Mathematical Analysis of Transport Properties of Polymer Films for Food Packaging. VII. Moisture Transport through a Polymer Film with Subsequent Adsorption on and Diffusion through Food

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SYNOPSIS

A system of partial differential equations was developed to describe the transient, three-step transport of moisture through packaged food products. The steps included (i) Fickian diffusion through the polymer package film; (ii) Langmuirian adsorption upon the food surface; and (iii) Fickian diffusion through the food material. A set of finite difference equations was derived to approximate the continuous model. These equations were solved for standard boundary conditions in each section of the food packages. The results can be used for the determination of the food package shelf life.

INTRODUCTION

One of the biggest concerns in the food industry is food deterioration by the penetration of moisture, oxygen, and, to a lesser degree, organic vapors. Storing food in the proper environment slows the deterioration and better preserves the food.[1-8] However, the food's useful lifetime is much further extended by the use of polymeric packaging films such as polyethylene, polystyrene, vinyl polymers, and various cellulose-based films. Generally, these polymers serve very well as barriers between the environment and the food.[9,10]

The problem of food packaging has been addressed recently in several important review articles.[11-13] Especially, Chao and Rizvi[12] have presented a thorough review and evaluation of various mathematical models that are used to predict moisture and oxygen transport behavior and the associated shelf life of food packages. A recent volume,[14] exclusively dedicated to the barrier properties of polymer packaging films, discusses the importance of the permeability coefficients in the packaging film selection.

During the course of food storage, oxygen, moisture, and organics permeate through the polymer package. Moisture subsequently adsorbs upon the surface of totally or partially dehydrated foods and penetrates into the food, while oxygen may react with the food surface. Eventually, both events lead to browning and rancidity.[4,5] The time required for these processes is in part dependent upon the physical and transport properties of the polymer. Therefore, the selection of the polymer to be used for a particular food packaging application strongly influences its useful lifetime.[14]

Past efforts of mathematical modeling in this field were focused on prediction of the shelf life by modeling the transport of moisture through polymeric packaging films[13,15-22] and its subsequent adsorption upon the food surface. Further investigations included food deterioration due to oxidation,[19] effects of varying external (storage) temperature and relative humidity,[21] and the simultaneous, coupled transport and adsorption of moisture and oxygen.[22] However, in all of these studies, only *steady-state moisture transport* was considered.

In the present study, transient Fickian diffusion of moisture through the polymer film and *through the food* is analyzed. The result of this analysis is a

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moisture-concentration profile as a function of space and time and the determination of a revised shelf life that takes into consideration the "delay" in deterioration due to the food transport.

MODEL DEVELOPMENT

The present analysis consists of three steps: diffusion across the polymer film; Langmuirian adsorption on the food; and diffusion through the food product. The following assumptions are used to simplify the analysis: (i) concentration-independent, binary moisture diffusion coefficients throughout the system; (ii) monolayer coverage by water molecules on the food surface; (iii) energetically uniform surface; (iv) slow or no chemical reactions; (v) condensation of the moisture that adsorbs upon the food surface; and (vi) constant external (storage) moisture concentration and temperature. The first assumption simplifies the modeling by treating the diffusion coefficient appearing in Fick's second law as a constant. The second and third assumptions are results of the assumed Langmuirian adsorption isotherm. The fourth assumption restricts the model to foods that deteriorate mainly by physical means.

Diffusion of Moisture across the Polymer Packaging Film

A representative diagram of the one-dimensional problem considered here is depicted in Figure 1. The basic differential equation describing the transport of moisture through the polymer packaging film is the following Fickian expression:

$$\frac{\partial c_1}{\partial t} = D_{wp} \frac{\partial^2 c_1}{\partial x^2} \qquad (1)$$

where c_1 is the moisture concentration in the polymer film, D_{wp} is the moisture diffusion coefficient in the polymer, x is position, and t is time.

