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Effect of Sherwood number on critical constants of diffusion

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Abstract—Critical constants of mass diffusion through a membrane were related to a critical time, t_c', which designates the conversion between transient and steady-state conditions of the diffusion process. The critical time t_c', is precisely defined and analytically derived. In their dimensionless form, these critical constants depend solely on the Sherwood number (*Sh*). Values of dimensionless critical constants were determined for the whole range of Sherwood numbers. The results are useful in cases where small amounts of diffused mass must be detectable. E.g.: in production from hazardous materials, in the design and evaluation of diffusion experimental processes and devices. The effect of measurement errors on the determination of the critical constants is also analyzed. The main results show that the evaluation of the critical constants is obtained with minimum errors, when experiments are being performed under convective boundary conditions ($Sh > 100$). The results of this study are applicable to heat transfer problems as well.

INTRODUCTION

The present work introduces critical constants of a point which separates between the transient and steady-state stages of mass diffusion through permeable thin walls. Quantitative prediction of this critical point is useful, especially in cases where minimum amount of the diffusant must be detected, like protection from hazardous materials and scientific experiments. Moreover, the critical point provides the basis for a wide range of industrial and scientific applications. The following examples illustrate the variety and extent of these applications.

(a) Stored food in plastic packaging may suffer damage due to penetration of small amounts of foreign materials and impurities through plastic covers (refs. [1, 2]). Evaluation of the required time for a critical mass of the undesired additives to penetrate the food, provides a control parameter for food storing.

(b) The adsorption of low molecular weight penetrants into solid polymers may change transport and mechanical properties of the polymer [3]. Relating the mechanical and mass transport properties to the critical diffusion parameters, enables prediction of these properties as a function of diffusion time.

(c) Transportation of hazardous liquids in polymer containers may be controlled by permeation test methods [4]. Storage life and transportation safety can be predicted and optimized by simple experiments determining the material geometry and diffusion properties of the container.

(d) Evaluation of polymers resistance to permeation may help assess their potential for use in chemical protection clothing applications [5].

(e) In Biology, medical polymeric membranes are used for transporting biological liquids [6]. Calculations of the critical point is necessary for designing and conducting experiments.

(f) Water absorbed in insulation of electric cables reduces their service life, by forming water trees in the insulation, which eventually break it [7]. Diffusion is the control mechanism of water penetration through these polymers.

(g) Permeation tubes are simple devices which are being used to generate a known low concentration of a desired gas in a carrier gas, utilizing known constant mass permeation rate of the desired gas through polymeric membranes. Permeation tubes are being used for example, in calibration of automobile exhaust gas and analyzers [8].

These applications are diffusion-controlled. Knowing the critical point for each case provides design information regarding the time and the amount of diffusing substance either in transient or in steady-state conditions.

The present analysis may also be used in designing and conducting diffusion based experiments by evaluating the critical point and its related critical constants prior to the beginning of the experimental and then refitting the critical point during the experiment.

THEORY

The simplest case, which accounts for the above applications, is the diffusion of a fluid through a plain

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NOMENCLATURE

C	C'/C_0
C_0	maximum diffusant mass concentration that a membrane can adsorb
C'	diffusant concentration within a membrane
D	diffusion coefficient
h_c	convective mass transfer coefficient
K	m_L/m_s, represents a closeness extent of m_s to m_L (Fig. 1)
L	membrane thickness
m	m'/m_0
m'	total mass per unit area which exits a membrane to the ambient
m_0	maximum diffused mass per unit area that a membrane can adsorb
m_c	m'_c/m_0
m'_c	critical diffused mass at time t'_c
m_L	m'_L/m_0
m'_L	mass per unit area at t', on the asymptotic line of $m'(t')$
m_s	m'_s/m_0
m'_s	total mass per unit area exits a membrane at t'_s
M	permeated mass in experiments
$\dot{M}$	rate mass permeated in experiments
Sh	h_cL/D, Sherwood number
t	$t'D/L^2$
t'	diffusion time
t'_b	minimum detectable (breakthrough) time of a diffused mass
t_c	t'_cD/L^2
t'_c	intercept time of the diffused mass asymptotic line
t_s	t'_sD/L^2
t'_s	start time of a steady-state flux
X	X'/L
X'	coordinate, normal to a membrane plane. Starts at the wet side of the membrane ($X' = 0$) and ends at the ambient side ($X' = L$).

Greek symbols

$\Delta()$	difference between two values of ( )
λ_n	nth eigen-value defined in equation (6)
χ^2	error measure of theoretical and experimental diffused mass.

sheet. It is a problem of heat or mass transfer through a membrane of thickness, L. The wet side of the membrane is in contact with the diffusant, while the other side is in contact with the ambient. The governing equation of this case is a one-dimensional diffusion equation (in its dimensionless form):

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial X^2} \tag{1}$$

with the initial condition

$$C = 0, \quad X > 0, \quad t = 0. \tag{2}$$

The boundary conditions at the wet side of the membrane

$$C = 1, \quad X = 0, \quad t \geqslant 0. \tag{3}$$

The mass flux across the other surface is transferred to the ambient by convection [9]

$$\frac{\partial C}{\partial X} = -Sh\,C, \quad X = 1, \quad t > 0 \tag{4}$$

where $Sh \equiv h_cL/D$ is the Sherwood number.

