Coupled Heat and Mass Transport in Unsteady Sublimation Drying

Sublimation drying is analyzed by considering coupled heat and mass transport at the ice-vapor interface. Since, the typical model of sublimation drying assumes a pseudo steady state heat transport limited process, these assumptions are critically analyzed to determine whether they are the cause of some of the limitations of the simplified model. It is shown that although total drying times can be substantially increased if there is heat leakage into the ice core and coupled heat and mass transport, this is not a problem in the conventional sublimation drying of foods. However, the results indicate that consideration of both coupled transport and heat leakage into the core result in time-varying ice temperatures which could exceed the triple point. In addition, the application of this analysis to the analogous heterogeneous chemical reaction problem is pointed out and appropriate conclusions can be drawn by inference.

E. C. FOX and W. J. THOMSON

Department of Chemical Engineering
University of Idaho
Moscow, Idaho 83843

SCOPE

Sublimation drying is a process in which a material to be dried is initially frozen and the water subsequently removed by direct sublimation. The most common example of this process is in the freeze drying of foods. The sublimation process is usually slow enough that it is modeled by the assumption of a uniform shrinking ice core under pseudo steady state conditions. Although the process involves both heat transport (to the ice core) and mass transport (water vapor from the ice core) many commercial processes are heat transport limited (King, 1971). These assumptions result in the prediction of a constant temperature (with time) in the ice core. However experiments have shown (Sandall, 1966) that this is not always a good assumption. This is an important consideration since it is critical that the temperature at the ice-vapor interface remain below the triple point. In addition the pseudo steady state model does not always give accurate predictions of total drying times.

The present work resulted from an effort to determine whether the assumptions made in the heat transfer limited pseudo steady state model were the causes of the limitations of this model. The two most important predictions of any model of sublimation drying are the total drying time and the temperature of the ice-vapor interface. Thus the major goal of this work was to determine whether the inclusion of the factors usually neglected in the pseudo steady state model would substantially alter either of these predictions. The analysis of this system also has added advantages since the basic model of a shrinking core also applies to many solid-fluid chemical reactions.

While the assumption of a heat transfer limited process is equivalent to decoupling the mass transport from the heat transport, our analysis considers coupled heat and mass transport at the ice-vapor boundary. With this as a starting point we then analyze the effects of both heat leakage into the ice core and the accumulation of energy and vapor in the dried portion of the sample. The importance of these considerations are given in terms of the pertinent dimensionless parameters. While the results are only strictly applicable to sublimation drying (since we used ice-vapor equilibrium data) the effects on heterogeneous chemical reactions can easily be inferred by analogy.

CONCLUSIONS AND SIGNIFICANCE

Sublimation drying has been analyzed by considering coupled heat and mass transport at the ice-vapor interface. In this context two separate models were developed to examine the effects of heat leakage into the ice core and accumulation of energy and vapor in the dried region of a sample. It was found that the total drying time is altered significantly whenever there is a unique combination of a high thermal capacity in the core, low sublimation energies (relative to the heat flux delivered to the core) and comparable heat and mass transport resistances in the dried region. Because of the values of the physical properties encountered in the sublimation drying of foods, the total drying time should be unaffected by any of these effects. Thus the reason for drying times longer than that predicted by the conventional model remains unanswered at this point. However, the conventional pseudo steady model for heterogeneous chemical reactions could be seriously in error since there is a potentially greater variation in physical properties for such problems.

Of more significance to sublimation drying are the results concerning the predictions of ice-vapor temperatures. Whenever mass transport resistance is comparable to or

Correspondence concerning this paper should be addressed to W. J. Thomson.

greater than the resistance to heat transport, the more sophisticated model predicts the ice-vapor temperature to increase with time. Accounting for heat leakage into the core also resulted in an ice core temperature which increased with time, similar to experimental results of previous investigators. Surprisingly, when finite heat leakage into the core accompanies significant mass transport resistance, the ice-vapor temperature was found to initially decrease with time. Such a phenomena might then prohibit local melting prior to complete drying.