According to Figure 1, position X_3 defines the atmosphere/polymer film interface, whereas position X_2 defines the polymer film/internal packaging atmosphere interface. Then, the following initial condition can be written:

$$t = 0 \quad X_2 \leq x \leq X_3 \quad c_1 = c_0 \qquad (2)$$

Here, c_0 is the initial moisture concentration at the time of packaging.

In addition, the following boundary conditions can be written:

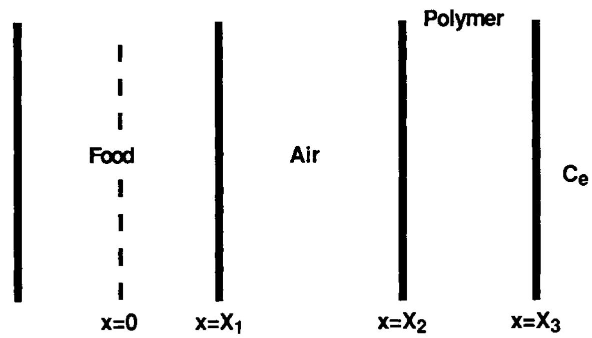

Figure 1 One-dimensional representation of the moisture transport problem. Moisture transport occurs from external conditions of c_e at $x > X_3$, throughout the polymer packaging film of thickness $X_3 - X_2$, into the air space, originally packaged at c_0, and then into the food of half-thickness X_1. In all simulations, $X_3 - X_1$ was assumed as 0.35 X_1.

$$t > 0 \quad x = X_3 \quad c_1 = c_e \qquad (3)$$

and

$$t > 0 \quad x = X_2 \quad c_1 = c_2 \qquad (4)$$

Here, c_1 is again the moisture concentration in the polymer, c_2 is the moisture concentration in the packaged air, and c_e is the external (storage) concentration after packaging.

Diffusion of Moisture through Packaged Air

The diffusional equation for moisture in the packaged air is similar to that for the polymer, but utilizes the moisture diffusion coefficient in air, D_{wa}:

$$\frac{\partial c_2}{\partial t} = D_{wa} \frac{\partial^2 c_2}{\partial x^2} \qquad (5)$$

It is subject to the initial condition

$$t = 0 \quad X_1 \leq x \leq X_2 \quad c_2 = c_0 \qquad (6)$$

where X_1 defines the food/packaged air interface. The boundary condition at $x = X_2$ is coupled with that of eq. (4), whereas the second boundary condition at $x = X_1$ is developed below.

To determine the boundary condition that couples the Langmuirian sorption with the Fickian diffusion, a molar balance for moisture is written at the food surface–air interface (at $x = X_1$). The balance contains the net rate of adsorption, r_{net}, the diffusion from the surface into the food, and the surface accumulation. The net rate of adsorption is the rate of adsorption less the rate of desorption:

$$r_{\text{net}} = r_a - r_d \quad (7)$$

The *adsorption rate* is proportional to the product of the bulk concentration near the surface and the fraction of the surface that is uncovered, $1 - \theta_w$:

$$r_a = k_1 c_w (1 - \theta_w) \quad (8)$$

The *desorption rate* is proportional to the fraction of the surface that is covered, θ_w:

$$r_d = k_2 \theta_w \quad (9)$$

The surface coverage is expressed as

$$\theta_w = c / c_m \quad (10)$$

The term, c_m, is the surface concentration corresponding to that of one monolayer and c is the moisture concentration near the food surface. Using eqs. (7)–(9), the molar balance for moisture at the $x = X_1$ interface is then expressed as

$$\frac{\partial c_s}{\partial t} = \frac{k_1 c(1 - \theta_w) - k_2 \theta_w}{V} - \left[- \frac{S D_{\text{wf}}}{V} \frac{\partial c_3}{\partial x} \right]_{x=X_1} \quad (11)$$

Here, c_3 is the moisture concentration within the food, c_s is the moisture concentration at the food surface, D_{wf} is the binary diffusion coefficient for moisture through the food, S is the surface area of the package, and V is the unfilled package volume. Equation (11) serves as the second boundary condition for solving eq. (5).

