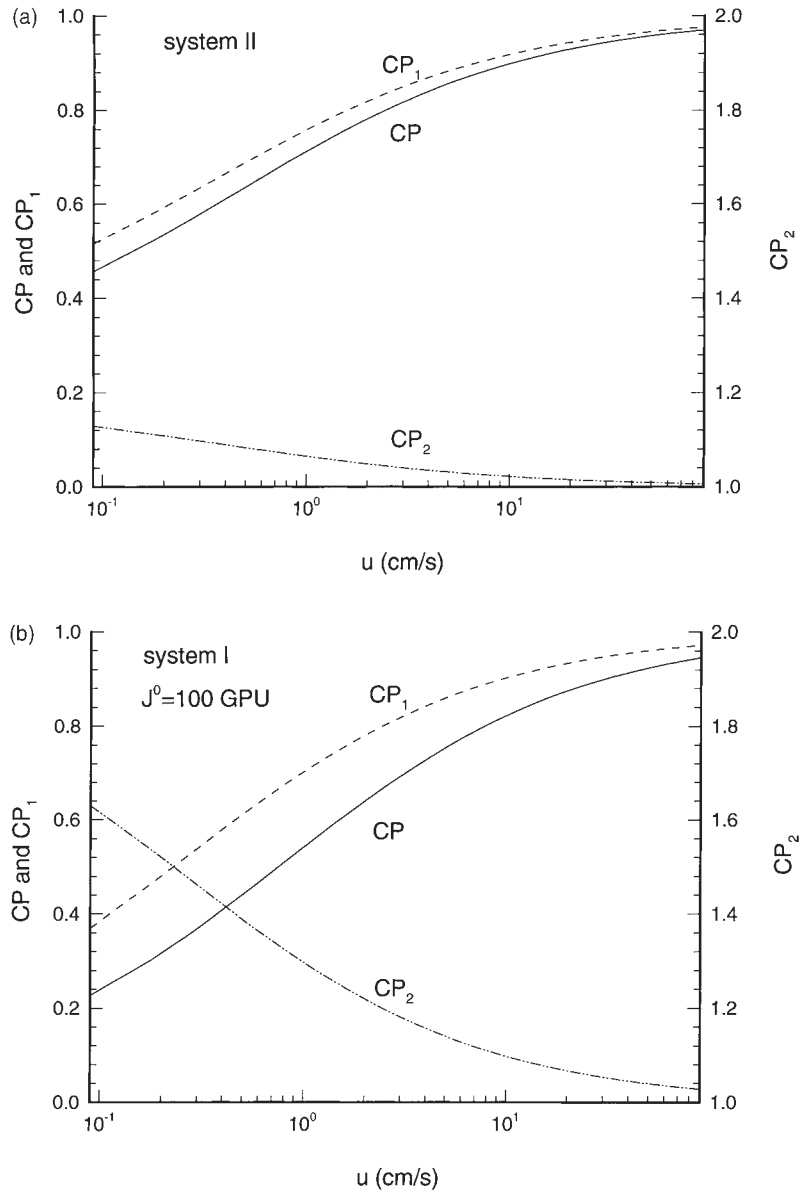


Fig. 5. Effect of feed gas velocity on concentration polarization: (a) System II; (b) System I with $J^0=100$ GPU; (c) System I with $J^0=1000$ GPU.

of the mass transfer due to the increase of kP_f/P_0 . Such an effect is similar to the increases of feed velocity. Thus, concentration polarization would be reduced. Fig. 6 illustrates the variation of CP_1 , CP_2 and CP with operation pressures for hydrogen recovery process. At a fixed permeate pressure of 1140 cmHg, a change of P_f from 1500 to 8000 cmHg resulted in a change of CP

from 0.85 to 0.47, as shown in Fig. 6(a). When the pressure difference of the feed and permeate sides is fixed at 3420 cmHg, CP changes only from 0.54 to 0.63 while P_f from 4000 to 8000 cmHg, as seen in Fig. 6(b). Such sample results point out that one should consider the concentration polarization effect on the separation results carefully when varying the

