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THEORY OF TRANSIENT PERMEATION THROUGH REACTIVE BARRIER FILMS I. STEADY STATE THEORY FOR HOMOGENEOUS PASSIVE AND REACTIVE MEDIA

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Polymeric barrier materials play an increasingly significant role in modern package engineering. Multilayer and composite structures are designed for rigid and flexible packaging to reduce permeation of undesirable species into and out of food, beverage, pharmaceutical, microelectronic products, and also for automotive applications. Utilizing chemical reaction to bind permeating oxygen, lower its transmission rate through packaging films and reduce oxygen amount present in a package is seemed as an attractive alternative to passive barrier solutions for extending shelf life of oxygen-sensitive products. A novel theory of transient permeation through homogeneous and multilayer reactive polymeric structures is developed in the article. Part I includes analytical solutions for the steady state model of permeation through a reactive film with immobile catalytic scavenger dispersed within the layer. The condition for zero effective transmission rate through homogeneous reactive layer is derived. Part II will introduce transient permeation theory for reactive films with non-catalytic scavenging action. Analysis of transient barrier performance as a function of material transport properties and scavenger reactivity will be presented in Part III.

Keywords: package engineering, active barrier, oxygen, scavenger, transient permeation, zero flux criterion, headspace oxygen

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TERMINOLOGY

Absorber: any material able to physically absorb (trap) permeating solute.

Active Barrier: membrane material containing activated scavenger able to irreversibly bind or convert permeating solute into neutral species.

Consumable Scavenger: scavenger with finite reactive capacity: once its capacity is exhausted by reacting with stoichiometric amount of solute, it is no longer active.

Diffusivity: kinetic diffusion coefficient of a particular solute in a particular material in $[\text{m}^2 \text{s}^{-1}]$.

Effective Flux: flux across the downstream (solute exit) boundary of a membrane; represents effective rate of permeation across the membrane.

Effective Transmission Rate (also **Permeance**): transmission rate of a solute across the downstream boundary of a membrane. For passive barriers in steady state, TR_{eff} is the same across any plane of the membrane normal to its thickness. For active barriers, TR_{eff} cannot be strictly defined because it depends on absolute values of solute partial pressures at the boundaries rather than solute pressure gradient Δp .

Exhaustion Lag Time: time during which the complete exhaustion of scavenger reactive capacity by permeating solute is achieved within a reactive layer after scavenger activation (assumed to be instantaneous). In this case the steady state flux across the membrane is achieved only after the exhaustion lag time. Exhaustion lag time is longer than the reference lag time for active barrier with consumable scavenger unless the reaction rate of scavenger with solute $K = \infty$: then both lag times are equal. Reactive capacity of renewable scavenger is infinite by definition, thus it is never exhausted: $t_{LE} = \infty$.

Flux (material): rate of mass transport of specified component i (solute) across unit area of arbitrary membrane plane normal to membrane thickness direction in $[\text{mol m}^{-2} \text{s}^{-1}]$, for gases it is commonly expressed in $[\text{m}^3(\text{STP})\text{m}^{-2} \text{s}^{-1}]$.

Induction Period: duration of the scavenger activation process throughout the reactive film by some external source (e.g., UV light or moisture). Some scavengers are immediately active upon manufacture; thus they have zero induction period.

Lag Time: when a permeating species is suddenly introduced on one side of the membrane, which is free of dissolved solute, steady state flux across the membrane is asymptotically achieved after some delay due to the finite rate of solute diffusion in membrane material.

The intercept of asymptotic permeant concentration growth downstream with time axis (zero concentration) is called the lag time, which is equal to $L^2/6D$ for homogeneous passive barriers. It represents an approximation of nonlinear transient permeation dynamics by two linear functions: zero flux across the membrane during the lag time and asymptotically steady state flux after it.

Passive Barrier: any material(s) made into a membrane that reduces solute flux across it in the presence of solute concentration gradient on the opposite sides of the membrane but does not chemically react with nor physically absorb the permeating solute.

Permeability: steady state transmission rate of a specific solute across a uniform membrane made from homogeneous passive barrier material, normalized to membrane thickness. Permeability is also equal to the product of diffusivity and solubility coefficients: $P = TR_{SS}L = DS$ in $[\text{mol m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}]$ or $[\text{m}^3(\text{STP})\text{m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}]$ for gases.

Reference Lag Time: lag time t_L for passive barriers including multilayer structures due to finite rate of solute diffusion across membrane material(s). It can be defined the same way for active barriers with renewable and consumable scavengers.

Renewable Scavenger: scavenger with infinite reactive capacity able to bind unlimited amount of solute without losing its efficiency. Catalysts for olefin polymerization converting unsaturated hydrocarbons into different species (polymers) are a good approximation of RS for these hydrocarbons.

Scavenger: chemically active species or functional groups incorporated in a passive barrier material and able to irreversibly bind (consume) permeating solute immediately on contact with it or upon activation by external source.

Solubility: thermodynamic equilibrium solubility coefficient of a particular solute in a particular material normalized to unit external partial pressure of the solute in $[\text{mol m}^{-3} \text{ Pa}^{-1}]$ or $[\text{m}^3(\text{STP})\text{m}^{-3} \text{ Pa}^{-1}]$ for gases.

Solute: any gas, liquid, or vapor with nonzero equilibrium solubility in a particular material at chosen temperature and external pressure.

Transient Permeation: dynamic process of establishing steady state solute concentration and flux profiles across a reactive film during scavenger capacity exhaustion time.

Transient Transmission Rate: effective transmission rate (permeance) as a function of time: it is a nonlinear function of time for films containing consumable scavengers until steady state transmission rate is achieved upon scavenger capacity exhaustion (true steady state is obtained only when fixed boundary conditions are maintained).