Diffusion of Moisture through the Food Product

The model for the diffusion through food is analogous to that of diffusion through the polymer film as in eq. (1). Again, the familiar form of Fick's second law, bounded between $x = 0$ and $x = X_1$, is

$$\frac{\partial c_3}{\partial t} = D_{\text{wf}} \frac{\partial^2 c_3}{\partial x^2} \quad (12)$$

subject to the initial condition

$$t = 0 \quad 0 \le x \le X_1 \quad c_3 = c_0' \quad (13)$$

and the boundary condition

$$t > 0 \quad x = 0 \quad \frac{\partial c_3}{\partial x} = 0 \quad (14)$$

Here, the initial condition is defined for a general case. Most likely, the initial moisture concentration in the food, c_0', is relatively small, and therefore c_0' may be assumed to be equal to zero. The boundary condition at $x = 0$ is the symmetry condition (flux at the center of the food is zero). The second boundary condition at $x = X_1$ is also derived from the discussion of the Langmuir isotherm. Thus, eq. (5) is coupled with eqs. (1) and (12). Because of this multiple coupling, determining an analytical solution for the system of eqs. (1), (5), and (12) is quite unattractive. However, a numerical solution is readily obtainable and is discussed in the following section.

MODEL PREDICTIONS

For the numerical solution of the previous model, it was necessary to use a finite differences technique. To use the explicit method of finite differences, the analytical system of equations must be transformed to difference equations. Figure 2 is the nodal grid used as an aid to write the difference eqs. (15)–(17). A centered finite divided difference is used to approximate the second-order derivative in x, and a forward finite difference is used to approximate the time derivative. The subscripts and superscripts denote the spatial and time dimensions, respectively.

For region I, with $0 < x < X_1$,

$$c_i^{l+1} = c_i^l + D_{\text{wf}} \frac{\Delta t}{(\Delta x)^2} (c_{i+1}^l - 2c_i^l + c_{i-1}^l) \quad (15)$$

For region II, with $X_1 < x < X_2$,

$$c_i^{l+1} = c_i^l + D_{\text{wa}} \frac{\Delta t}{(\Delta x)^2} (c_{i+1}^l - 2c_i^l + c_{i-1}^l) \quad (16)$$

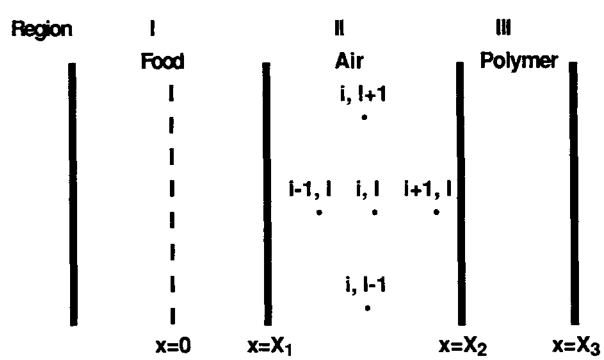

Figure 2 Nodal grid of moisture transport problem for the finite difference method, where the subscript i represents the spatial dimension and the subscript l represents time.

For region III, with $X_2 < x < X_3$,

$$c_i^{l+1} = c_i^l + D_{wp} \frac{\Delta t}{(\Delta x)^2} (c_{i+1}^l - 2c_i^l + c_{i-1}^l) \quad (17)$$

The transformed initial and boundary conditions are listed as eqs. (18)–(23). The initial condition for region I is

$$c_i^0 = c_0' \quad (18)$$

For region II,

$$c_i^0 = c_0 \quad (19)$$

Finally, for region III,

$$c_i^0 = c_0 \quad (20)$$

The boundary conditions become

$$c_0^{l+1} = c_0^l + 2D_{wf} \frac{\Delta t}{(\Delta x)^2} (c_1^l - c_0^l) \quad (21)$$