Simultaneous mass and heat transport in heterogeneous systems is important in sublimation drying and in noncatalytic reactions. There have been many analyses of these problems by the so-called "Uniform Shrinking Core Model." This model assumes that the system is at a pseudo steady state so that the core (unreacted or unsublimed material) retreats uniformly with time.

In one of the earlier works Sandall et al. (1967) utilized the pseudo steady state approach to analyze the sublimation drying of turkey meat. They assumed that there was no heat leakage into the core and no heat or mass accumulation in the dried portion of the sample. The equations were solved for a slab geometry and it was assumed that the temperature and concentration at the core boundary (the ice front) remained constant with time. However Sandall's experimental work (1966) showed that in a number of cases the ice front temperature varied with time. This was particularly evident toward the latter stages of his runs and is a potentially serious problem since it is possible for local melting to occur prior to complete drying. Hill and Sunderland (1971) have taken much the same approach except that they allowed for thermal conduction through the back face of the frozen slab. Dyer (1964) solved the unsteady state heat transport equation for the sublimation drying problem again with the assumption of zero heat leakage into the ice core and a constant temperature ice front. Accumulation of heat within the dried portion of the material was accounted for by McCulloch and Sunderland (1971) but once again the heat and mass transfer were assumed to be uncoupled.

In the field of heterogeneous noncatalytic chemical reactions, Hills (1968) has analyzed the thermal decomposition of $CaCO_3$ by assuming pseudo steady state conditions and accounting for heat leakage into the core. He showed that the analysis of kinetic data was very dependent on the accuracy of the model utilized to describe the transport and kinetic phenomena. Wen (1968, 1971) has done some of the more extensive work in this area. He has solved the heat and mass transport equations utilizing the pseudo steady state assumption but expressing the reactant concentrations at the surface of the core as a function of temperature (1968). In addition, he has solved the unsteady heat and mass transport equations by assuming a constant temperature at the reaction front and that the mass and energy equations were uncoupled (1971).

Isheda et al. (1970) solved the unsteady heat and mass transport equations for an instantaneous chemical reaction at the core boundary. They assumed the core boundary to be at a constant temperature and considered the mass transport to be independent of the heat transport. They did not consider heat leakage into the core and concluded that under certain conditions the total reaction time increased considerably when accumulation was accounted for.

In all of the work accomplished to date there has not been an unsteady state analysis of either the sublimation drying problem or the noncatalytic reaction problem under conditions where the heat and mass transport are coupled. Consequently we seek to investigate the importance of coupling the heat and mass transfer at the ice front. It is well known that many sublimation drying processes are heat transfer limited (King, 1971) in such cases it is justifiable to decouple the mass transfer problem by assuming constant temperature and concentration boundary conditions at the ice front. However, as King (1971) points out, the drying can become mass transfer controlled at higher ambient pressures and also in the sublimation drying of liquid foodstuffs. In addition the pseudo steady state solution is at odds with Sandall's results (1966) and does not correctly predict the drying time for the removal of the last 10 to 35% of the water (King, 1971). In view of these limitations an analysis of the effects of the various assumptions upon which previous models are based would seem to be in order. Specifically, the analysis would include the consequence of decoupling the heat and mass transfer, assuming zero heat leakage into the ice core, and neglecting accumulation in the dried region.

While the specific problem dealt with here is concerned with sublimation drying, the results should be equally applicable to those reacting systems which can be described by a retreating core model. Throughout the paper we will attempt to point out the appropriate analogies with the heterogeneous reaction problem.

ANALYSIS

The coordinate system and geometry of the model is shown in Figure 1. The heat and mass transport in the dried portion of the sample (I) and the core (II) are

$$\frac{\partial T_1}{\partial t} = \alpha_1 \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial T_1}{\partial r}\right) \tag{1}$$

$$\frac{\partial T_2}{\partial t} = \alpha_2 \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial T_2}{\partial r}\right) \tag{2}$$

While the mass transport in region I is described by

$$\frac{\partial C}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) \tag{3}$$