Equations (3) and (4) are boundary conditions of the diffusion equation (1). Equation (4) appears in various forms. It is known as a linear mixture of a Dirichlet and Neumann boundary condition in the case of heat conduction in a thin rod [10], Fourier and Newton laws in the heat transfer case [11], or Fick's law [9] in the mass transfer case. Therefore, analysis results of equations (1)–(4) are equally applicable for both heat and mass transfer. In this article, without loss of generality, we shall consider the mass transfer case only.

The Sherwood number, Sh in equation (4) represents a velocity ratio of the diffused mass, i.e., convective velocity relative to mass velocity within the membrane. Alternatively, it represents the absorbability of the diffusant by the ambient relative to the membrane ability to supply the diffused mass. Therefore, the concentrations at $X = 1$ [equation (4)] and along the membrane thickness are Sh dependent. When Sh is close to zero, the surrounding inhibits mass transfer, and when Sh tends to infinity, the surrounding absorbs the transferred mass from the membrane as fast as it can supply due to the forced convection of the ambient fluid [16]. In equation (4) it is assumed that the concentration of the diffusant, within the ambient is negligible relative to the concentration at the membrane surface.

The solution of equation (1) with the conditions set in equations (2)–(4) provides the following concentration function:

$$C(X,t) = 1 - \frac{Sh\,X}{1+Sh} - 2\sum_{n=1}^{\infty} \frac{e^{-\lambda_n^2 t}\sin\lambda_n X}{\lambda_n - \sin\lambda_n\cos\lambda_n} \tag{5}$$

where λ_n is given implicitly by:

$$\lambda_n \cos \lambda_n + Sh \sin \lambda_n = 0. \tag{6}$$

The total mass $m(t)$, which exits the membrane to the ambient, is obtained by integration of the diffusion flux at the membrane surface over the diffusion time, t, using equations (4)–(6):

$$m(t) = 1 - \frac{Sh\,t}{1+Sh} + 2\sum_{n=1}^{\infty} \frac{(1-e^{-\lambda_n^2 t})\cos \lambda_n}{\lambda_n(\lambda_n - \sin \lambda_n \cos \lambda_n)}. \tag{7}$$

The first term on the right hand side of equation (7) is the mass which exits the membrane to the ambient, after time long enough to achieve steady-state conditions.

When the second term is significant, it indicates that part of the diffused mass is still adsorbed inside the membrane, i.e., an existence of a transient time dependent stage, until a saturation level in the membrane is achieved. Therefore, for small vaues of t, as long as the contribution of the second term of equation (7) is significant, the flow out of the membrane is considered to be in the transient stage.

CRITICAL CONSTANTS

Diffusion based industrial applications and laboratory experiments need critical criteria to separate the transient-state from the steady-state stages. Other critical constants such as minimum allowable (or detectable) diffused mass, are described in the introduction. As the diffusing mass, $m(t)$, in equation (7) is a continuous function, it is difficult to determine a reference point in this function for the above critical constants. However, there is a way to define precisely such a reference point in the $m(t)$ function [equation (7)].

Critical time

Equation (7) has the following asymptotic line:

$$m_L(t) = \frac{Sh}{1+Sh}(t-t_c) \tag{8}$$

where t_c is the intercept point of the asymptote line with the time axis (Fig. 1).

$$t_c = 2(1+Sh)\sum_{n=1}^{\infty} \frac{\sin \lambda_n}{\lambda_n^3 + \lambda_n Sh \sin^2 \lambda_n}. \tag{9}$$

The time t_c is uniquely determined by equations (6) and (9). Therefore, it is convenient to relate other diffusion constants either to t_c or $m_c = m(t_c)$ [equation (7)], the critical diffused mass.

The critical time t_c depends only on the Sherwood number, Sh [equation (9)]. In the limit values of Sh, the t_c range is derived from equations (6) and (9):

$$\tfrac{1}{6} < t_c < \tfrac{1}{2}. \tag{10}$$

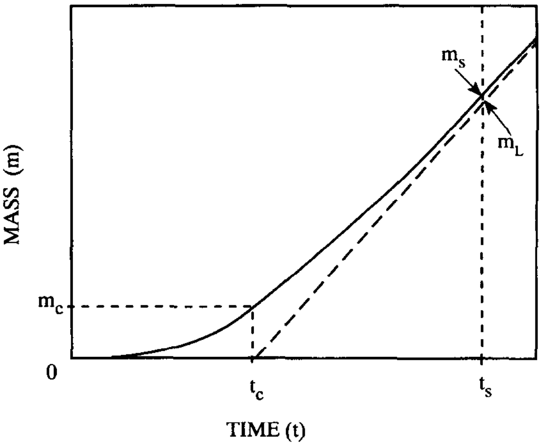

Fig. 1. Typical diffused mass–time curve. Definitions of critical values t_c, m_c, m_L and t_s at a start-time of a steady-state mass flux.