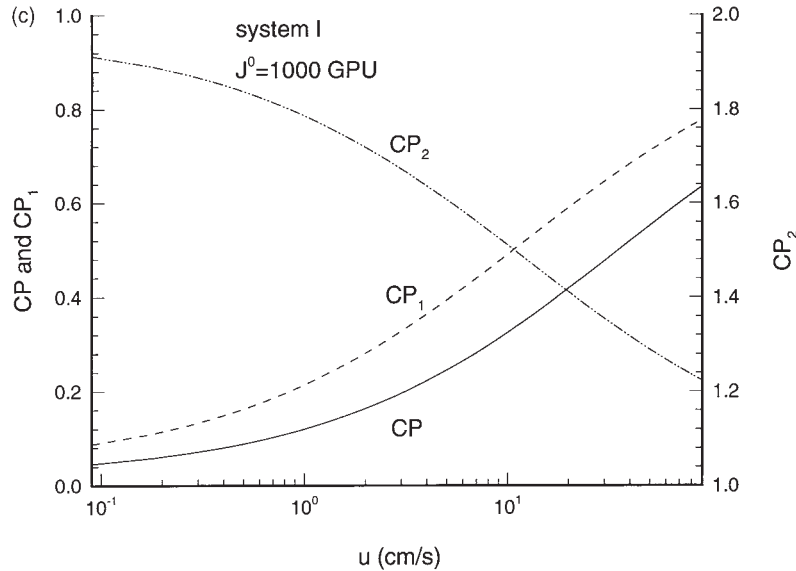


Fig. 5. (Continued)

pressure driving force. These results are consistent with the analysis of the $CP-J^0$ effects.

4.5. Effect of feed gas composition

The feed gas molar fraction changes from case to case for different separation processes. Even for a given gas separation process, the membrane at different location sees a different gas composition due to its selective permeation. From Eqs. (18) and (19), one can obtain:

$$CP_1 = \frac{k + J^0 F \beta}{k + J^0 F - x J^0 F (1 - \beta)}, \quad (36)$$

$$CP_2 = \frac{k + J^0 F}{k + J^0 F - x J^0 F (1 - \beta)}. \quad (37)$$

When $x=1$, the system is a single-component system of the more permeable gas, and $CP_1=x_s/x=1$ naturally. Similarly when $x=0$, $CP_2=(1-x_s)/(1-x)=1$ as expected. For realistic mixed gas cases with infinite dilution conditions, Eqs. (36) and (37) reveal interesting limiting cases. To simplify the discussion, consider constant boundary layer thickness and other parameters in these equations, with only composition (i.e., x) varying. Interestingly, at $x=1$, CP_2 resumes a constant value other than 1 and when $x=0$, CP_1 is also

constant but not 1. When $x \rightarrow 0$, the presence of the less permeable gas is large, and there is very little of the more permeable gas in the system. However, the boundary layer and the concentration gradient still exist as usual. For the less permeable gas, the concentration gradient is small, $1-x_s$ is equal to $1-x$ approximately, thus $CP_2 \rightarrow 1$; but for the more permeable gas, x_s is lower than x obviously because of the fast permeation, thus CP_1 is less than 1. CP_2 is constant when $x=1$ can be explained similarly. To better illustrate the significance of these results, consider two different concentrations of the fast component. Suppose the molar fraction of the fast component is 80% for Case A and 60% for Case B. When the J and P_f are assumed to be the same in both cases, and for simplicity, let $P_p=0$ and $\alpha \rightarrow \infty$, then, $N_1=JP_f x$, $N_2=0$.

If 100 mol feed is considered, and suppose the permeate in Case A is 40 mol, then the permeate in Case B would be $(40\% \times 60\%) / 80\% = 30$ mol. In extreme conditions, the concentration of the fast component on the membrane surface is $(80-40)/(80-40+20)=67\%$ and $(60-30)/(60-30+40)=43\%$ for Cases A and B, respectively. Therefore the concentration difference of the fast component between bulk and membrane surface is 13% and 17% for Cases A and B, respectively.