Transmission Rate: material flux across a membrane normalized to external pressure gradient Δp of permeating solute in $[\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}]$ or $[\text{m}^3(\text{STP})\text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}]$ for gases. *TR* can be strictly defined only for passive barriers where the permeating solute is conserved during transport.

1. INTRODUCTION

Plastics widely replace metal and glass containers in food and beverage packaging and also find a variety of new uses in pharmaceutical, microelectronic, and automotive industries. The most important property of metals and glass for packaging applications is that they are thought to be nearly absolute barriers to gas and vapor permeation. Although polymeric materials provide numerous documented advantages over metal and glass, they all allow the permeation of gases, solvents, and vapors to some degree. Overcoming the permeability limitations of polymers is a major goal of barrier material development in modern package engineering. Barrier materials find a wide acceptance in the packaging industry for their ability to restrict permeation of undesirable species like oxygen into the package or loss of desirable species like carbon dioxide and water vapor out of the package, and thus extend product shelf life. Multilayer laminates and composite structures are designed to combine useful properties of several materials and to reduce permeation rates even more compared to homogeneous barriers.

Barrier materials can be classified as either passive or active. Although any dense material (as opposed to highly porous structures) may serve as a passive barrier to solute permeation, the general understanding in the field is that material is called a barrier for specified solute if its permeability coefficient $P \leq 1$ [$\text{cc}(\text{STP})\text{mil}/(100 \text{ in}^2 \text{ day atm})$] = 4.5×10^{-20} [$\text{m}^3(\text{STP})\text{m m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$] for structural polymers and $P \leq 100$ [$\text{cc}(\text{STP})\text{mil}/(100 \text{ in}^2 \text{ day atm})$] for elastomers at specified temperature and relative humidity. This article shall use the term (passive) *barrier material* to denote any homogeneous dense polymeric structure without such quantitative limitations. Passive barrier polymers like EVOH, PVDC, PET and other polyesters, aliphatic polyamides, etc. have been known for a long time. Newer high barrier materials like partially aromatic polyamides and composite polymeric structures with inorganic nanoclays (nanocomposites) are actively studied and commercialized. Passive barriers work by restricting solute permeation due to limited solubility of the solute in a barrier material and lower diffusivity of the solute in it compared to carrier media (vacuum for gases and vapors, solute itself for liquids).

Active barrier materials work by scavenging the permeating solute during diffusive transport: either by chemically binding it or by chemically converting it into other (neutral) species. Reactive capacity of active barriers to *permanent gases* and *water vapor* is inherently limited. The reason is that the scavenger is consumed in chemical reaction binding the solute, whereas catalytic reactions converting permanent gases and water into other substances without consuming the catalyst cannot proceed without continuous energy input. It is also noted that the conditions for such reactions to proceed at meaningful rates are far from ambient. When the reactive capacity of active barrier is exhausted by reaction the active barrier turns into a passive one. Reactive barrier films (mostly incorporating oxygen scavengers) recently started to attract an increasing attention due to their ability to reduce oxygen transmission rates to nearly zero during the *exhaustion lag time* when the scavenger is still active, and their claimed ability to reduce headspace oxygen by generating oxygen flux from the package into the film. Here the headspace oxygen refers to oxygen trapped inside the package after capping because the product filling level is usually below the full volume of the package: this oxygen is often deleterious to shelf life of the products sensitive to oxidation (Figure 1). There is always some oxygen dissolved in the product in equilibrium with headspace oxygen, though its effect on permeation through its partial pressure is the same as that of headspace oxygen provided its equilibrium concentration is below its solubility limit in the (liquid) product.

In package engineering curricula [1–2] and in general textbook treatment of reactive-diffusive transport [3–6] in solid media there exist only separate elements of a comprehensive permeation theory. The main reason for that is a lack of analytical solutions for the equations describing reaction-diffusion dynamics in most but the simplest special cases. The fundamental work of Crank [3] describes many solved problems in purely diffusive transport but few methods are available to solve problems of reactive-diffusive transport. These methods are unable to solve industrially important problems of transport through reactive media with finite reactive capacity; thus, numerical simulations are the only recourse to study specific cases. Pioneering work of Yang et al. [7] introduced a method to analytically treat reactive-diffusive transport in case of fast reactions somewhat similar to self-propagating combustion waves, but the assumptions made in it effectively reduced transient permeation effects to zero.

From the authors' perspective, the existing lack of understanding of factors affecting the transient performance of active barriers leads to difficulty in correctly evaluating shelf life gains and determining