The extreme value, $t_c = 1/6$, is obtained at high values of Sh ($Sh \to \infty$). As $Sh \to 0$, $t_c = 1/2$. As $Sh \to \infty$, the concentration $C(1) \to 0$ [equation (4)]. This special case is discussed in ref. [14] which resulted in the same value of $t_c = 1/6$, as in equation (10) for $Sh \to \infty$. A graphical presentation of t_c [equations (6) and (9)] for the whole range of Sh is shown in Fig. 2. This figure shows that there are three mass conductivity zones; (i) An "isolative zone" in which the ambient inhibits mass transfer out of the membrane. It exists at $Sh < 0.03$, and $t_c \approx 1/2$, independent of Sh. (ii) At the other end, when $Sh > 30$, the boundary conditions accelerate mass transfer and $t_c \approx 1/6$, regardless of Sh values. This zone is defined as a "conductive zone", meaning that the ambient allows convection of all diffusants that reach the boundary. (iii) The intermediate or "mixed zone", at the range of $0.03 \leqslant Sh \leqslant 30$, is characterized by Sh dependent t_c, as shown in equations (6) and (9).

Critical mass m_c

Once t_c is analytically determined, the respective mass m_c is calculated by substituting t_c values in equation (7), i.e., $m_c = m(t_c)$. A plot of m_c vs. Sh is shown in Fig. 3. In the isolative zone, $m_c \approx 0.039$ for $Sh > 30$, regardless of Sh values. In the mixed zone, $0.03 \leqslant Sh \leqslant 30$, m_c is Sh-dependent according to equations (6) and (7) and has a maximum value of $m_{c\max} = 0.042$ at $Sh = 7.3$.

Definition of t_s, *the start-time of a steady-state mass flux*

As has already been mentioned, diffusion is a continuous process and is an asymptotic function [equation (7)]. In such problems arbitrary definition is needed to decide when a steady-state starts practically. For example, the entrance length of a flow in a duct is arbitrarily defined as a distance at which the centerline velocity is 0.98–0.99 of the fully developed value [12]. Similarly, the velocity field boundary layer thickness of a fluid along a flat plate, is arbitrarily defined as a

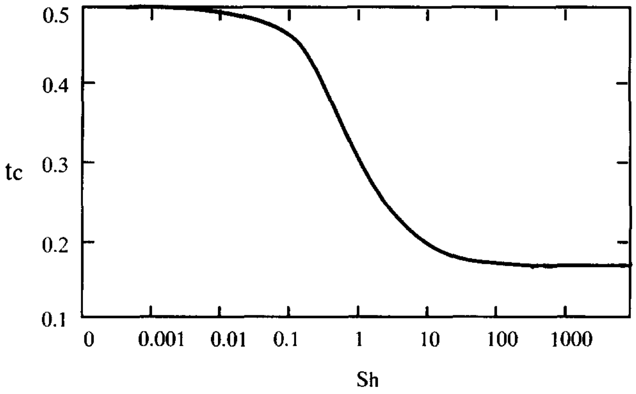

Fig. 2. Changes of t_c with Sherwood number, *Sh* ($1/6 < t_c < 1/2$).

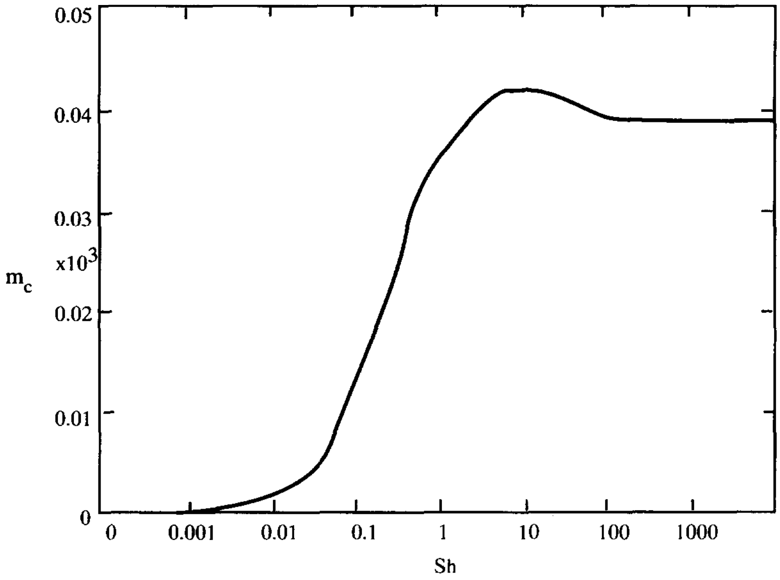

Fig. 3. Critical mass $m_c = m(t_c)$ as a function of *Sh* ($0 < m_c < 0.039$ with $m_{c\max} = 0.042$ at $Sh = 7.3$).

distance from the plate surface for which the velocity of the fluid reaches 0.99 of the free stream velocity [13].