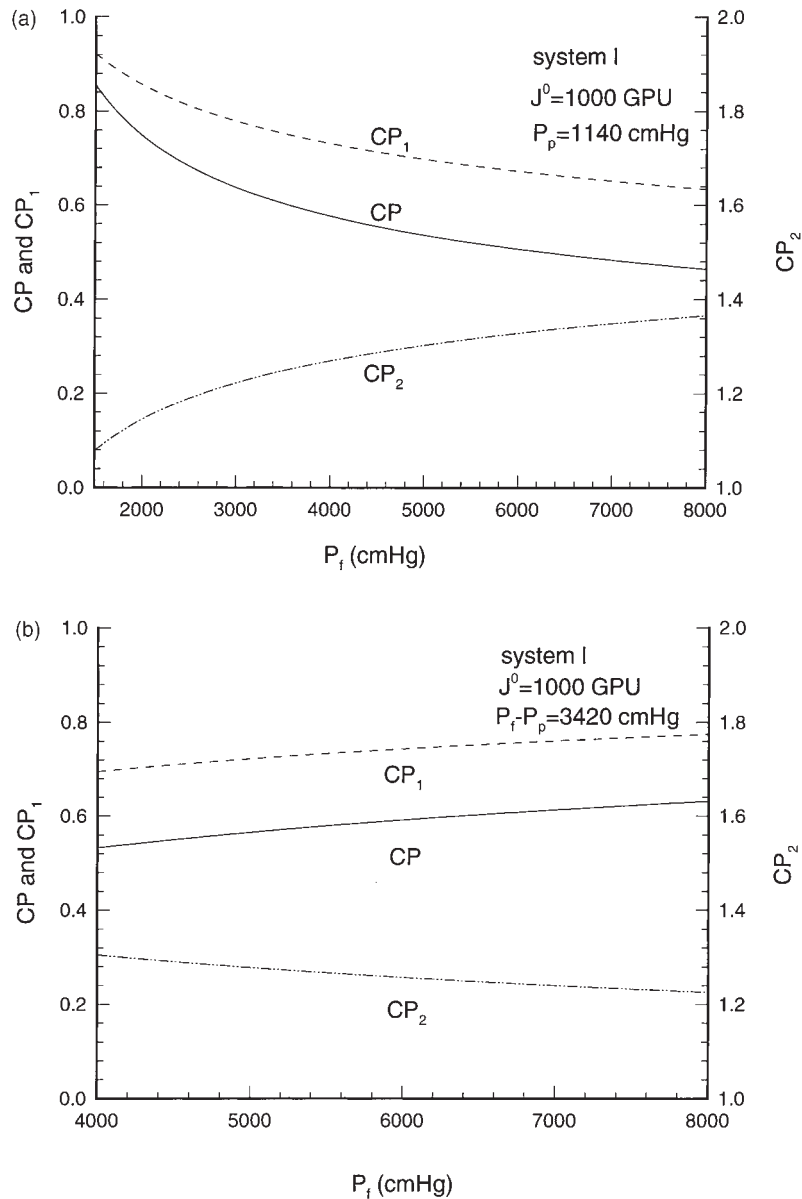


Fig. 6. Effect of operation pressure on concentration polarization for System I with $J^0=1000$ GPU: (a) $P_p=1140$ cmHg; (b) $P_f-P_p=3420$ cmHg.

Thus, the higher concentration of the fast component yields a lower concentration gradient of the fast component and hence a lower grade of concentration polarization.

Eqs. (36) and (37) also show that both CP_1 and CP_2 increase with the increase of x , the molar fraction of the more permeable gas in bulk feed, Fig. 7. Such a

phenomenon is in clear contrast to those discussed in the previous sections where CP_1 and CP_2 change in opposite directions. The unique feature of CP_1 and CP_2 changes with x in the same direction can be better understood based on the previous analysis and the concentration profiles of the more and the less permeable gases shown in Fig. 1. From Fig. 1, one sees that

