Int. J. Heat Mass Transfer. Vol. 14, pp. 625–638. Pergamon Press 1971. Printed in Great Britain

SUBLIMATION–DEHYDRATION IN THE CONTINUUM, TRANSITION AND FREE-MOLECULE FLOW REGIMES*

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(*Received* 25 *March* 1970 *and in revised form* 17 *August* 1970)

Abstract—A theoretical analysis is presented for heat and mass transfer during sublimation–dehydration. The energy equations in the dried and frozen regions are solved. Equations are presented for hydrodynamic and diffusional flow in the dried region for free-molecule, transition, and continuum flow regimes. The energy and vapor flow equations are coupled to give closed form solutions for the interface temperature as a function of the flow regime, interface position, transport property data, and externally controlled boundary conditions. The equations are valid for simultaneous hydrodynamic and diffusional flow in the continuum and transition flow regimes, and are valid for molecular diffusion in the free-molecule regime. Closed form equations are presented for the interface position as a function of time for cases where the interface temperature is either constant or a linear function of the interface position.

The results indicate that if heat is transferred through both the dried and frozen layers, the interface temperature will change as the interface position changes. Numerical calculations for freeze-drying beef show that this relationship is approximately linear for chamber pressures between 0·5 and 4·0 torr. It is also found that the pressure which gives the fastest drying rate for beef is between 0·5 and 1·0 torr. For all beef samples 1·5 inches thick or less, drying is faster when it takes place from both faces than when it takes place from only one face and heat is conducted through the back face. Numerical calculations are presented which show the feasibility of atmospheric freeze-drying of thin samples.

NOMENCLATURE

A,	defined by equation (29) [lbf^{2}s/lbm ft^3];
B,	defined by equation (30) [lbf^2/ft^4];
C,	defined by equation (31) [lbm lbf^2/s ft^5];
C_2,	defined by equation (25) [1/ft^2];
C_3,	defined by equation (37) [B/s];
C_4,	defined by equation (38) [B/fts];
C_5,	defined by equation (39) [B/ft^2 s];
C_6,	defined by equation (40) [B/ft^3];
C_7,	defined by equation (41) [B/ft^2];
C_8,	defined by equation (42) [B/ft^4];
C_p,	specific heat [B/lbm °R];
D,	mutual diffusion coefficient [ft^2/s];
D_K,	Knudsen's diffusion coefficient defined by $(2/3)r_c\bar{v}$ [ft^2/s];
F_2,	parameter defined by equation (8) [1/ft];
g_c,	constant equal to 32·2 [ft lbm/lbf s^2];
ΔH,	heat of sublimation [B/lbm];
k,	thermal conductivity [B/s ft °R];
Kn,	Knudsen number $(\lambda/2r_c)$ [dimensionless];
l,	length of capillary tube [ft];
L,	thickness of freeze-drying sample [ft];
M,	molecular weight;
N,	mass flow rate [lbm/ft^2 s];
$\bar{N}$,	molar flow rate [moles/ft^2 s];
P,	total pressure [lbf/ft^2];
$\bar{P}$,	partial pressure [lbf/ft^2];

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*This investigation was supported by the Public Health Service Research Grants UI 00093–04, UI 00712–01 and UI 00712–02 from the National Center for Urban and Industrial Health and FD–00156–03 from the Food and Drug Administration.

ΔP, pressure difference [lbf/ft^2];
Q, parameter defined by equation (22) [lbm/ft s];
r_0, constant defined by equation (35) [°R];
r_1, constant defined by equation (35) [°R/ft];
r_c, capillary radius [ft];
R, gas constant [ft lbf/lbm °R];
$\bar{R}$, universal gas constant [ft lbf/mole °R];
R_2, parameter defined by equation (26) [lbm^2/ft^{4}s^2];
R_3, parameter defined by equation (27) [lbm/ft^3 s];
S. reflection coefficient [dimensionless];
t, time [s];
T, temperature [°R];
u, macroscopic gas velocity [ft/s];
$\bar{v}$, average molecular velocity [ft/s];
x, freeze-dried model coordinate [ft];
X, position of interface between dried and frozen regions [ft];
y, molar concentration, moles of component divided by moles of mixture;
β, function defined by equation (5) [1/ft];
Γ, first-order correction for nonroundness and other irregularities of the capillary [dimensionless];
ε_D, permeability in the continuum regime [ft^2];
ε, permeability in the transition regime [ft^2];
η, viscosity [lbf s/ft^2];
λ, mean free path [ft];
μ, viscosity [lbm/ft s];
ρ, density [lbm/ft^3];
σ, porosity, pore volume divided by total volume [dimensionless];
τ, tortuosity factor [dimensionless].

Subscripts
a, air;
e, effective;
i, ice;
L, position at frozen back face;
w, water vapor;
X, position of interface;
0, position at dried surface;
I, dried region;
II, frozen region.