Strictly speaking the thermal diffusivity α_1 will depend on the porosity of region I as well as on the properties of the vapor within the pore. Similarly the mass diffusivity D can result from Knudsen diffusion and/or molecular diffusion depending on the operating pressure and the pore dimensions. However since it is not our purpose to investigate these properties we take the pragmatic approach of assuming them to be effective values which remain constant throughout region I. The initial and boundary conditions are given by

at $t = 0$, all r

$$T_1 = T_2 = T_I \tag{4}$$

$$C = 0 \tag{5}$$

at $r = R,\ t > 0$

$$T_1 = T_R \tag{6}$$

$$C = C_R \tag{7}$$

at $r = s,\ t > 0$

$$T_1 = T_2 \tag{8}$$

$$k_1 \frac{\partial T_1}{\partial r} = -\lambda D \frac{\partial C}{\partial r} + k_2 \frac{\partial T_2}{\partial r} \tag{9}$$

$$C = f^e(T_2) \tag{10}$$

In these equations, (8) is a statement of the continuity of temperature at the ice front, (9) is the energy balance at the ice front, and (10) expresses the equilibrium relationship between concentration (vapor pressure) and temperature which exists there. Equations (9) and (10) add the greatest degree of complexity to the models which have been considered previously. It is through these equations that the heat and mass transfer equations are coupled. In the absence of any rate limiting assumptions, concentration and temperature at the ice front are free to change with time. In view of the highly nonlinear nature of the equilibrium function f^e, it is entirely possible that the temperature here could rise above the triple point and produce local melting.

To complete the mathematical description of the problem, a mass balance yields the instantaneous relationship between the ice front position and time.

$$\frac{ds}{dt} = \frac{M_w D}{\rho} \left.\frac{\partial C}{\partial r}\right|_{r=s} \tag{11}$$

It should be noted that the analogous reaction rate problem can also be described by Equations (1) to (9) if λ is replaced by the heat of reaction and Equation (10) is replaced by either a reaction rate or an expression of chemical equilibrium (both of which are temperature dependent).

The solution of these equations becomes very complex even with numerical analysis techniques. In this paper the solution is approached from two extreme cases; the case where heat leakage into the core is important (Heat Leakage Model) and the case where mass and heat accumulation in region I is important (Accumulation Model).

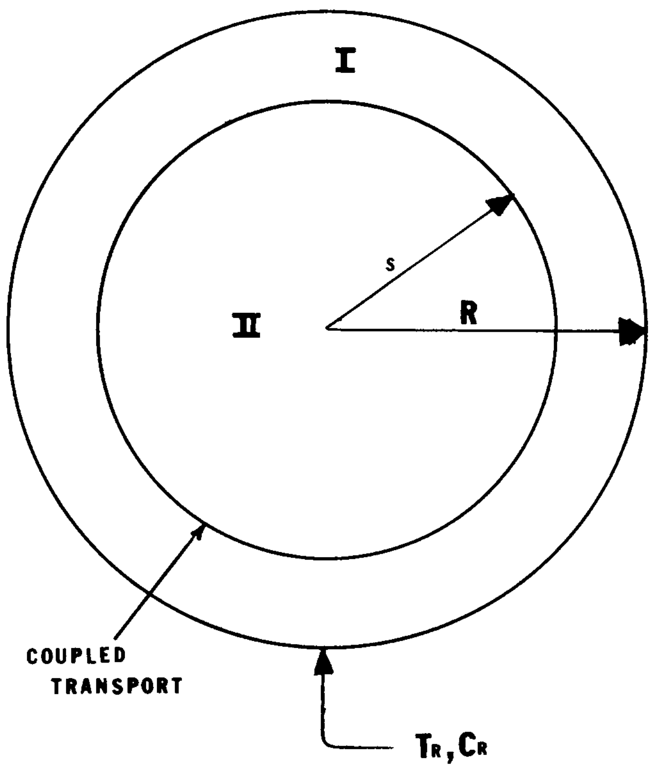

Fig. 1. Diagram of model.