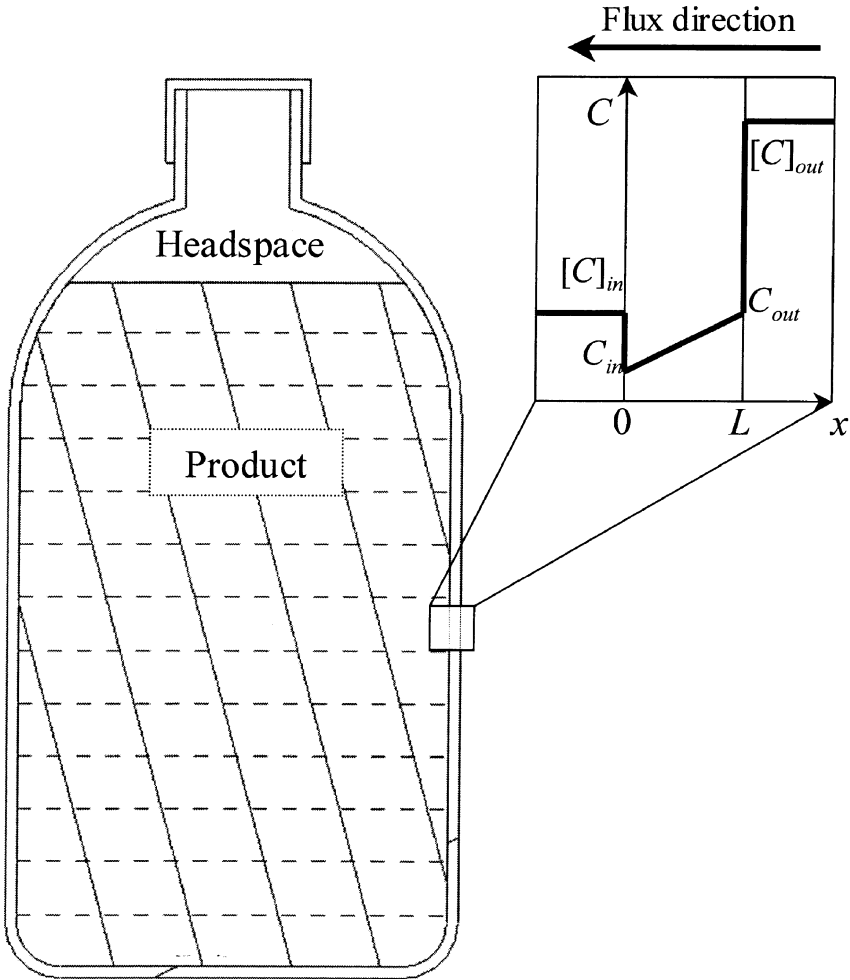


FIGURE 1 Plastic package schematic: notation, coordinate system, and flux direction are preserved throughout the article.

optimal material structures in active packaging design. In this work a theoretical treatment of reactive methods of reducing the effective transmission rates through the barrier is proposed. It is believed that this work will be a useful supplement in teaching modern courses on package engineering and will also help scientists and engineers who desire practical analytical solutions for systems with reactive-diffusive transport in solids.

Permeation of a solute through a solid film containing dispersed immobile reactive species able to chemically bind the solute is inherently a dynamic process accompanied by consumption of the reactive species (thereafter called non-catalytic scavenger), thus the steady state transmission rate through the film is only achieved when the scavenger reactive capacity is exhausted [6–7]. Although the exhaustion lag time to reach the steady state encompasses a transient process for which an exact analytical solution cannot be obtained in general case, it is useful to initially approximate that period as a steady state permeation process with fixed boundary conditions and catalytic scavenger. That would allow the derivation of analytical solutions for transmission rates through different multilayer film structures, introduce zero flux criterion, estimate the initial rate of the solute reduction in the package headspace, and also establish *conditions for realizing such effects in practical applications*. However, the reactive capacity of any scavenger is always finite, thus the analysis of cumulative ingress through the actual films requires estimation of the scavenger lifetime if the results are to be applicable to real packaging structures.

In Parts II and III, the catalytic scavenger assumption is relaxed, and analytical results are presented for the scavenger exhaustion lag time and the transient transmission rate using the developed steady-unsteady solution matching method for the narrow reaction wavefront approximation and dynamic reactive-passive interface approach. These results present a practical value to a packaging engineer wishing to design optimized reactive barrier structures, to minimize the permeant ingress into the package and to extend the useful life of the scavenger.

2. GOVERNING EQUATIONS AND MODEL ASSUMPTIONS

Diffusion of gaseous permeating species (solute concentration C inside the polymer) through an infinite homogeneous polymer membrane with thickness L and its reaction with immobile reactive species (concentration of active sites R) uniformly dispersed within the polymer are described by the following one-dimensional dynamic material balance equations, neglecting accumulation of reaction products in the matrix and matrix polymer property changes due to reaction:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \mu KRC \quad (2.1)$$

$$\frac{\partial R}{\partial t} = -KRC \quad (2.2)$$

for $C = C(x, t)$ and $R = R(x, t)$, assuming the irreversible reaction of the first order by both species with reaction rate constant $K = K(T)$ and the stoichiometric coefficient μ . Most currently available commercial oxygen scavenging systems involve irreversible oxidation reactions, whereas the first order is commonly assumed for diffusion-controlled reactions. Here D is the concentration-independent diffusivity of the solute in the matrix polymer, and it is assumed that D is not affected by the presence of the scavenger or by products of the reaction. It is also assumed that the scavenger is fully activated and at 100% of its capacity by the time $t = 0$, thus R is affected only by its reaction with C . The triggering mechanism and the effect of the induction period of the scavenger on transient transmission rate are out of the scope of this work. The induction period is the duration of the scavenger activation process throughout the film by some external source, and it should not be confused with the lag time that refers to the time of establishing a steady state diffusive transport across a (passive) membrane.

The scavenger and the products of its reaction with the solute are assumed to be immobile, thus there is no diffusion in the system other than solute diffusion. This case corresponds to most currently studied scavenging systems in polymers. As has been shown by Cussler et al. [7–8], only the reaction of solute with immobile scavenging species will enhance transient barrier properties, but reaction with mobile species will not (the case of facilitated diffusion [8]). The enhancement appears as an increased lag time before steady state is reached upon scavenger capacity exhaustion. The steady state refers to the constant solute flux or transmission rate (dynamic property) across any membrane cross-section normal to the external solute concentration gradient. During the lag time the effective transmission rate through the film will evolve exhibiting *transient behavior*. That time is called the *exhaustion lag time* t_{LE} to distinguish it from the commonly observed *reference lag time* t_L to reach steady state permeation through passive barriers and reactive barriers with catalytic type (not consumable) scavenger. The exhaustion lag time resulting from finite reactive capacity of the scavenger may increase 3–4 orders of magnitude for some systems compared to the reference lag time, thus the transient improvement of film barrier properties can last for months and years. Understanding and controlling transient barrier properties, rather than steady state permeation and the lag times, become increasingly important for practical applications. The focus of this work is on transient barrier properties of the reactive films as most relevant for the packaging industry. Analysis of the rate of permeant ingress into the package *during the exhaustion lag time* is one of the current objectives: further work will focus on optimization of structural design in

terms of minimization of cumulative permeant ingress during an application-driven timeframe.