An equivalent definition of the start-time of a steady-state diffusion rate, is the time, t_s, at which

$$\frac{m_L(t_s)}{m(t_s)} = K, \quad K < 1. \tag{11}$$

The constant K in equation (11) represents the closeness extent of the total diffusion mass $m(t)$ [equation (7)] to the asymptotic mass m_L [equation (8)] at time t_s. The constant K may be taken as 0.99, the same as in boundary layer problems, or other values (<1), which satisfy specific application needs. For example, Figs. 4 and 5 graphically show equation (11) for t_s with $K = 0.9$ and equation (7) $m_s = m_s(t_s)$ vs. Sherwood number, *Sh*, respectively. Both the time t_s and the mass m_s have similar functions of *Sh* as t_c and m_c (Figs. 2 and 3). These functions have the same three zones: isolative, convective and mixed zones. Steady-state start time t_s (defined for $K = 0.9$ [equation (11)] range is $0.281 \leqslant t_s \leqslant 0.47$, and the respective mass range $m_s = m(t_s)$ is $0 \leqslant m_s \leqslant 0.127$, with $m_{s\max} = 0.132$ at $Sh = 10$ (Table 1).

Table 1 shows the relationship between the constant t_s and m_s vs. t_c, m_c, m_c/m_s and t_c/t_s for three cases of Sherwood numbers.

Non-monotonic behavior of the critical mass constants

Boundary conditions, represented by the Sherwood number, *Sh*, affect critical masses m_c and m_s non-monotonically, as shown in Figs. 3 and 5. Their peak values are within $6 < Sh < 15$. A physical interpretation, based on the boundary condition equation (4), is suggested for this peak.

The mass flux diffuses from a membrane is proportional to the concentration of the diffused mass at the membrane surface, $C(1, t)$, and to the Sherwood

Table 1. Dimensionless constant values of mass diffusion

Sh	t_c	m_c	t_s^*	m_s	m_c/m_s	t_c/t_s
< 0.02	1/2	0	0.947	0	0.302	0.528
> 20	1/6	0.039	0.281	0.127	0.308	0.593
max ($Sh=$)	—	0.042 (7.3)	—	0.132 (10)	0.365 (1.5)	0.652 (1.5)

*t_s is the time at which the steady-state starts. It is arbitrarily defined as the time in which $m_L(t_s)/m(t_s) = 0.9$, where $m_L(t) = Sh(t-t_c)/(1+Sh)$ is the asymptotic line of the $m(t)$ curve equation. If the definition of t_s is different, then the last four columns of Table 1 must be fitted accordingly.

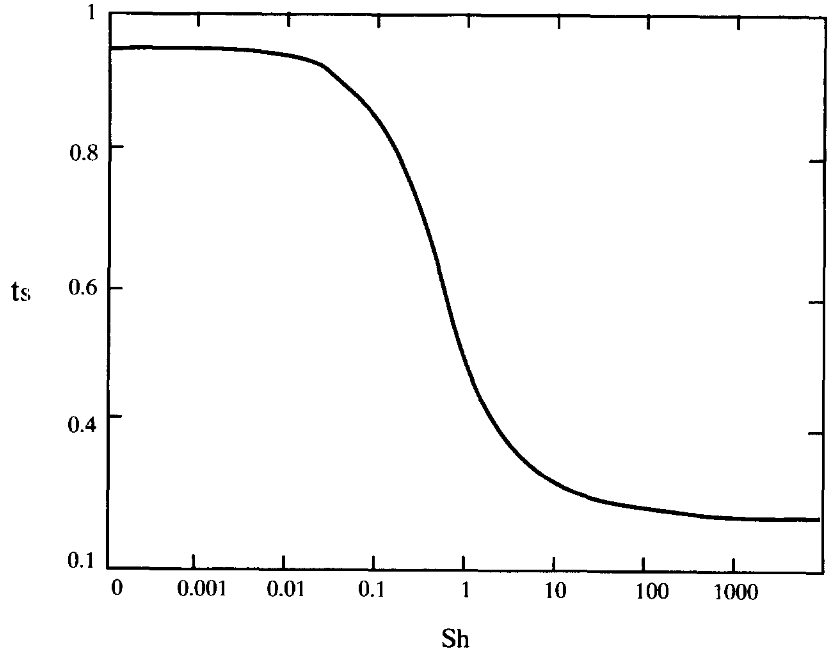

Fig. 4. Start-time of the steady-state mass flux, t_s, as a function of Sh for $m_L/m_s = 0.9$ ($0.281 < t_s < 0.947$).