Heat Leakage Model

For the Heat Leakage Model we take the accumulation terms of Equations (1) and (3) to be zero so that

$$\frac{d}{dr}\left(r^2 \frac{dT}{dr} \right) = 0 \tag{12}$$

$$\frac{d}{dr}\left(r^2 \frac{dC}{dr} \right) = 0 \tag{13}$$

To be rigorous, the heat leakage into the ice core should be accounted for by solving Equation (2) simultaneously with Equations (6) to (13). Since this process is nearly as complicated as solving the original set of equations, we define a heat leakage parameter δ which is defined by

$$\rho_2 C_{p_2}\ s \frac{dT_2}{dt} = \frac{k_2}{\delta}(T_s - T_2) \tag{14}$$

Thus we are assuming that the only temperature gradients which exist within the ice core are linear over some radial thickness δ. The remaining portion of the core is assumed to undergo a uniform temperature change with time. Viewed in this context, δ is an adjustable parameter which determines the resistance to heat leakage into the core. A maximum value for this resistance can be estimated by setting $\delta = s$. Note that in general it can change with time which is consistent with the behavior of Equation (2). Rewriting the boundary condition given by Equation (9) in terms of δ

$$k_1 \frac{dT_1}{dr} = -\lambda D \frac{dC}{dr} + \frac{k_2}{\delta}(T_s - T_2) \tag{15}$$

In dimensionless form, Equations (12) and (13) become

$$\frac{d}{d\phi}[(1 - s^*)\phi + s^*] \frac{dT_1^*}{d\phi} = 0 \tag{16}$$

$$\frac{d}{d\phi}[(1 - s^*)\phi + s^*] \frac{dC^*}{d\phi} = 0 \tag{17}$$

where ϕ is the transformed independent variable defined by

$$\phi = \frac{r - s}{R - s} \tag{18}$$

The dimensionless boundary conditions are

at $\phi = 1$,

$$T^* = C^* = 1 \tag{19}$$

at $\phi = 0$,

$$C^* = f^e(T^*) \tag{20}$$

$$\frac{dC^*}{d\phi} = -\Gamma \frac{dT_1^*}{d\phi} + \Omega(T_s^* - T_2^*)(1 - s^*) \tag{21}$$

The dimensionless parameters Γ and Ω describe the ratios of heat conducted to the core boundary to the sublimed mass and the heat leakage into the core to the sublimed mass. These parameters are easily extended to the analogous chemical reaction problem.

The ice front position can be calculated from Equation (11) which in dimensionless form is

$$\frac{ds^*}{d\tau} = \frac{N_{Le}\ \Psi}{(1 - s^*)}\ \frac{dC^*}{d\phi}\bigg|_{\phi=0} \qquad (22)$$

where the product of the Lewis number and Ψ is a relative measure of the core recession rate corresponding to a given sublimation mass flux.

Equations (16) and (17) are solved by initially guessing at a value of T_s^* and then iterating about Equations (20) and (21). Once agreement is reached between the previous guess and the calculated value, the ice core temperature T_2^* is updated by solving Equation (14) over a small time increment $\Delta\tau$. In dimensionless form this can be expressed by

$$T_2^*\bigg|_{\tau+\Delta\tau} = T_s^* + (T_2^*\bigg|_{\tau} - T_s^*) \exp\left[\frac{\Delta\tau\Lambda}{s^*}\right] \qquad (23)$$

where the dimensionless parameter Λ is a ratio of the heat leakage between regions I and II to the thermal capacity of the ice core.

Accumulation Model

To account for accumulation within region I Equations (1) and (3) were placed in the same dimensionless variables as in the heat leakage model so that

$$\frac{\partial T_1^*}{\partial \tau} = \frac{1}{(1 - s^*)^2}\ \frac{\partial^2 T_1^*}{\partial \phi^2} + \frac{2}{(\phi(1 - s^*) + s^*)(1 - s^*)}\ \frac{\partial T_1^*}{\partial \phi} \qquad (24)$$

$$\frac{\partial C^*}{\partial \tau} = \frac{N_{Le}}{(1 - s^*)^2}\ \frac{\partial^2 C^*}{\partial \phi^2} + \frac{2N_{Le}}{(\phi(1 - s^*) + s^*)(1 - s^*)}\ \frac{\partial C^*}{\partial \phi} \qquad (25)$$

with boundary conditions

at $\tau = 0$, all ϕ

$$C^* = 0, \quad T_1^* = T_2^*$$

at $\phi = 1,\ \tau > 0$

$$T_1^* = C^* = 1$$

at $\phi = 0,\ \tau > 0$

$$C^* = f^e(T_2^*)$$

$$\frac{\partial C^*}{\partial \phi} = \Gamma \frac{\partial T_1^*}{\partial \phi}$$