The constant boundary conditions *outside the film* corresponding to gaseous permeant equilibrium on the film surface and resembling transmission rate testing conditions common in packaging industry are set as:

$$\text{Inside the package: } x \leq 0, \text{ permeant partial pressure } p(0) = p_{in} \quad (2.3)$$

$$\text{Outside the package: } x \geq L, \text{ permeant partial pressure } p(L) = p_{out} > p_{in} \quad (2.4)$$

The equilibrium boundary concentrations C_{in} and C_{out} of the permeant *within the film* are then found from Henry's law, assuming linear sorption isotherms for all materials:

$$\text{Inner film boundary (downstream): } x = 0, \quad C(0, t) \equiv C_{in} = Sp_{in} \quad (2.5)$$

$$\text{Outer film boundary (upstream): } x = L, \quad C(L, t) \equiv C_{out} = Sp_{out} \quad (2.6)$$

Here S is the equilibrium solubility coefficient of the particular permeant in the particular film material. Alternatively, the dimensionless partition coefficient H of the permeant in the film material may be used should we decide to utilize permeant concentration $[C]$ outside the film instead of external partial pressure p :

$$C_{in} = Sp_{in} = H[C]_{in} \quad (2.7)$$

$$C_{out} = Sp_{out} = H[C]_{out} \quad (2.8)$$

The initial conditions within the film are set as follows:

$$C(x, 0) = C_{in} + (C_{out} - C_{in}) \frac{x}{L} \quad (2.9)$$

$$R(x, 0) = R_0 \quad (2.10)$$

Here $C(x, 0)$ is an established steady state concentration profile for the homogeneous *passive* film with the same material transport properties as the reactive film (see derivation of the result in Eq. 2.9 in section 6). This profile is more complex for multilayer structures, although exact analytical solutions are available, and the two-layer film case is analyzed in Part II.

It is assumed that the scavenger is instantly activated at time $t = 0$, which is equivalent to saying that the reaction rate constant K jumps from 0 to K_A :

$$K(t) = K_A h(t) \quad (2.11)$$

where $h(t)$ is the Heaviside step function. Thus, we initially have the passive film with steady state permeation defined by boundary conditions (Eqs. 2.5 and 2.6) and then start considering the system behavior from the moment of complete scavenger activation while maintaining the same boundary conditions.

Foundation for the Choice of Initial Conditions

The choice of the initial condition (Eq. 2.9) is different from that used as a reference in the literature [3,6] on passive and active diffusive transport where it is common to write $C(x,0) = 0$. Then at $t > 0$ there is a permeant build-up inside the sealed test chamber meaning the downstream concentration $C(0,t)$ is not fixed. However, the present set of conditions is thought to be most relevant for packaging films. The reason is that the standard method of film permeability testing [9] (e.g., using MOCON oxygen sensory equipment) involves continuous removal of the species permeated through the film by a carrier gas (usually nitrogen), thus maintaining preset permeant concentration at the inner boundary. Preset zero concentration at $x = 0$ is the common choice, but any other value may be used. The relevance of this setup for packaging applications stems from the fact that barrier packaging is routinely used for oxygen-sensitive products (containing vitamins C and E, for example), thus it can be safely assumed that nearly all permeating oxygen will immediately react with the product, preventing any significant free oxygen accumulation in the package headspace and in the product. Thus, all oxygen that passed through the film and reacted with the product does not build up inside in free form, and as a result some constant (pseudo equilibrium) oxygen concentration inside the package (headspace and product) can be assumed. This pseudo equilibrium will exist provided there is a stoichiometric excess of oxygen sensitive product in the package, and the rates of oxygen diffusion into and reaction with the product are balanced by the oxygen ingress rate through the film (see Figure 1). When the oxygen consumption rate in the package is much higher than the ingress rate, the condition $C_{in} = 0$ can be assumed.

It is noted that using the initial condition (Eq. 2.9) effectively excludes the reference lag time from consideration because the steady state is already established within the passive barrier by the time $t = 0$ when the scavenger is activated. Establishing the relationship between the reference and the exhaustion lag times as a function of scavenging reaction rate and scavenger capacity is one of the subjects of this work, and it is analyzed in detail in sections 13–16 in Part II.

Catalytic Scavenger Assumption

The authors consider the following simplifying assumption to be able to reduce the system of Eqs. 2.1 and 2.2 to an analytically solvable steady state reaction-diffusion problem: the concentration of active scavenging sites R is in excess of the stoichiometric amount of oxygen present anywhere within a film, and the active site concentration available for reaction is changing slowly (not necessarily due to slow reaction rate: morphology of scavenger particles may provide sufficiently high reactivity on particle surface only, then when the surface layer reacted completely, the permeant has a chance of reacting within untapped inner layers, provided reaction products do not interfere with permeant access to active sites). This assumption is similar to the scavenger acting as a catalyst without active site depletion, where $R = \text{const}$. It is also postulated that reaction products do not affect the material properties of the film such as permeant diffusivity and solubility in it as well as its geometric dimensions, which is generally true for low scavenger loading in the film material. Then a substitution can be made:

$$k = \mu KR \quad (2.12)$$

The material balance and rewritten (Eq. 2.1) with the apparent rate constant k for the pseudo first order reaction:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC \quad (2.13)$$

3. STEADY STATE SOLUTION

This article shall initially focus on a steady state solution for Eq. 2.13 with boundary conditions (Eqs. 2.5 and 2.6), that is, consider the equation

$$\frac{\partial^2 C}{\partial x^2} = \frac{k}{D} C \quad (3.1)$$

The general solution of Eq. 3.1 is found as

$$C(x) = \beta_1 \exp\left(x\sqrt{\frac{k}{D}}\right) + \beta_2 \exp\left(-x\sqrt{\frac{k}{D}}\right) \quad (3.2)$$

where the constants β_1 and β_2 are determined from the boundary conditions. Introducing dimensionless x coordinate $\zeta = [0..1]$:

$$\zeta = \frac{x}{L} \quad (3.3)$$

the solution in Eq. 3.2 is rewritten in a more convenient form:

$$C(\xi) = \beta_1 \exp(\xi\phi) + \beta_2 \exp(-\xi\phi) \quad (3.4)$$

where ϕa is a dimensionless complex called Thiele modulus, which is a square root of the second Damkohler number Da^{II} representing the ratio of characteristic time of diffusion to characteristic time of reaction within the film:

$$\phi \equiv \sqrt{Da^{\text{II}}} = L\sqrt{\frac{k}{D}} \quad (3.5)$$

Large Thiele moduli, $\phi \gg 1$, correspond to the case of fast reactions. Although this article is not limited to fast reactions for most presented results, the exhaustion lag time analysis will be based on this assumption.