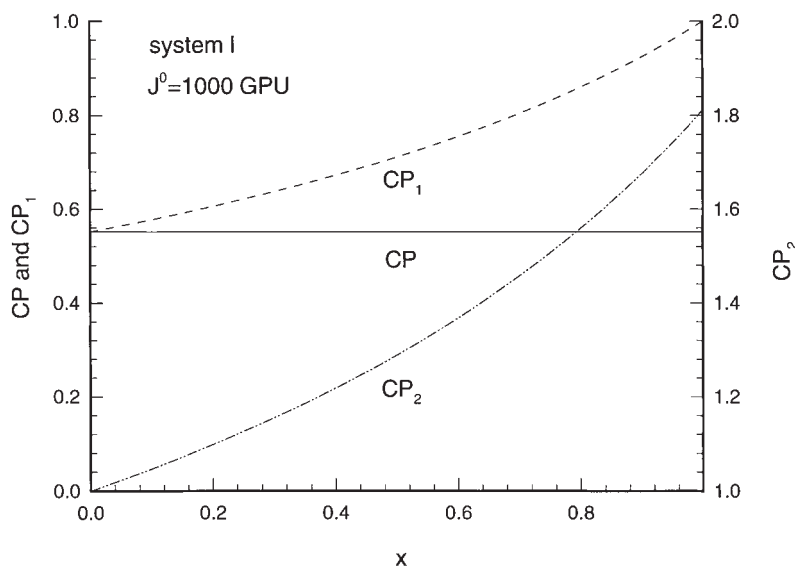


Fig. 7. Effect of feed gas molar fraction x on concentration polarization for System I with $J^0=1000$ GPU.

x_s is always lower than x and $(1-x_s)$ is always higher than $(1-x)$ except at the two end points of x , i.e., $x=0$ and $x=1$. When x is away from either 0 or 1, we would have $CP_1 < 1$ and $CP_2 > 1$. While it has been established that $x=0$, $CP_2=1$, then CP_2 should initially increase as x increases to satisfy $CP_2 > 1$. In addition, the larger the

x , the higher the possibility of concentration polarization, hence CP_2 would increase monotonically with x . Similarly since $x=1$, $CP_1=1$, then as x decreases, CP_1 should initially decrease to have $CP_1 < 1$. Actually following the similar analysis for CP_2 we can say that such a decreasing trend would extend to the region of

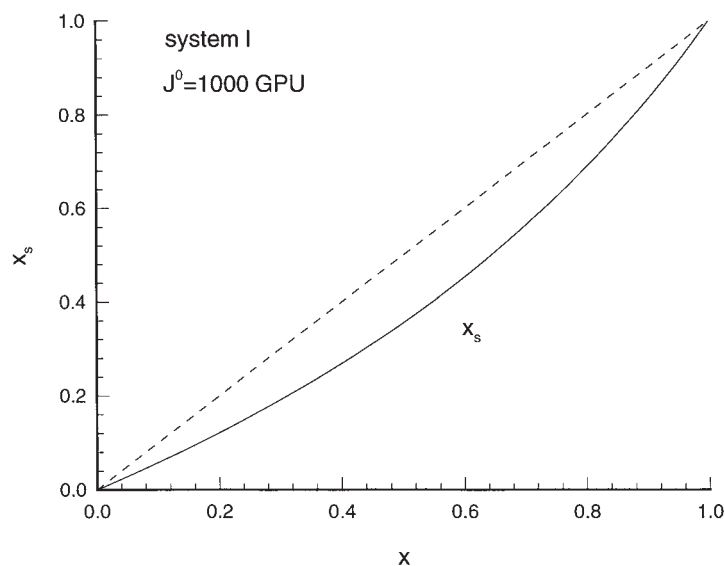


Fig. 8. The variation of the molar fraction of the more permeable gas at the membrane surface with its bulk concentration under the operation conditions of Fig. 7.

$x \rightarrow 0$. The last statement can also be expressed alternatively as “CP₁ increases as x increases”. This effect will be more clearly illustrated subsequently.

Divide Eq. (36) by Eq. (37), one gets

$$CP = \frac{k + J^0 F \beta}{k + J^0 F}. \quad (38)$$

The gas mixture composition does not affect the overall concentration polarization degree, CP. Of course, the change of the composition will result in a change in the physical properties hence k may change slightly. As analyzed in the previous sections, the effect of permeation flux, J^0 , is the dominating factor in influencing CP. Thus the slight variation of k does not change CP appreciably. The constant CP implies that for a given set of operating conditions, the molar fraction of the more permeable gas at the membrane surface, x_s , varies only with its bulk concentration, x . While

$$CP = \frac{CP_1}{CP_2} = \frac{x_s}{x} \frac{1 - x}{1 - x_s}. \quad (39)$$

Thus,

$$x_s = \frac{CPx}{1 - (1 - CP)x}. \quad (40)$$

This x_s and x relationship is illustrated in Fig. 8 for the operating conditions of Fig. 7 where $CP=0.553$. The convex curve demonstrates clearly the increase of CP₁, the ratio of x_s to x , with x . It would be ideal to experimentally verify the theoretical results shown in this study. Due to the shortage of suitable membranes and membrane separation facilities, the present work focused on the theoretical analysis only.