with

$$c_{X_1}^{l+1} = c_{X_1}^l + \frac{\Delta t k_1}{V} c_{X_1+1}^l \left(1 - \frac{c_{X_1}^l}{c_m}\right) - \frac{\Delta t k_2}{V} \frac{c_{X_1}^l}{c_m} + \frac{\Delta t S D_{wf}}{V 2\Delta x} (c_{X_1}^l - c_{X_1-2}^l) \quad (22)$$

and

$$c_{X_3}^l = c_e \quad (23)$$

As for all parabolic partial differential equations, use of the explicit method requires that the system of difference equations be subject to eq. (24), the requirement for stable solutions. Of the three diffusion coefficients, D_{wa} is chosen as the value to be used in the stability relation because it corresponds to the *limiting* time interval:

$$\frac{D_{wa}\Delta t}{(\Delta x)^2} \leq \frac{1}{2} \quad (24)$$

Using a computer to iterate over the space and time dimensions, the moisture concentration profile is finally obtained.

DISCUSSION

Numerical solution of the previous model provides the moisture concentration profile as a function of normalized position and time. For solution simulations, it was necessary to use typical values of the various parameters involved in the model. In a previous communication by Howsmon and Peppas,[22] packaging of freeze-dried seafood was considered for such an analysis. Table I summarizes the necessary parameter values for this system. The equilibrium value of moisture uptake is based upon that reported by Iglesias and Chirife.[23] The estimates for the Langmuir sorption rate constants are based upon the reported equilibrium constant by Iglesias and Chirife[23] as well. Other values chosen for this packaging situation are package surface area, $S = 129.03$ cm^2; unfilled package volume, $V = 73.74$ cm^3; storage temperature of the package, $T = 30°$C; initial moisture concentration in the food = 0.05 (5% RH); initial moisture concentration in the packaged air = 0.15 (15% RH); and a constant external (storage) concentration of 0.70 (70% RH).

Figures 3 and 4 describe the moisture penetration concentration through the food-package system being considered. Normalized moisture concentration for different values of Fourier time is plotted as a function of position. The food product is assumed to have a thickness $2X_1$. Thus, position is plotted as a ratio of the distance from the center of the food, $x = 0$, to the food's half-thickness, X_1. For this illustration, the distance between the food and polymer film is arbitrarily chosen to be 35% of the food's half-length, which is

$$X_3 - X_1 = 0.35 X_1 \quad (25)$$

The Fourier time, τ, is expressed as

$$\tau = \frac{D_{wf} t}{X_1^2} \quad (26)$$

Table I Physical Properties of Packaged, Freeze-Dried Seafood[a]

Parameter	Value
Moisture diffusion coefficient in food product, D_{wf}	1×10^{-6} cm^2/s
Moisture diffusion coefficient in air, D_{wa}	1×10^{-1} cm^2/s
Moisture diffusion coefficient in polymer film, D_{wp}	1×10^{-7} cm^2/s
Adsorption rate constant, k_1	30×10^{-14} s^{-1}
Desorption rate constant, k_2	1×10^{-14} RH s^{-1}
Monolayer concentration, c_m	0.30 (30% RH)

[a] Adapted from Howsmon and Peppas.[22]