INTRODUCTION

SUBLIMATION-dehydration is a process where biological substances are preserved by drying in the frozen state. The substance to be dried is frozen and then placed in a vacuum chamber where the pressure is lower than the triple point of water. Heat is supplied to the product whereupon the frozen water component sublimates and the vapor passes out into the chamber. The vapor is then collected or carried away. The process can be depicted as a one-dimensional situation where the ice front recedes into the product as heat is continually supplied. The vapor flows through the resulting dried layer under the influence of a total pressure gradient and a partial pressure gradient of the water vapor.

There have been previous heat and mass transfer analyses reported on the freeze-drying process. In [1–6], various assumptions were made to limit the generality of the results. These include considering either hydrodynamic or diffusional flow but not both, considering heat transfer only through the dried region, not considering all the flow regimes, considering the interface temperature and pressure constant or not specifying how to determine them. Dyer and Sunderland [7] present an analytical solution for freeze-drying by coupling the energy, diffusion and hydrodynamic equations. They consider the general case where heat is transferred through both the dried and frozen regions and the interface parameters vary throughout the process. However, they only consider drying in the transition regime, and assume that the temperature distribution in the dried region is linear. This seems to be quite valid for drying of beef, but might limit the application to other processes. In addition, the calculation procedure involves trial and error solutions that must be carried out on a computer.

There is a need for a general analysis of the freeze-drying process that will yield useful results, yet still adequately represent the physical situation. The purpose of this paper is to present an analysis giving closed form solutions for the drying time when hydrodynamic and diffusional flow at all pressures, as well as heat transfer through the dried and frozen regions are considered.

ANALYTICAL INVESTIGATION

A one-dimensional model of the freeze-drying process is illustrated in Fig. 1. As drying proceeds, a dried layer forms and is distinctly separated from the frozen layer of the product. The interface thickness between the dried and frozen layers has been measured during drying of beef by Hatcher [8] and found to be less than 5 mm thick. Hatcher also found that after the phase front passed a specific position in the meat, there was no more than a 3 per cent variation in the moisture content for the remainder of the process. In addition, there was less than a 3 per cent change in the moisture content of the frozen section until the passage of the phase front. Most foods have a structure similar to wood in that they have a grain growth in a certain direction. This grain or fiber direction is usually oriented parallel to the heat and vapor transport, because the thermal conductances are larger in this direction. The pore structure of the dried region is a complex path in one general direction which can be idealized as a tortuous bundle of capillary tubes of non-uniform cross section. Heat required for sublimation may be transferred by conduction through the porous dried layer, or it may be conducted through the frozen layer, or it may be conducted through both. The sublimated vapor flows through the dried layer under the influence of both a total pressure gradient and a partial pressure gradient. The model described above can be adapted to the special case of equal drying from both sides by simply letting $x = L$ be the center line of the product and setting the heat transfer through the frozen layer equal to zero.

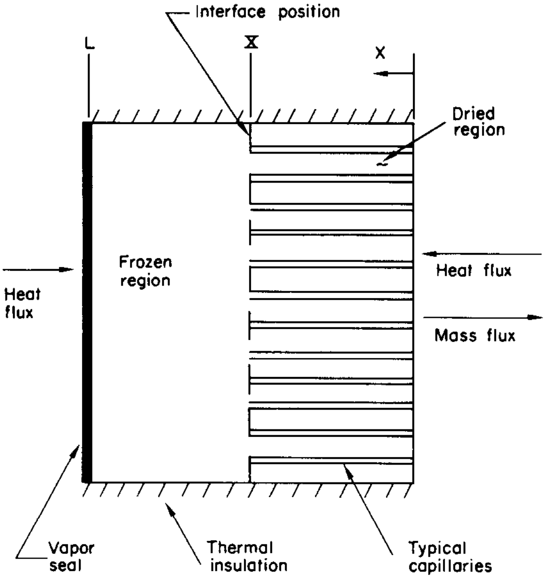

FIG. 1. Model of freeze-drying process.

The theoretical analyses involve solving the energy equation for both the dried and frozen regions, solving the continuity and momentum equations for the vapor flux in the continuum, transition, and the free-molecule flow regimes, and combining the equations to determine how the interface temperature varies throughout the drying process. With the interface temperature established, equations will be derived for both the drying rate and the drying time as a function of the sample thickness and drying regime.

All transport properties which are pressure and/or temperature dependent will be evaluated at the vacuum chamber pressure and mean temperature, respectively. Thus, for a given vacuum chamber pressure and fixed boundary temperatures, all transport properties will be treated as constants. In addition, at any point in the dried layer, the vapor temperature and the dried food product temperature are assumed equal.

All of the energy, continuity and momentum equations used will be one-dimensional and "quasi-steady." The latter assumption implies that the time rates of change of properties (except the change of enthalpy with phase change) are assumed negligible in comparison to the space rates of change. Due to the slow drying rates this assumption appears to be valid; for example, it takes approximately 30 h to dry a slab of beef 1·5 in. thick. In addition, Dyer [9] solved the "exact" and "quasi-steady" energy equations assuming that the interface temperature remained constant. He used the results to get drying times and found that the two separate methods differed by only 2 per cent.