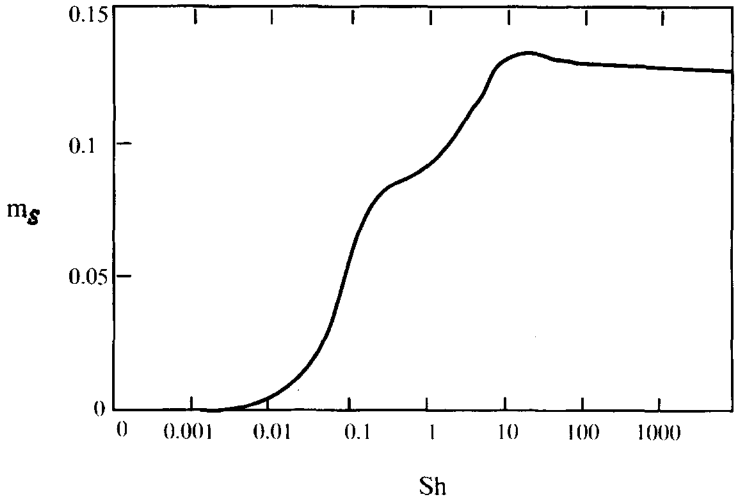

Fig. 5. Diffused mass, $m_s(Sh)$ ($=m(t_s, Sh)$) curve for $m_L/m_s = 0.9$ ($0 < m_s < 0.127$, with $m_{smax} = 0.132$ at $Sh = 11$).

number, Sh, which represents the rate at which the ambient absorbs the diffused mass relative to the mass velocity within the membrane. At low Sh (<6), the ambient inhibits absorption of the diffused mass (low changes of $C(1,t)$), which results in its accumulation at the membrane surface ($C(1,t) = 0(1)$). In this case, $m(t)$ increases with Sh, including $m(t_c)$ and $m(t_s)$ [equation (4)]. At high Sh (>15), $C(1,t)$ decreases with increasing Sh, since the ambient sucks the diffused mass as fast as it exits the membrane. As $Sh \rightarrow \infty$, $C(1,t) \rightarrow 0$, m_c and m_s reach finite values shown in Table 1. At a certain combination of $c(1,t)$ and Sh (at $Sh = 3$ for $m_{c\max}$ and $Sh = 11$ for $m_{s\max}$), the critical constants reach their maximum values.

Illustrative example

The following example shows the applicability of this study in designing and conducting experiments of diffusion-based products.

Suppose that maximum protection from hazardous material leakage is required. For any value of Sh, say $Sh > 20$ (good ventilation), the following equations for the critical points, t_c, m_c and t_s, m_s can be derived from Table 1:

$$t'_c = \frac{L^2}{6D}; \quad t'_s = \frac{0.281L^2}{D};$$

$$m'_c = 0.039m_0; \quad m'_s = 0.127m_0. \qquad (12)$$

Equations (12) show that maximum protection is achieved where one selects a membrane as thick as possible and of material which minimizes m_0 and D. Given values of the actual diffusion parameters m_0 and D, critical times and masses, may be calculated by equations (12).

Experimental determination of diffusion parameters: D, m_0 and Sh

Diffusion experiments provide N data points of permeated mass, M, or mass rate, $\dot{M}$, as a function of time, t. A fit procedure of equation (7) and its derivative may be applied to the experimental data yielding the required set of diffusion parameters D, m_0 and Sh, which minimizes:

$$\chi^2 = \Sigma[M_i - m(t_i, D, m_0, Sh)]^2;$$

$$\chi_1^2 = \Sigma[\dot{M}_i - \dot{m}(t_i, D, m_0, Sh)]^2, i = 1, 2 \ldots N \qquad (13)$$

for permeated mass, χ^2, and permeated mass rate, χ_1^2.

In the following numerical examples, actual values of the diffusion parameters, m_0, D and Sh, are obtained. These examples demonstrate various aspects of the theoretical contribution to better understanding of the meaning of experimental data.

Example 1: *breakthrough time*

A fit procedure of time derivative of equation (7) was applied to experimental data of ref. [5]. The data is of a permeation resistance of flexed metallized low density polyethylene to dichloromethane (film A-1 flexed). Several points which were taken from this graph are presented in Fig. 6 as experimental data. The curve in Fig. 6 is the time derivative of equation (7) with $D = 0.333 \times 10^{-7}$ cm^2 s^{-1}, $m_0 = 1.14$ g cm^{-3} and $Sh = 5$.

Reference [5] has defined a breakthrough time as the time at which a minimum permeation rate of 15.8 μg cm^2-min^{-1} was detected using Miran 80A Infrared Spectrometer. With the above values of D, m_0 and Sh, it is obtained, from Fig. 6, that the breakthrough time (defined in Fig. 2) is:

$$t_b = 0.11t_c. \qquad (14)$$

Equation (14) provides an idea of the detectable breakthrough time of a diffusant through a membrane, in terms of characteristic constant of a permeation process, based on the detection capability of the experimental instrumentation.