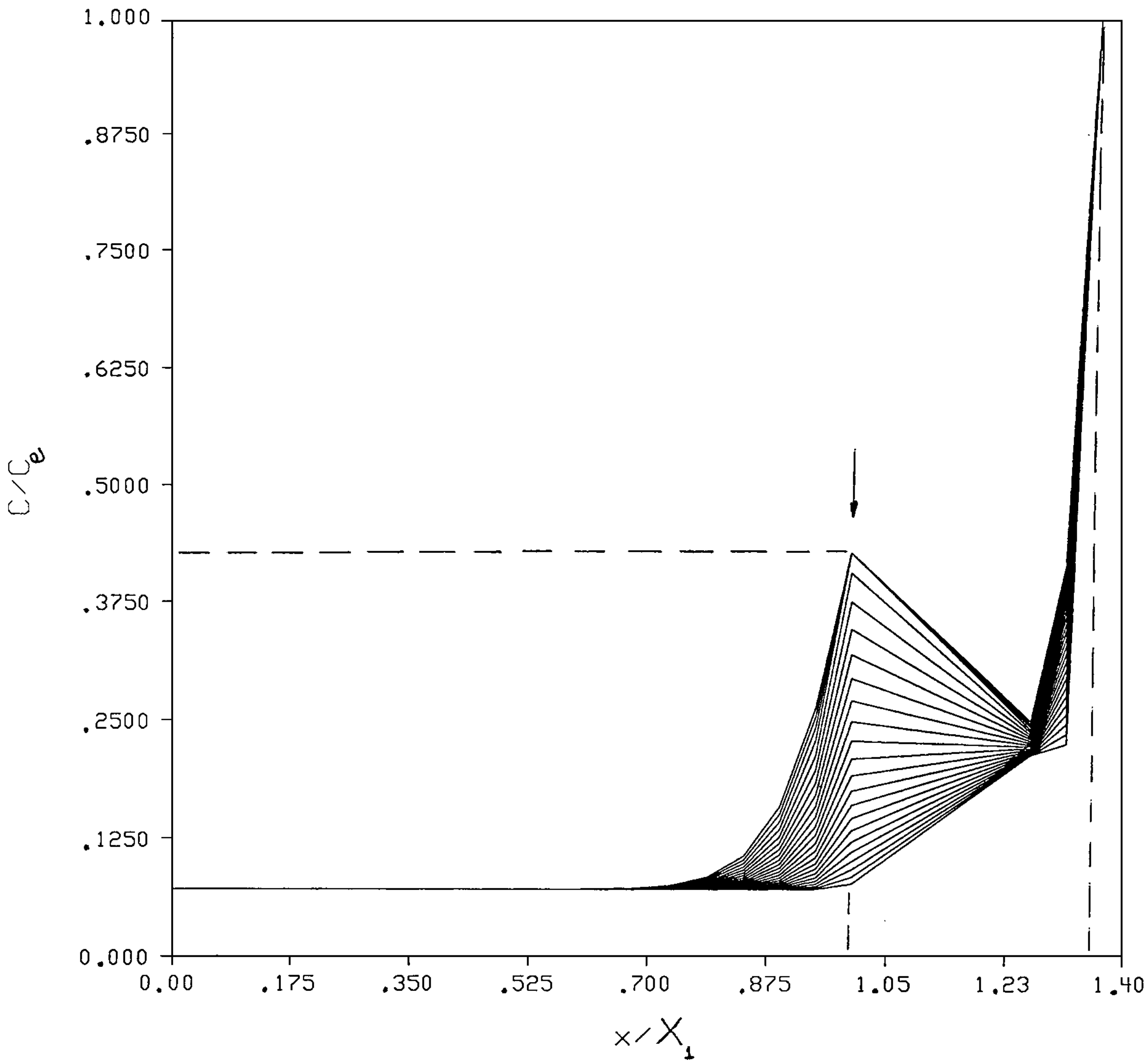

Figure 3 Early time (1–21 h) transport behavior of packaged food product. Normalized moisture-concentration profile, c/c_e, as a function of normalized position, x/X_1, for various dimensionless times, $\tau = D_{wf}t/X_1^2$. From bottom to top, curves represent Fourier times increasing by $\tau = 4 \times 10^{-4}$, which correspond to actual increase times of 1 h. Arrow indicates the food product surface and $X_3 - X_1 = 0.35\ X_1$.

Figure 3 contains the early time data where each interval of τ is 4×10^{-4} corresponding to 1 h. Figure 4 presents the long-term data with τ intervals of 9.6×10^{-3} (1 day). The profiles are quite consistent with what one would expect *a priori*. The profiles across the polymer are similar to profiles observed in thin films, while the profiles across the food appear to be very similar to error function-type concentration decays typically observed in diffusion through solids.