5. Conclusions

A mathematical model was established successfully to investigate the effects of both the membrane separation properties and operation parameters on the concentration polarization in gas separation processes. The concentration polarization was analyzed in terms of permeation fluxes of the more and the less permeable gases and separation factor. The operation parameters and membrane properties of two typical industrial applications, hydrogen recovery and air separation, were used for sample calculations.

Permeation rate is a dominating factor in affecting concentration polarization, higher permeation rate always gives more serious concentration polarization. For the two systems studied here, separation factor drops more than 10% when permeation rate of the more permeable gas is higher than 100 GPU. Thus it is necessary to consider the concentration polarization in process design and analysis. For a given permeation rate, the membrane that gives higher separation factor would experience more serious concentration polarization effect. When the separation factor is large enough, its further increase shows insignificant influences on the concentration polarization. This limit value changes along with the value of the permeation rate. For $J^0=1000$ GPU, it is about 20, and for $J^0=100$ GPU, it is about 10.

The effects of permeation rate and separation factor are coupled. When $J^0>200$ GPU and $\alpha^0>10$ or when $J^0>300$ GPU and $\alpha^0>3$, concentration polarization is serious, and when $100<200$ GPU and $\alpha^0>10$, concentration polarization may be serious with its exact degree depending on the operation parameters such as feed gas velocity.

Increasing gas feed velocity is a helpful operational technique to decrease but not eliminate concentration polarization. The effects of actual operation pressures on concentration polarization are relatively small for a fixed pressure difference across the membrane. While for a given permeate pressure, the change of gas feed pressure would result in change in the permeate fluxes and concentration polarization degree. Gas composition is found not to affect the overall concentration polarization degree, CP, although it can change the permeation fluxes of both the more and the less permeable gases.

The model analysis and sample calculation demonstrate the importance of considering and studying concentration polarization for process design and analysis with the ever increasing improvement of the gas separation membranes.

6. Nomenclature

CP concentration polarization degree, the ratio of separation factor with concentration polarization to that without concentration polarization

CP ₁	ratio of permeation flux with concentration polarization to that without concentration polarization for the more permeable gas
CP ₂	ratio of permeation flux with concentration polarization to that without concentration polarization for the less permeable gas
d_e	hydraulic diameter, four times the cross-sectional area divided by the wetted perimeter (cm)
d_o	outside diameter of fiber (cm)
D	diffusion coefficient of the feed gas ($\text{cm}^2 \text{s}^{-1}$)
D_0	diffusion coefficient of the feed gas at standard temperature and pressure ($\text{cm}^2 \text{s}^{-1}$)
F	defined as in Eq. (9)
J	superficial permeation rate of the more permeable gas with concentration polarization (GPU, $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$)
J^0	permeation rate of the more permeable gas without concentration polarization (GPU, $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$)
k	mass transfer coefficient (cm s^{-1})
N_1	permeation flux of the more permeable gas ($\text{cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1}$)
N_2	permeation flux of the less permeable gas ($\text{cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1}$)
N_1^0	N_1 without concentration polarization effect ($\text{cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1}$)
N_2^0	N_2 without concentration polarization effect ($\text{cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1}$)
P_0	standard pressure, 76 cmHg or $1.013 \times 10^5 \text{ Pa}$
P_f	total pressure on the feed side (cmHg)
P_p	total pressure on the permeate side (cmHg)
T	temperature on the feed side (K)
T_0	standard temperature $T_0 = 273.15 \text{ K}$
u	velocity of the feed gas along the hollow fiber (cm s^{-1})
x	molar fraction of the more permeable gas in feed bulk
x_s	molar fraction of the more permeable gas on the membrane surface
y	molar fraction of the more permeable gas on the permeate side

Greek letters

α	superficial separation factor with concentration polarization
----------	---

α^0	separation factor without concentration polarization
β	defined as in Eq. (10)
ν	kinematic viscosity of feed gas ($\text{cm}^2 \text{s}^{-1}$)
μ	viscosity of the feed gas ($\text{g cm}^{-1} \text{s}^{-1}$)
ρ	density of the feed gas (g cm^{-3})
ρ_0	density of the feed gas at standard temperature and pressure (g cm^{-3})

Subscripts

0	condition at standard temperature and pressure
1	the more permeable gas
2	the less permeable gas
o	outside
p	permeate side
f	feed side

Superscripts

0	without concentration polarization
---	------------------------------------

Acknowledgements

We are grateful to Prof. R. Xu and late Prof. B. Zhu of Dalian Institute of Chemical Physics for their helpful comments and discussions.