Note that in this model we are neglecting heat leakage into the core and thus the temperature in the ice core T_2^* is taken to be uniform. This is not to imply that T_2^* is constant since it will change with time depending on the extent of the coupling between the heat and mass transport at the ice front.

The above equations were placed in finite difference form and solved by utilizing a straight forward Crank-Nicolsen method. The resulting algebraic equations were of a tridiagonal form and solved by the method of Thomas (Carnahan et al., 1969) on an IBM model 360-40 computer. Again the ice front position was updated by solving Equation (22) over each finite time interval. A radial grid size of 0.1 and a $\Delta\tau$ of 0.1 proved to be sufficiently accurate ($\sim$ .1%) yielding computational times of about seven minutes. The stability of the numerical solutions were found to be sensitive only to the initial guess of the ice front position. Assuming an initial s^* of 0.99 proved to be satisfactory in all cases considered.

It should also be pointed out that in the actual calculations it was necessary to choose absolute values of C_R and T_R so that the ice-vapor equilibrium could be calculated. However this is not detrimental to the generality of the results.

ANALYTICAL RESULTS

Heat Leakage Model

To determine the conditions under which heat leakage is important, a plot of the ratio of drying time with and without heat leakage is shown in Figure 2 for various values of the dimensionless parameters Γ, Ω, and Λ. It was found that whenever Ω was less than 10 heat leakage did not affect the drying time no matter what the value of Λ. Similarly, if Λ was equal to one or greater, heat leakage is insignificant even for very high Ω. The reason for this dependency of heat leakage on Ω is obvious since it represents the ratio of heat leakage into the core to the energy absorbed in the sublimation process. However if Λ is large, the ice core thermal capacity is low relative to the heat leakage and its temperature rises rapidly to T_s which then reduces the driving force for heat leakage into the core. Thus the total drying time is only affected when the heat leakage is greater than the sublimation energy and the thermal capacity of the core is large. It is also interesting to note the dependency of the drying time on Γ as shown in Figure 2. Since Γ is a measure of the heat flux delivered to the ice front relative to the sublimation ability of the core, heat leakage is insignificant at both low and high values of Γ. At low values of Γ the heat flux to the ice front is low enough so that heat leakage is no problem. At high values of Γ, the heat flux is large but so is the sublimation rate (low λ for example). As a result the total drying time is very short and the effect of heat leakage is minimized.

Since the heat of sublimation for ice is large, it would

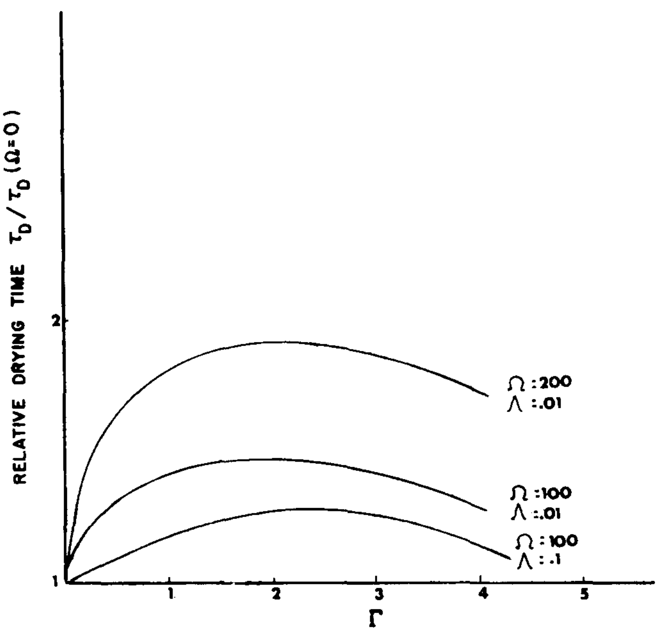

Fig. 2. The effect of heat leakage on drying time ($N_{Le}\Psi = .1$).