As it can be seen from the comparison of Figures 3 and 4, during the early times of the packaging process a relatively sharp gradient of moisture concentration is established between the external conditions, c_e, at $x = 1.35X_1$. Because of the quasi-equilibrium conditions of the Langmuir adsorption at the food surface, $x = X_1$, the moisture concentration is kept at a somewhat higher level and eventually achieves the steady-state value of $c_m/c_e = 0.4285$ or $c_m = 0.30$ (since $c_e = 0.70$), which is achieved at $\tau = 8.4 \times 10^{-3}$, i.e., in 21 h. Beyond this point, the moisture concentration *in the food* builds up (see Fig. 4), whereas the moisture-concentration profile between the food product and the polymer film

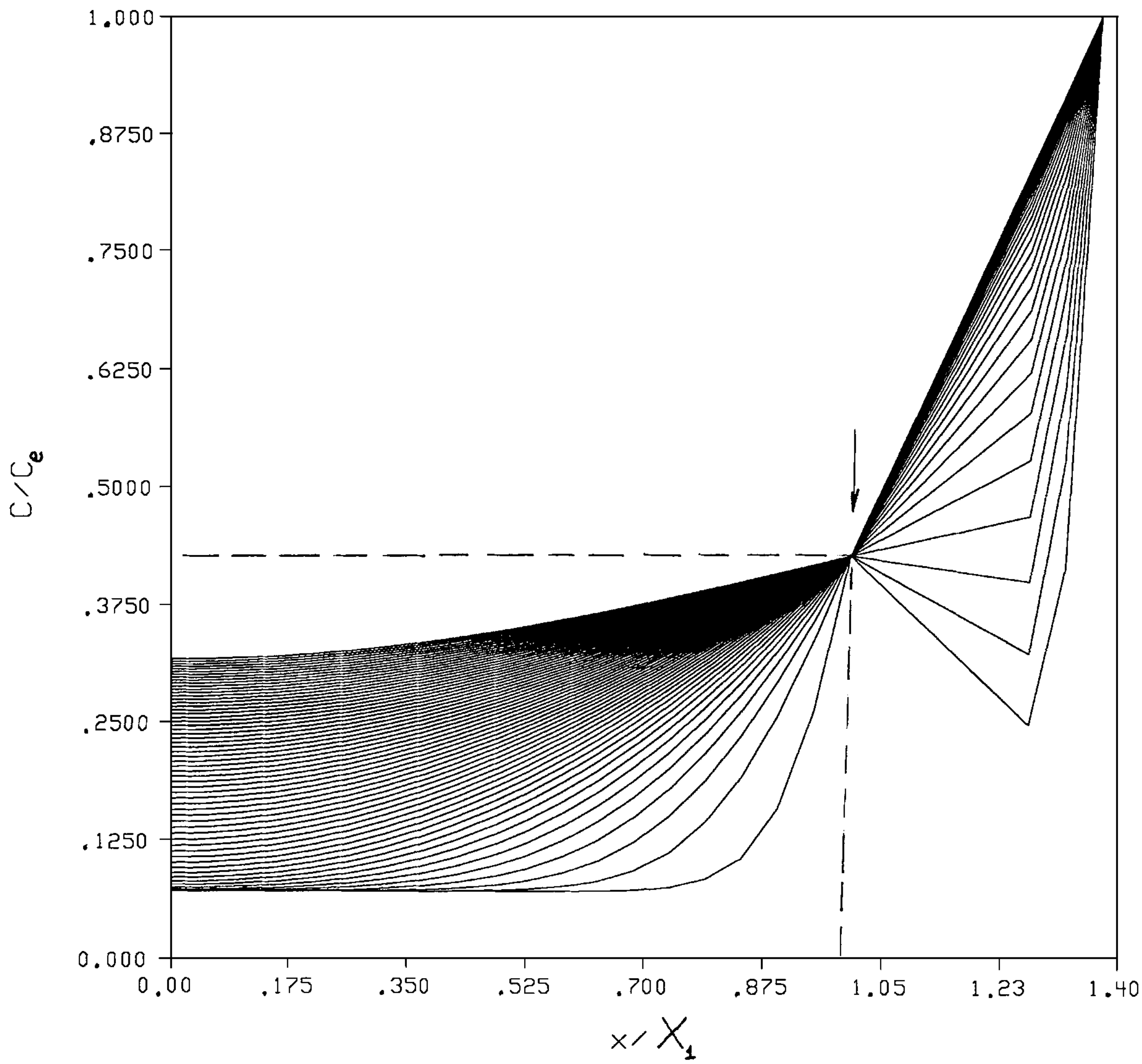

Figure 4 Late-time (1–60 d) transport behavior of packaged food product. Normalized moisture-concentration profile, c/c_e, as a function of normalized position, x/X_1, for various dimensionless times, $\tau = D_{wf}t/X_1^2$. From bottom to top, curves represent Fourier times increasing by $\tau = 9.6 \times 10^{-3}$, which correspond to actual increase times of 1 d.

achieves an almost straight line, indicating a linear steady-state moisture transport from $c_e = 0.70$ to $c_m = 0.30$.

The application of the Figures 3 and 4 is very straightforward as they may be used to determine the shelf life of food products. One must first define the key conditions for which the food becomes of no use, that is, the position in the food (usually $x = 0$) and the maximum allowable moisture concentration at that position relative to the storage concentration. By simply referring to the time curves, one can determine the time that corresponds to the key conditions. This value then is the shelf life. If the type of freeze-dried food is varied, then only the value of D_{wf} is affected. The profiles in Figures 3 and 4 remain the same.

The application of such an analysis may further be extended to the selection of the optimum polymer packaging system. By varying the value of the moisture diffusion coefficient in the polymer film, D_{wf}, and generating the corresponding profiles, a large data base of profiles may be developed and stored on a computer. User friendly software could then be written that would readily access the data. By again defining the conditions for which the food becomes of no use, one would specify the shelf life to the computer and the corresponding value of D_{wp} would be calculated. In turn, this value would be used to determine the necessary polymer packaging film for the system in consideration.