References

- [1] H. Strathmann, Membrane separation processes, J. Membr. Sci. 9 (1981) 121–189.
- [2] R.T. Chern, W.J. Koros, B. Yui, H.B. Hopfenberg, V.T. Stannett, Selective permeation of CO_2 and CH_4 through Kapton polyimide: Effects of penetrant competition and gas-phase nonideality, J. Polym. Sci. 22 (1984) 1061–1084.
- [3] R. Rautenbach, R. Albrecht, Membrane Processes, Wiley, New York, 1989.
- [4] B.-K. Sea, K. Kusakabe, S. Morooka, Pore size control and gas permeation kinetics of silica membranes by pyrolysis of phenyl-substituted ethoxysilanes with cross-flow through a porous support wall, J. Membr. Sci. 130 (1997) 41–52.
- [5] Y.-T. Chern, B.-S. Wu, Preparation of composite membranes with polyimides and poly(amide-imide)s skin via interfacial condensation for air separation, J. Appl. Poly. Sci. 63 (1997) 693–701.
- [6] X.-G. Li, M.-R. Huang, Water-casting ultrathin-film composite membranes for air separation, Sep. Sci. Tech. 31 (1996) 579–603.

- [7] S.-Y. Lee, S.-J. Lee, S.-J. Kwon, S.-M. Yang, S.B. Park, Preparation of sol–gel driven alumina membrane modified by soaking and vapor-deposition method, *J. Membr. Sci.* 108 (1995) 97–105.
- [8] K. Kusakabe, Z.Y. Li, H. Maeda, S. Morooka, Preparation of supported composite membrane by pyrolysis of polycarbosilane for gas separation at high temperature, *J. Membr. Sci.* 103 (1995) 175–180.
- [9] R.S.A. de Lange, K. Keizer, A.J. Burggraaf, Analysis and theory of gas transport in microporous sol–gel derived ceramic membranes, *J. Membr. Sci.* 104 (1995) 81–100.
- [10] J.C.S. Wu, H. Sabol, G.W. Smith, D.L. Flowers, P.K.T. Liu, Characterization of hydrogen-permselective microporous ceramic membranes, *J. Membr. Sci.* 96 (1994) 275–287.
- [11] A. Sengupta, K.K. Sirkar, Membrane Separation, in: R.J. Wakeman (Ed.), *Progress in Filtration and Separation*, Elsevier, Amsterdam, 1986, pp. 289–415.
- [12] S.A. Stern, Polymers for gas separation: the next decade, *J. Membr. Sci.* 94 (1994) 1–65.
- [13] K.L. Wang, S.H. McCray, D.D. Newbold, E.L. Cussler, Hollow fiber air drying, *J. Membr. Sci.* 72 (1992) 231–244.
- [14] I.-J. Chung, K.-R. Lee, S.-T. Hwang, Separation of CFC-12 from air by polyimide hollow-fiber membrane module, *J. Membr. Sci.* 105 (1995) 177–185.
- [15] S. Bhattacharya, S.-T. Hwang, Concentration polarization, separation factor, and Peclet number in membrane processes, *J. Membr. Sci.* 132 (1997) 73–90.
- [16] K. Haraya, T. Hakuta, H. Yoshitome, A study of concentration polarization phenomenon on the surface of gas separation membrane, *Sep. Sci. Tech.* 22 (1987) 1425–1438.
- [17] D.A. Donohue, Heat transfer and pressure drop in heat exchangers, *Ind. Eng. Chem.* 41 (1949) 2499–2511.
- [18] T. Matsuura, *Synthetic Membranes and Membrane Separation Processes*, CRC Press, Boca Raton, 1994.