Example 2: *lag time* (*critical time*, t$_c$)

Mass permeation data was reported by ref. [3] and is represented by full squares in Fig. 7. These data are of Toluene vapor, at 40 ppm concentration and at water activity of 86%, permeated through a two-sided PVDC coated oriented polypropylene film. The curve in Fig. 7 is calculated from equation (7) with $m_0 = 0.0105$ g cm^{-3}, $D = 7.06 \times 10^{-12}$ cm^2 s^{-1}, and $Sh = 16.6$. Using these constants, the value of the calculated time is $t'_c = 184$ h, while its experimental value, derived by ref. [3], is 55 h. This difference suggests that the experimentally determined lag time was based on data measured in the transient rather than steady-state stage of the permeation process. Theoretically, on the other hand, it is possible to calculate the asymptotic line of the permeation curve (Fig. 7), and thereby calculate the exact lag time, t'_c, which is the intercept point of the asymptotic line with the time axis.

Example 3: *diffusion mechanism*

Reference [2] studied the diffusion through dry and preswelled polymer films. They concluded that preswelling increases diffusion rate, shortens the induction time and leads to linear plots. The linearity of preswelled films from a simple diffusion process, while dry films exhibit nonlinearity due to their complex diffusion process.

The present approach to the diffusion process can account for all of the ref. [2] observations in one diffusion mechanism, expressed quantitatively by equation (7).

The theoretical approach of the diffusion mechanism deals with the two sub-processes simultaneously: adsorption of a part of the diffusant by the membrane, while the other part of it passes through the membrane out to the ambient (transient

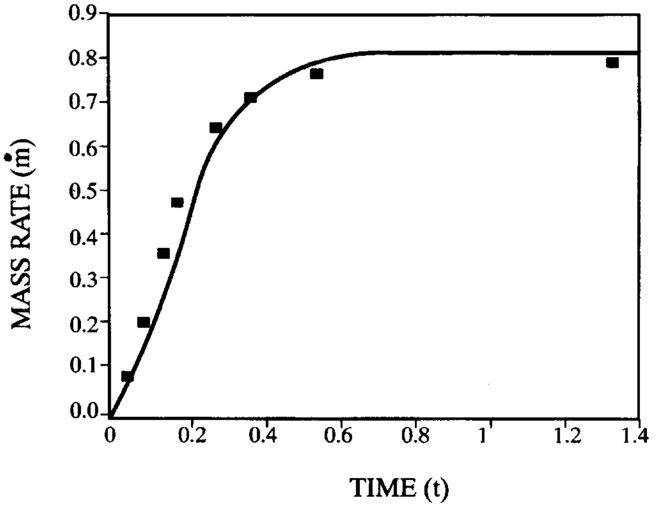

Fig. 6. Mass permeation rate with diffusion time. The full squares were extracted from ref. [5] (film A-1 flexed). The curve was calculated from equation (7) with $D = 0.333 \times 10^{-7}$ cm^2 s^{-1}, $m_0 = 1.4$ g cm^{-3} and $Sh = 5$.

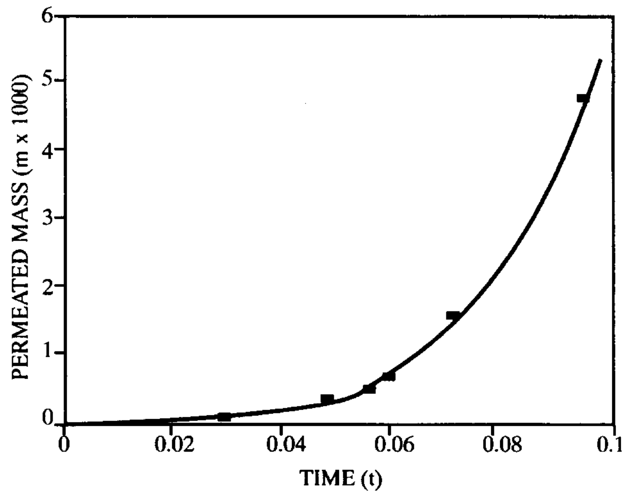

Fig. 7. Permeated mass time $m(t)$ curve. A fit of equation (7) to ref. [3] data (full squares) with $D = 7.06$ 10^{-12} cm^2 s^{-1}, $m_0 = 0.0105$ g cm^{-3} and $Sh = 16.6$.

state). When the membrane reaches equilibrium, a steady-state permeation is reached (a linear curve).

On this ground the two curves of ref. [2] of ethyl-laurate diffusion through preswelled polypropylene film (a) and dry film (b) could be united into one graph, since it is a one diffusion process, which starts with transient-state and ends with steady-state. Figure 8 shows ref. [2] data points for dry and preswelled films, and the theoretical curve calculated from equation (7), where the maximum percentage of ethyl-laurate in the PP films is $m_0 = 67.7$, the diffusion coefficient of the whole process is $D = 2.66 \times 10^{-12}$ cm^2 s^{-1} and $Sh = 0.59$. The group of data on the right side of Fig. 8, is of preswelled PP film in ethyl-laurate for 24 days [2]. Since no record was reported on the diffused mass percentage during preswelling period of time, a constant amount of mass percentage ($\Delta m = 27.8$) was added to each of the upper seven points in Fig. 8, in order to fit it to a single curve.