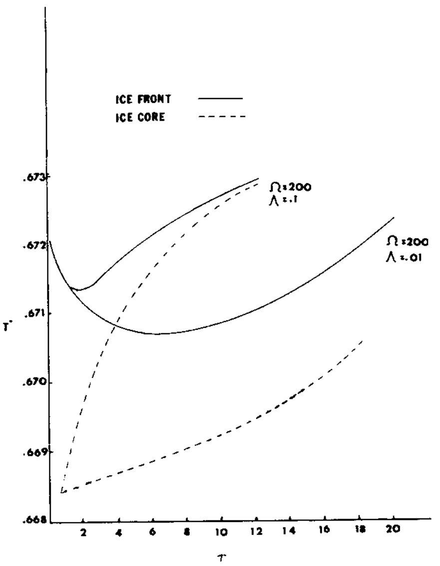

Fig. 3. The effect of heat leakage on the ice temperature ($\Gamma = .5$, $N_{Le}\Psi = .01$).

appear that heat leakage into the core does not account for the erroneous drying times sometimes predicted by the pseudo steady state model.

However it is also important to evaluate the effect of heat leakage on the temperatures at the ice front since local melting will occur if the triple point of water is exceeded. Figure 3 shows the relationship between the ice core and the ice front temperatures as a function of time. While results are shown only for a Γ of 0.5, it was found that the magnitude of the ice front temperatures varied directly with Γ. This would be expected since large values of Γ correspond to large heat fluxes and/or low diffusivities and it becomes necessary for the local vapor concentration at the ice front to increase so that the mass transport driving force increases. The ice-vapor equilibrium relationship would then dictate a higher ice front temperature.

In Figure 3 the cases with high values of Λ exhibit a dip at the beginning of the run. This can be attributed to the interrelationship of the heat leakage into the core and the ice-vapor equilibrium at the ice front. That is, at the beginning of the run the ice core temperature is low thereby encouraging large heat leakage. Since there is a correspondingly lower sublimation rate, the ice front temperature must dip so that the vapor concentration at the ice front is low enough to reduce the mass transport driving force. Later in the run the ice core temperature begins to rise and the subsequent reduction in heat leakage requires a higher sublimation rate and a correspondingly higher ice front temperature. Thus when Γ is large there is a definite danger that the ice front temperature may exceed the triple point. In this case heat leakage into the core is an advantage since it delays the increase in the ice front temperature and can in fact result in a temporary reduction in the ice front temperature as shown in Figure 3. It is then to be hoped that the drying time will be less than the time required for the ice front temperature to exceed the triple point.

These results can be extended directly to the chemical reaction problem. In such a case the total reaction time could be significantly increased due to heat leakage provided that the heat of reaction is not very large. Also, decreases in the unreacted front temperature as predicted in Figure 3 would cause a decreased reaction rate and longer reaction times.

Accumulation Model

The results obtained with the Accumulation Model are shown in Figures 4 and 5. As can be seen from Figure 4, at low values of $N_{Le}\Psi$ or when the ice core is shrinking slowly [see Equation (22)], the drying time is inversely proportional to Γ. Note also that when $N_{Le}\Psi$ is low the pseudo steady state solution is identical to solutions obtained with the Accumulation Model. However as $N_{Le}\Psi$ increases, the core front recedes at a faster rate and accumulation in region I begins to become important. Thus at $N_{Le}\Psi = 9.0$, the drying time as predicted by the Accumulation Model is more than twice that predicted by the pseudo steady state model.