4. EFFECTIVE TRANSMISSION RATE

The material flux J_x of a species across any membrane plane $x = X$ is determined from Fick's first law of diffusion as

$$J_x = -D \frac{dC}{dx} \quad (4.1)$$

The transmission rate TR through the film plane x refers to the flux J_x normalized to the imposed external pressure difference Δp

$$\Delta p = p_{out} - p_{in} \quad (4.2)$$

The accepted practice in the literature on passive barrier films is to state a positive global TR as a system property of the film material, nature of permeant and external conditions (analogous to chemical reaction rates) because it is assumed that transport always occurs in a direction opposite to the concentration gradient as in Eq. 4.1 or to external pressure difference Δp in Eq. 4.2. In reactive films it is possible to have permeant transport from both sides of the film into the film despite the existing pressure gradient outside. To distinguish these cases we need to define *local* TR_x across the film plane $x = X$ through local flux J_x . Keeping up with current notation this article defines positive local TR_x when positive global Δp is imposed and local flux J_x is negative as

$$TR_X \equiv \frac{-J_X}{\Delta p} = \frac{D}{\Delta p} \frac{dC}{dx} \Big|_{x=X} \quad (4.3)$$

Then, reporting negative TR_X would mean that there is a case of local flux through the plane $x = X$ into the film against generally expected flow direction commanded by the external (global) pressure gradient.

For any homogeneous material it is possible to define positive permeability P as a material property [3] in terms of transmission rate normalized to membrane thickness L (as discussed in the earlier work [10]):

$$P = TR \cdot L \quad (4.4)$$

This definition of permeability is applicable only to passive homogeneous barriers that are not very thin and at permeant external pressures close to atmospheric. For passive heterogeneous barriers, P defined according to Eq. 4.4 lacks physical meaning [10], and only TR may be used to characterize permeation. Because for reactive films TR_x is a transient property (possibly negative by the authors' definition), it depends on the absolute values of boundary conditions (apart from remaining scavenging capacity) and as such cannot be considered a basis for defining the absolute pressure independent film and material properties TR and P , respectively.

Thus, for any particular film: reactive or passive, single or multilayer, the (transient) effective transmission rate TR_{eff} (also called permeance or pressure normalized flux) can be defined as TR_x at the permeant *downstream (exit) boundary* with $p = p_{in}$ to characterize film barrier properties. In this case the exit boundary is $x = 0$ by default, thus we utilize flux J_0 and obtain from Eq. 4.3

$$TR_{eff} \equiv \frac{-J_{eff}}{\Delta p} = \frac{-J_x|_{x=0}}{\Delta p} \equiv \frac{-J_0}{\Delta p} = \frac{D_0 dC}{\Delta p dx} \Big|_{x=0} \quad (4.5)$$

Eq. 4.5 is the general effective transmission rate equation applicable to any film. It should be stressed here that Δp is the *external* permeant pressure gradient measured outside the film, C is the permeant concentration within the film, and in the case of multilayer film, $D_0 \equiv D|_{x=0}$ is the diffusivity of the material layer exposed to the *inside* of the package, that is, the side exposed to p_{in} , and the condition set in Eq. 2.4

$$p_{in} < p_{out} \quad (4.6)$$

is enforced, that is, the boundary is called *inner* if the external permeant pressure at it is strictly less than the permeant pressure at the other boundary. Otherwise, there is a problem with the definition in Eq. 4.5 when the condition

$$0 < p_{in} = p_{out} \quad (4.7)$$

is met, and the scavenging action is present: it would produce unphysical infinitely large TR_{eff} when the actual permeant fluxes into

the film from both its sides are finite and opposite in direction. The alternative definition to Eq. 4.5 can then be written utilizing p_{out} instead of Δp as

$$\overline{TR}_{eff} = \frac{-J_{eff}}{p_{out}} = \frac{D_0}{p_{out}} \frac{dC}{dx} \Big|_{x=0} \quad (4.8)$$

Definitions 4.5 and 4.8 become equivalent when $p_{in} \equiv 0$, but in general they are different. It is noted that definition 4.8 is not mathematically correct for passive barriers although it is often repeated in the literature [11] in the assumption of $p_{in} \equiv 0$. Therefore, definition 4.8 will be used for the film field performance calculations when p_{in} is close to zero and $p_{in} \ll p_{out}$, leaving definition (4.5) for comparative evaluation of the special case of reactive films with fluxes into the film from both sides when

$$0 < p_{in} \cong p_{out} \quad (4.9)$$

Within the TR definition, positive TR_{eff} means the permeant at the exit boundary passing through the film in the direction opposite to the internal global concentration gradient, whereas negative TR_{eff} shows the presence of the countercurrent from inside the package into the film despite the imposed global concentration gradient. The latter situation is only possible when permeant scavenging action is present, and that would mean an effective reduction of the permeant amount present in the package headspace.