Effect of measurement errors on diffusion parameters and critical constants

Given a set of experimental data, $M(t)$, its appropriate diffusion parameters, D, m_0 and Sh, can be evaluated as previously discussed. The minimum number of data required for first estimation of the diffusion parameters, is three points of M_i, t_i $(i = 1, 2, 3)$. Each additional experimental point upgrades the parameter

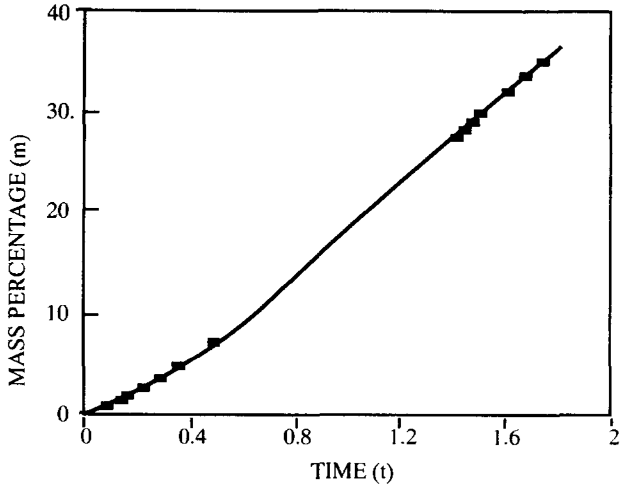

Fig. 8. A fit of equation (7) (with $D = 2.66 \times 10^{-12}$ cm^2 s^{-1}, $m_0 = 67.7$ g cm^{-3} and $Sh = 0.59$) to the data of ref. [2] for dry and preswelled polypropylene films (lower and upper squares, respectively).

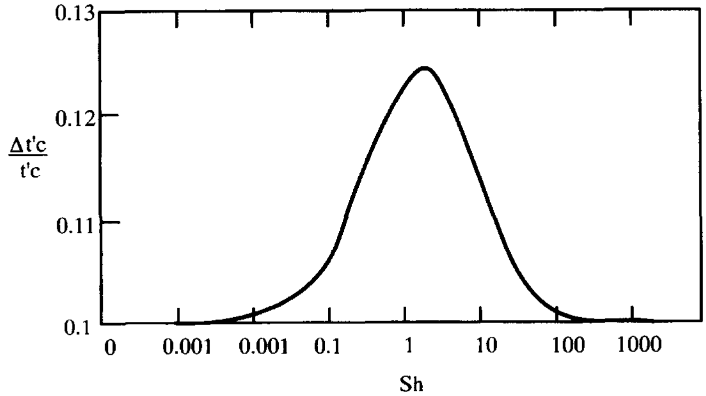

Fig. 9. Relative deviation of the critical time $\Delta t'_c/t'_c$ variation with Sh, for $\Delta Sh/Sh = \Delta D/D = \Delta m_0/m_0 = 0.1$.

values. Final values of the parameters are obtained using all available data at the end of the experiments. These changes affect the critical constants according to the following equations derived from equations (7) and (9):

$$\frac{\Delta t'_c}{t'_c} \cong \frac{\Delta t_c}{t_c} + \frac{\Delta D}{D}; \quad \frac{\Delta m'_c}{m'_c} \cong \frac{\Delta m_c}{m_c} + \frac{\Delta m_0}{m_0}. \tag{15}$$

Each term in equations (15) is an absolute value of a relative deviation. The primes indicate dimensional variables. Plots of $\Delta t'_c/t'_c(Sh)$ and $\Delta m'_c/m'_c(Sh)$ are shown in Figs. 9 and 10, with absolute relative deviations $\Delta Sh/Sh = \Delta D/D = \Delta m_0/m_0 = 0.1$. In these figures, relative deviations of the critical constants are of the order of the parameter deviations.

Minimum errors in evaluating the critical constants t'_c and m'_c, are achieved in highly convective boundary conditions ($Sh > 100$).

Deviations in a start point of the steady-state mass flux, may be obtained from the following equations derived from equations (7), (8) and (11)

$$\frac{\Delta m'_s}{m'_s} \cong \frac{\Delta m_s}{m_s} + \frac{\Delta m_0}{m_0}; \quad \frac{\Delta t'_s}{t'_s} \cong \frac{\Delta t_s}{t_s} + \frac{\Delta D}{D}. \tag{16}$$

Similar to equations (15), each term in equations (16) represents an absolute value, and the primes indicate dimensional variables. Graphic presentation of equations (16) for $K = 0.9$ [equation (11)], is very close to Figs. 9 and 10.