Figure 5 shows the temperature response of the ice front as a function of time for various Lewis numbers. When the Lewis number is high, the ice front temperature drops at the end of the run. This is because at high Lewis numbers heat accumulation dominates and at the end of the run there is a large volume available for accumulation to take place. Thus the sublimation rate decreases and the ice front must cool in order to lower the mass transport driving force. At low Lewis numbers the opposite takes place and the ice front temperature increases at the end of the run. In this case mass accumulation is dominant and the mass transport driving force must increase in

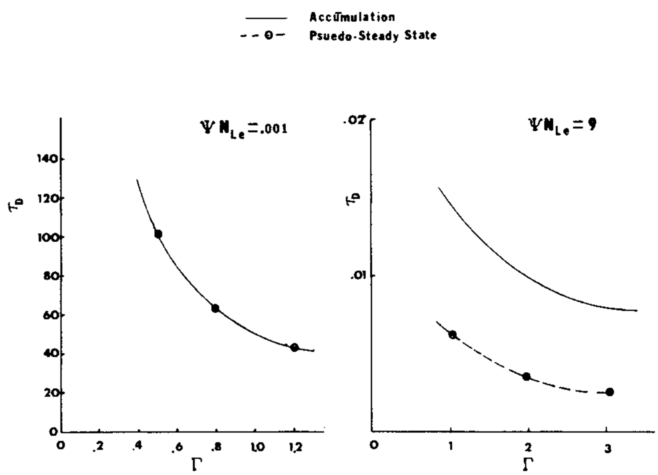

Fig. 4. The effect of accumulation on drying time.

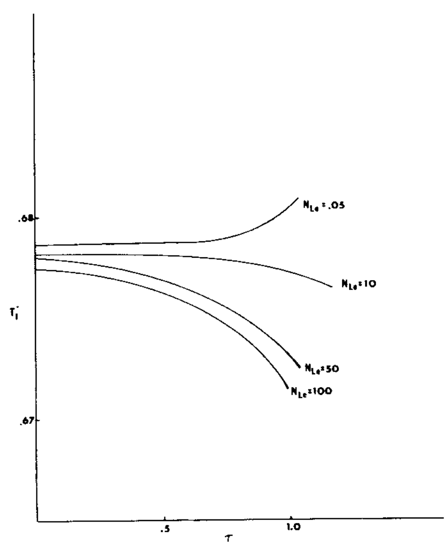

Fig. 5. The effect of accumulation on the ice front temperature ($\Psi = .2$, $\Gamma = 1$).

order to remove the vapor from the sample. In this latter case heat leakage could also be important and the two models would have to be joined in order to obtain quantitative results.

The results shown in Figure 5 are for $\Psi = 0.2$. As the magnitude of Ψ increases, the temperature response in Figure 5 would be more severe and would occur earlier in the run. Lower values of Ψ require larger (or smaller) values of the Lewis number to produce the trends shown in Figure 5.

CONCLUSIONS

The objective of this work has been to determine the conditions under which pseudo steady solutions are not descriptive of sublimation drying problems and certain noncatalytic, heterogeneous reactions. By analyzing for the two extreme conditions which would alter the pseudo steady state predictions (heat leakage and accumulation) in a separate manner, results have been obtained which yield the critical values of the pertinent dimensionless parameters.

As far as total drying time (or total reaction time) is concerned, heat leakage will be important only when both the thermal leakage parameter and the thermal capacitance of the core are high (high Ω, low Λ) and then only for intermediate values of Γ. Accumulation affects total drying time only when the core recedes relatively fast (high values of Ψ). For the sublimation drying of most foods, none of these dimensionless parameters are of sufficient magnitude to warrant anything but a pseudo steady state solution to predict total drying time. Thus we can conclude that the inability of the pseudo steady state solution to give accurate predictions of total drying time is not due to the decoupling of heat and mass transport, the neglect of heat leakage into the ice core, or to the neglect of accumulation in the dried region. Neither does it appear that the total reaction time for the thermal decomposition of $CaCO_3$ will be affected by either heat leakage or accumulation. However this latter conclusion should be verified by replacing the ice-vapor equilibrium with the reaction rate as a function of temperature. For other applications, calculations should be made of Ω, Λ, Γ, and Ψ before deciding on whether a pseudo steady state analysis is adequate.