Having these results available we are ready to analyze cases of single layer and multilayer films with and without reaction to establish the effects of the reaction and the boundary conditions on the steady state TR_{eff} . For consumable scavengers with instantaneous activation throughout the active layer the steady state results constitute the *initial* TR_{eff} since the apparent reaction rate constant k in Eq. 2.12 becomes variable after non-catalytic scavenger activation: $k = k(x, t)$.

5. NORMALIZATION OF PARAMETERS

The authors selected some typical values of material properties for a base polymer film and typical boundary and initial conditions to normalize all input parameters and reported results. The base case parameters were selected to represent average passive barrier material with relatively slow reaction and under 0.2 atmosphere of external pressure gradient simulating atmospheric oxygen. That allowed them to clearly see the effects of reaction rate increase and variation in material properties in the analysis of structural designs.

Base Case Scaling Parameters

The chosen base case scaling parameters correspond to the initial Thiele modulus $\phi_0 = 1$ for the reactive layer, and the passive layer permeability $P = 10^{-18} \text{ m}^3(\text{STP})\text{m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} = 22.23 \text{ cc mil}/(100 \text{ in}^2 \text{ day atm})$ in SI units and units common in US package engineering references, respectively.

$$\begin{aligned}
 L_B &= 10^{-4} \text{ m} \\
 D_B &= 10^{-12} \text{ m}^2 \text{ s}^{-1} \\
 S_B &= 10^{-6} \text{ m}^3(\text{STP})\text{m}^{-3} \text{ Pa}^{-1} \\
 k_B &= 10^{-4} \text{ s}^{-1} \\
 p_{in.B} &= 0 \text{ Pa} \\
 p_{in.B} &= 0.2 \cdot 10^5 \text{ Pa} \\
 J_B &= -10^{-10} \text{ m}^3(\text{STP})\text{m}^{-2} \text{ s}^{-1}
 \end{aligned} \tag{5.1}$$

(the *negative* flux scaling for all reported fluxes)

From this point all variations shall be normalized in the system parameters to the values in data set 5.1 and report dimensionless values shall be reported. For example, table entry $D_1 = 10$ would mean that its dimensional value is $D_1 = 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and so on. Note that the solute flux through the passive base film found according to Eq. 4.1: $J_x = -2 \times 10^{-10} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} = +2$ in normalized units, whereas for the reference double thickness PP-film with $L_1 = L_2 = 1$: $J_{PP} = -10^{-10} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} = +1$.

6. SINGLE PASSIVE LAYER (P-FILM)

In the case of non-reactive homogeneous membrane, Eq. (3.1) is reduced to

$$\frac{\partial^2 C}{\partial x^2} = 0 \tag{6.1}$$

then, taking the boundary conditions in Eqs. 2.5 and 2.6 into account, the steady state solution $C(x)$ is

$$C(x) = C_{in} + \frac{C_{out} - C_{in}}{L} x = C_{in} + (C_{out} - C_{in}) \xi \tag{6.2}$$

and the flux J_x is constant through any membrane plane $x = X$ (including $x = 0$) and equal to

$$J_x = J_0 = -\frac{D}{L}(C_{out} - C_{in}) \quad (6.3)$$

The effective transmission rate is found according to Eq. 4.5 as

$$TR_{eff} = \frac{D}{L\Delta p}(C_{out} - C_{in}) \quad (6.4)$$

Using solubility relations from the boundary conditions in Eqs. 2.5 and 2.6, Eq. 6.4 is reduced to the well-known result (Eq. 4.4):

$$TR_{eff} = \frac{DS}{L} \equiv \frac{P}{L} \quad (6.5)$$

Figure 2 shows the concentration profile inside the film corresponding to solution 6.2 without reaction ($\phi = 0$).

7. SINGLE REACTIVE LAYER (R-FILM)

Solving Eq. 3.4 for β_1 and β_2 with the fixed boundary conditions in Eqs. 2.5 and 2.6 we obtain

$$\beta_1 = \frac{C_{out} - C_{in} \exp(-\phi)}{\exp(\phi) - \exp(-\phi)} \quad (7.1)$$

$$\beta_2 = \frac{C_{in} \exp(\phi) - C_{out}}{\exp(\phi) - \exp(-\phi)} \quad (7.2)$$

Figure 2 shows concentration profiles for $p_{in} = 0$ and several nonzero Thiele moduli. After differentiating (Eq. 3.2) by x we obtain the local flux J_x as

$$\begin{aligned} J_x &= -D \frac{dC}{dx} = -\sqrt{kD} \left(\beta_1 \exp\left(x\sqrt{\frac{k}{D}}\right) - \beta_2 \exp\left(-x\sqrt{\frac{k}{D}}\right) \right) \\ &= -\sqrt{kD} (\beta_1 \exp(\zeta\phi) - \beta_2 \exp(-\zeta\phi)) \end{aligned} \quad (7.3)$$

and at the inner boundary $x = 0$:

$$\begin{aligned} J_0 &= -\sqrt{kD}(\beta_1 - \beta_2) = -\sqrt{kD} \cdot \frac{2C_{out} - C_{in}(\exp(\phi) + \exp(-\phi))}{\exp(\phi) - \exp(-\phi)} \\ &\equiv -\sqrt{kD} \cdot (C_{out} \operatorname{csc} h(\phi) - C_{in} \operatorname{coth}(\phi)) \end{aligned} \quad (7.4)$$