DISCUSSION

Mass (or heat) transfer through a membrane begins with a transient-state, in which part of the diffused mass is being absorbed into the membrane, and another part permeates through the membrane out to the ambient. With time, the membrane reaches equilibrium and the mass flux reaches a steady-state.

For such a process it is useful to define a critical point, which will serve as a reference point between the transient and steady-state stages. The required point is being uniquely defined as the intercept point

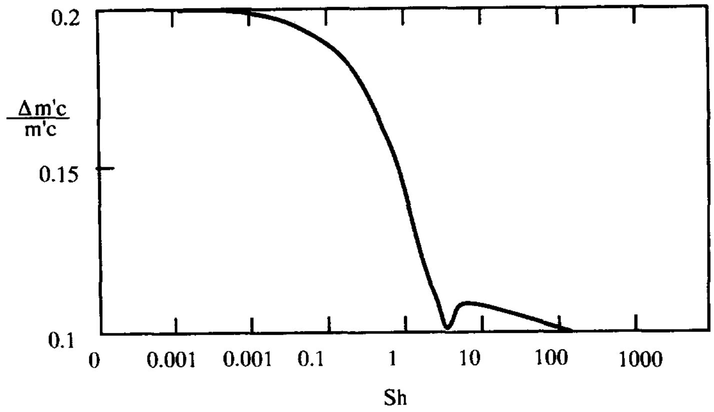

Fig. 10. Relative deviation of the dimensional critical mass $\Delta m_c'/m_c'$ vs. Sh for $\Delta Sh/Sh = \Delta m_0/m_0 = \Delta D/D = 0.1$.

of the asymptotic line of $m(t)$ with the time axis (t_c, m_c (Fig. 1)). The critical point, t_s, m_s which related to the reference point t_c, m_c, is also defined in this study. The boundary conditions effect on the critical constants of diffusion, at the external side of the membrane, were also discussed in this work.

Analytical function of $t_c(Sh)$ was derived from where it was found that $1/6 < t_c < 1/2$, as shown in Fig. 2. The total mass, m_c, which exits the membrane up to time t_c reveals that m_c is a function of Sh with peak value of 0.0418 at $Sh = 7.3$. Figures 2 and 3 clearly demonstrate the difference between the following three types of boundary conditions:

1. Convective Boundary Conditions ($Sh > 20$): In this range, the critical constants are practically Sh-independent. The surroundings are able to absorb the diffused mass as fast as the membrane can transfer it. Alternatively, the mass concentration at the external surface of the membrane, $C(1, t)$, tends to zero regardless of the Sh value. Therefore, the boundary conditions have a negligible effect on the critical constants.
2. Inhibitive Boundary Conditions ($Sh < 0.02$): In this range, the membrane is able to transfer the diffused mass faster than the environment is able to absorb it. Any amount of diffused mass, which is being transferred to the environment, will accumulate at the external surface of the membrane independently of the Sherwood number, which means a negligible effect of the boundary conditions on the critical constants. Therefore, this condition is also characterized by critical constants, which are independent of Sh.
3. Mixed Boundary Conditions ($0.02 < Sh < 20$): The critical constants in this region are strongly Sh-dependent. Moreover, m_c in Fig. 3 has a peak value in this range, although t_c monotonically decreases with Sh, as seen in Fig. 2. The non-monotonic behavior of m_c is due to the opposite effects of $C(1, t)$ and Sh [equation (4)].

Based on the exactly defined critical point, t_c, m_c, practical critical points such as start time and initial mass, t_s, m_s, of a steady-state mass flux were defined and related to t_c, m_c. Figures 4 and 5 depict graphs of t_s, m_s, similar to those of t_c, m_c. The start time of a steady-state mass flux, t_s, changes with Sh more than three fold. This implies, for example, that in applications of protecting people and products from contaminants and hazardous materials, inhibitive boundary conditions are required in order to maximize t_s and minimize m_s (Figs. 4 and 5).

A fit procedure of $m(t)$ [equation (7)] to three existing experimental data sets is carried out. Specific values of the diffusion parameters, D, m_0 and Sh, for each data set was obtained. Additional results of the fit procedure are:

1. Empirical detectable breakthrough time, t_b, of a diffusant through a membrane is related to t_c, $t_b = 0(0.1t_c)$. This specific relationship provides a first guess of t_b for diffusion based design of products and experiments.
2. Empirical determination of t_c may wrongly be based on transient rather than steady-state data, since it may take an unknown amount of time to achieve a steady-state mass flux. However, applying equations (7) to the experimental data yields diffusion parameters by which t_c is exactly calculated and therefore m_c, t_s and m_s may be calculated accordingly from equation (9).

Measurement errors cause deviations in the calculated diffusion parameters and critical constants. Relationships, which were developed between the deviations, show that minimum errors in evaluating the critical constants (Figs. 9 and 10) are achieved in convective boundary conditions ($Sh > 100$). A possible explanation for this effect is that at high Sherwood numbers the exit mass flux is governed by the diffusion process through the membrane only, and changes in the boundary conditions have a negligible effect on the process critical constants.

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