The new model has one major advantage over the models of Peppas and Khanna[18] and Peppas and Kline.[21] It allows moisture to enter the food product, thus relaxing the stringent conditions of previous models. Indeed, whereas before[18,21] the calculation of shelf life was based on unacceptably high values of the relative humidity (or c) in the packaged air (region $X_1 < x < X_2$), with the new model this decision is based on actual humidity values *in the food* (region $x < X_1$).

We wish to thank Lance K. Safford of the Chemistry Department for his valuable assistance with the Cyber 205 computer.

APPENDIX
COMMENTS ON THE NUMERICAL ALGORITHM

Few systems of partial differential equations describe diffusion through multiple media and even fewer contain such equations that are coupled to one another through differential boundary conditions, like the system discussed here. Thus, the system presented here requires the development of a modified version of the explicit finite difference method if an accurate solution is to be obtained.

The numerical algorithm that was developed gives special attention to the food surface air interface ($x = X_1$). The algorithm allows moisture to build upon the surface until it reaches the Langmuirian constraint. Once the constraint is met, the moisture concentration is not allowed to change with time. Therefore, within the transient process, an equilibrium state (steady-state) is reached at the interface. The moisture diffusion through the polymer, the air, and the bulk food remains transient. The other sections of the algorithm are most likely what one would expect. However, the algorithm does possess some key steps to accommodate the different diffusion coefficients encountered. The algorithm was written in FORTRAN and was compiled and run on one of Purdue University's CYBER 205 supercomputers. The concentration profiles in Figures 3 and 4 are the final results of the simulation.

The explicit method offers a simple, concise way by which the solution for the problem discussed here is realized; however, it presents one drawback. Since air is present between the food and the polymer, its high diffusion coefficient limits the time increment in the computer routine to a very small value. The time increment is determined from the stability requirement. Because of this small value, millions of iterations are necessary to generate meaningful results. Therefore, utilizing this method requires a substantial amount of cpu time and may take several hours for it to finish. There exist, however, other finite difference methods that do not require stability relations. These methods could quite possibly be used to solve the system of partial differential equations without using large numbers of iterations.

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