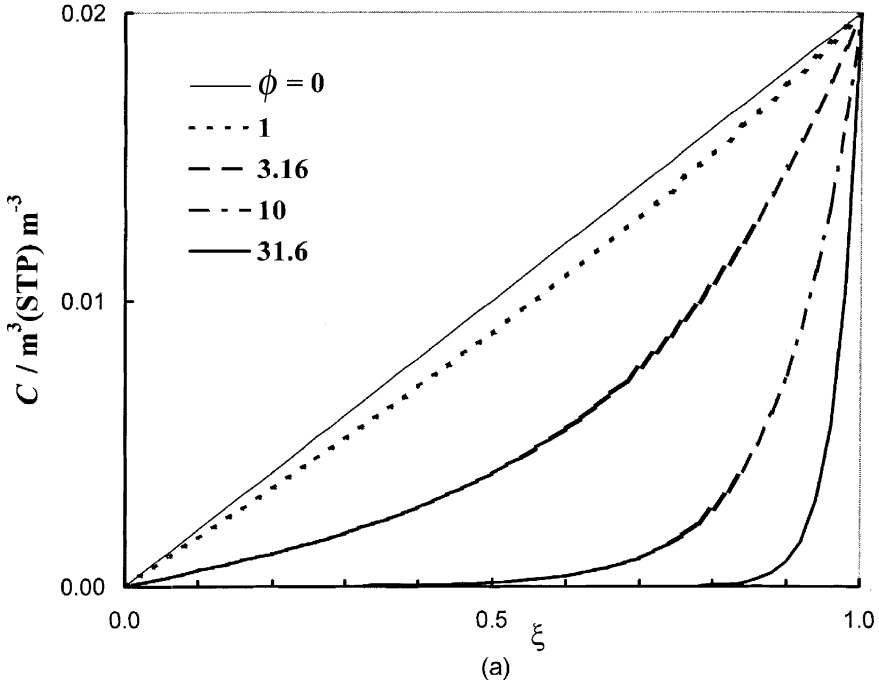


FIGURE 2 (a) Solute concentration profiles in P- and R-films. $C_{in} = 0$, $R = \text{const.}$ (b) Solute flux profiles through P- and R-films. $C_{in} = 0$, $R = \text{const.}$

The effective transmission rate through the reactive film is then found according to Eq. 4.5:

$$TR_{eff} = \frac{\sqrt{kD}}{\Delta p} (\beta_1 - \beta_2) = \frac{D}{L\Delta p} \phi (C_{out} \csc h(\phi) - C_{in} \coth(\phi)) \quad (7.5)$$

If $p_{in} = 0$ ($C_{in} = 0$), then TR_{eff} can be reduced to the known result of Siegel [11], which is a special case of solution 7.5:

$$TR_{eff} = \frac{DS}{L} \phi \csc h(\phi) \quad (7.6)$$

It is also observed from Eq. 7.6 that in this special case for any positive value of Thiele modulus two important inequalities are always true: $J_0 < 0$ and $TR_{eff} > 0$, if $p_{out} > 0$.

Figure 3 represents the case when $p_{in} > 0$, and both positive and negative values of J_0 and \overline{TR}_{eff} can be observed. Note that the alternative \overline{TR}_{eff} definition in Eq. 4.8 was used for this comparison for the reasons described earlier. Actually, normalization of J_0 by Δp to get

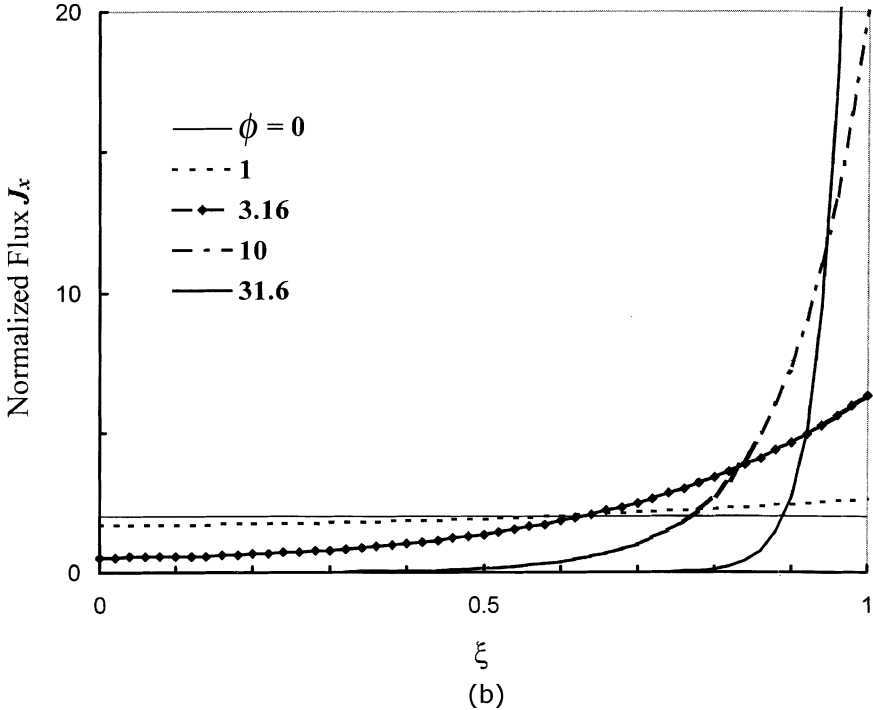


FIGURE 2 (Continued).

TR_{eff} is provided here only to make possible a comparison with common passive barrier results: in reactive films Δp cannot be used as a scaling factor in general because TR_{eff} depends on both absolute values of p_{in} and p_{out} rather than their difference as seen from Eq. 7.5. A better choice would be to use the effective flux J_0 dependent on absolute boundary concentrations from Eq. 7.4 to characterize reactive film barrier performance while keeping in mind the discussed sign convention for J_x and TR_x .

It is also noted that solutions 3.4, 7.1, and 7.2 are applicable only when $\phi > 0$, that is, when the reaction rate constant $k > 0$. For $k \equiv 0$, The passive barrier solution (Eq. 6.2) should be used instead because the coefficients in Eqs. 7.1 and 7.2 become degenerate (the case of 0/0 singularity).