However it was found that the ice front temperatures were very sensitive to both heat leakage and accumulation. This becomes very important in sublimation drying since the ice front temperature must remain below the triple point of water. Similarly, in reaction problems the reaction rate is very often a sensitive function of temperature. While the ice front temperatures would not be influenced by heat leakage or accumulation for heat transfer limited sublimation drying, calculations indicate that both could be significant in some applications. Thus values for Γ could be high in the sublimation drying of some liquid footstuffs and the Lewis number can be low in some heterogeneous reaction problems. In any case, calculations of the Lewis number along with Ω, Λ, and Ψ will at least provide a quantitative basis for an appropriate analytical decision.

ACKNOWLEDGMENT

The authors express their gratitude to Potlatch Forest Inc. for their financial support of Mr. Fox during this work. The authors would also like to thank Mr. Harvey Harding for his assistance in the numerical analysis.

NOTATION

C = vapor concentration
C^* = dimensionless concentration, C/C_R
C_p = heat capacity
D = diffusivity
f^e = equilibrium function
k = thermal conductivity
M_w = molecular weight
N_{Le} = Lewis number, D/α
r = distance from center of sphere
R = outer radius of sample
s = radius of core
s^* = dimensionless core radius, s/R
T = temperature
T^* = dimensionless temperature, T/T_R
T_s = ice front temperature
t = time
α = thermal diffusivity, $k/\rho C_p$
$\Gamma = \dfrac{kT_R}{M_w C_R D \lambda}$
$\Lambda = \dfrac{\alpha_2}{\alpha_1}\dfrac{R}{\delta}$
λ = heat of sublimation
ρ = density
τ = dimensionless time $\dfrac{\alpha_1 t}{R^2}$
τ_D = dimensionless drying time
ϕ = dimensionless radius $\dfrac{r-s}{R-s}$
$\Psi = C_R M_w/\rho$
$\Omega = \dfrac{k_2 T_R}{M_w C_R D \lambda}\dfrac{R}{\delta}$
* = dimensionless variable
$_R$ = outer radius of the sphere
$_1$ = dried region
$_2$ = core region

LITERATURE CITED

Carnahan, B., H. A. Luther, and J. O. Wilkes, Applied Numerical Methods, Wiley, New York (1969).

Dyer, F. D., "Transport Phenomena in Sublimation Dehydration," Ph.D. thesis, Georgia Inst. Technology, Atlanta (1964).

Hill, J. E., and J. E. Sunderland, "Sublimation-Dehydration in the Continuum, Transition and Free Molecule Flow Regimes," *Intern. J. Heat Mass Transfer*, **14**, 625 (1971).

Hills, A. W. D., "The Mechanism of the Thermal Decomposition of Calcium Carbonate," *Chem. Eng. Sci.*, **23**, 297 (1968).

Ishida, M., Y. Kishio, and S. Takashi, "The Applicability of the Pseudo-Steady State Approximation to Moving Boundary Problems for Spheres," *Chem. Eng. of Japan*, **3**, 49 (1970).

King, C. J., Freeze Drying of Foods, CRC Press, Cleveland, Ohio (1971).

McCulloch, J. W., and J. E. Sunderland, "Integral Techniques Applied to Sublimation Drying with Radiation Boundary Condition," *J. Food Sci.*, **35**, 834 (1970).

Sandall, O. C., "Interactions Between Heat and Mass Transfer in Freeze Drying, Ph.D. thesis," Univ. of Calif., Berkeley (1966).

———., C. J. King, and C. R. Wilke, "The Relationship Between Transport Properties and Rates of Freeze-Drying of Poultry Meat," *AIChE J.*, **13**, 428 (1967).

Wen, C. Y., "Non-Catalytic Heterogeneous Solid Fluid Reaction Models," *Ind. Eng. Chem.*, **60**, 34 (1968).

———., and L. Y. Wei, "Simultaneous Nonisothermal Noncatalytic Solid-Gas Reactions," *AIChE J.*, **17**, 272 (1971).

Manuscript received August 27, 1971; revision received March 15, 1972; paper accepted March 16, 1972.