8. ZERO FLUX CONDITION

The zero flux condition through the reactive film is easily obtained from Eq. 7.5 if we set $TR_{eff} = 0$. Then, the critical equilibrium concen-

tration of the permeant at the downstream film boundary is

$$C_{in.crit} = \frac{2C_{out}}{\exp(\phi) + \exp(-\phi)} \equiv C_{out} \operatorname{sch}(\phi) > 0 \quad (8.1)$$

Thus, if $C_{in} < C_{in.crit}$ (as is the case when C_{in} is set to zero in the standard TR measurement method according to ASTM Procedures [9] E96 and F372) then $TR_{eff} > 0$, and there is no way to reduce oxygen in the package headspace no matter what the reactivity of the scavenger is. However, if $C_{in} > C_{in.crit}$, then negative TR_{eff} is obtained for this particular ϕ value and one is able to effectively reduce headspace oxygen while the scavenger reactive capacity is not yet exhausted. The rate r_{HS} of permeant reduction in headspace is then given by J_0 from Eq. 7.4 multiplied by the total area A of the active barrier surface:

$$r_{HS} = A\sqrt{kD}(\beta_1 - \beta_2) \quad (8.2)$$

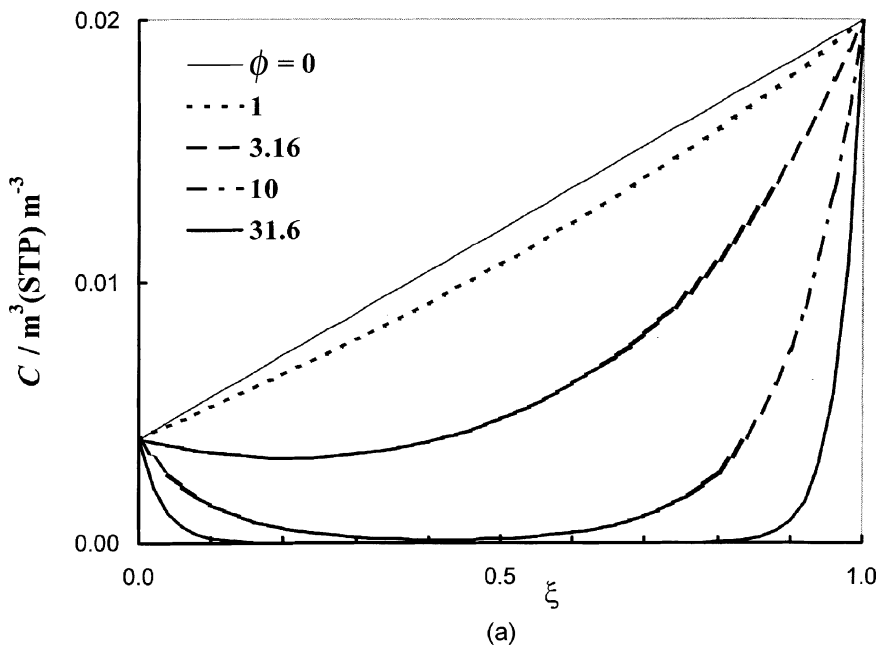


FIGURE 3 (a) Solute concentration profiles in P- and R-films. $C_{in} > 0$, $R = \text{const.}$ (b) Solute flux profiles through P- and R-films. $C_{in} > 0$, $R = \text{const.}$

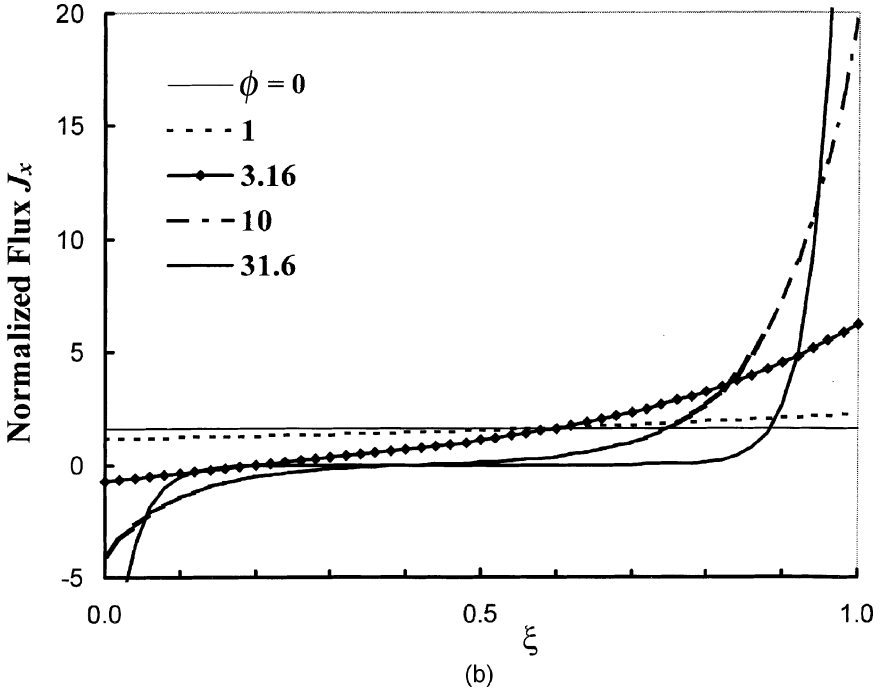


FIGURE 3 (Continued).

Note that the result in Eq. 8.2 refers to the catalytic scavenger case and thus constitutes the *initial* rate of permeant reduction in headspace for the consumable scavenger upon its instantaneous activation.

SUMMARY

Part I introduced the foundation of steady state permeation theory for homogeneous passive films and reactive films with catalytic scavenger. Important results include the effective transmission rate dependence (Eq. 7.5) on boundary conditions, zero flux criterion (Eq. 8.1), and the rate of permeant reduction in the headspace (Eq. 8.2). In Part II the dynamics of permeation across multilayer structures with active and passive layers will be analyzed, leading to the formulation of transient permeation theory based on dynamic reactive-passive interface approach and developed steady-unsteady solution matching method.

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