The type of flow in the capillary channels depends upon the ratio of the mean-free path of the vapor molecules to the capillary diameter, the Knudsen number. Continuum flow exists for $Kn < 0{\cdot}01$, transition flow exists for $0{\cdot}01 < Kn \leqslant 2$, and the free-molecule flow exists for $Kn > 2$.

Energy equation

The following equation for the temperature distribution in the dried region can be obtained by making an energy balance on a differential element:

$$\frac{\mathrm{d}^2 T_I}{\mathrm{d}x^2} + \frac{C_p \rho_i \sigma}{k_I} \frac{\mathrm{d}X}{\mathrm{d}t} \frac{\mathrm{d}T_I}{\mathrm{d}x} = 0. \tag{1}$$

The first and second terms represent conductive and convective heat transfer respectively. If the mass-transfer rate were small so that the convective effect could be neglected, the governing equation would simply be the one-dimensional steady state heat conduction equation, and the solution would be a linear temperature profile. Therefore, the mass transfer accounts for the non-linearity of the temperature distribution in the dried region. The boundary conditions are

$$T_I = T_0 \quad \text{at } x = 0 \tag{2}$$

$$T_I = T_X \quad \text{at } x = X. \tag{3}$$

The solution to equation (1) is

$$\frac{T_I - T_0}{T_X - T_0} = \frac{1 - \mathrm{e}^{-\beta x}}{1 - \mathrm{e}^{-\beta X}} \tag{4}$$

where

$$\beta = \frac{\rho_i \sigma C_p}{k_I} \frac{\mathrm{d}X}{\mathrm{d}t}. \tag{5}$$

It will be seen later that T_X actually varies during the drying process if heat is conducted through both the dried and frozen layers. Since the interface movement is extremely slow, it will be assumed that equation (4) adequately represents the temperature distribution in the dried region at any instant. Since there is no mass transfer occurring in the frozen region, the temperature distribution is linear and given by:

$$\frac{T_{II} - T_L}{T_X - T_L} = \frac{x - L}{X - L}. \tag{6}$$

Equation (4) cannot be used if closed formed solutions are desired because the interface position and its derivative both appear in the argument of the exponential term. Some approximation to the above profile must then be used. Dyer and Sunderland [7] expanded the exponential terms in a Taylor series and neglected all terms of higher order than one. This amounts to the same thing as assuming a linear temperature profile in the dried region, which is quite acceptable for most freeze-drying processes where the mass-transfer rates are low. However, a second ordered polynomial will be used in this analysis to be as general as possible. By using the boundary conditions (2) and (3) with an energy balance at the interface, the assumed profile reduces to:

$$\frac{T_I - T_0}{T_X - T_0} = \frac{x}{X} + \left[1 - \frac{x}{X}\right]\left[\frac{x}{X} - F_2 x\right] \tag{7}$$

where

$$F_2 = \frac{\Delta H \rho_i \sigma \dfrac{\mathrm{d}X}{\mathrm{d}t} - k_{II}\left[\dfrac{T_X - T_L}{X - L}\right]}{[T_0 - T_X]\, k_I}. \tag{8}$$

Continuity equations

For either the sublimated vapor or air, from the conservation of mass for steady, one-dimensional flow, it follows that the flow rate is constant. Since for the air species the flow rate is zero at the interface, it is zero throughout the entire dried layer.

Momentum equations

Free-molecule flow regime. The momentum equation for a gaseous mixture in the free-molecule flow regime, in a capillary tube of uniform cross-section and length is given by Present [10]

$$N = \frac{2r_c}{3}\bar{v}\frac{\Delta P}{lRT} \tag{9}$$

where $\bar{v}$ is the average molecular speed given by $(8\bar{R}T/\pi M)^{\frac{1}{2}}$. Equation (9) was derived for isothermal flow. Therefore, in order to use this equation, it will be assumed that the temperature gradient in the dried region has no effect on the flow rate, and the vapor properties can be evaluated at an average temperature. Dyer [9] showed both experimentally and analytically that this thermal transpiration effect is negligible in the transition regime. It was shown by Hill [17] that the effect is also negligible in the free-molecule and continuum regimes. According to Present, if a free-molecule flow of a binary gas mixture takes place, the component gases will diffuse along the tube independently of each other and equation (9) can be applied to each gas separately, if ΔP is interpreted as the partial pressure drop.

Several corrections must be made to equation (9) in order to make it applicable to flow in porous media. The flow is for a unit area of the capillary tube. In order to convert the flow to a unit surface area of the food sample, the equation must be multiplied by the porosity, σ. The vapor actually travels a longer, tortuous path through the food, so the equation is corrected by multiplying the equation by a constant Γ. The temperature of the vapor in equation (9) will be taken as the average temperature between the interface and the surface. Therefore, the momentum equation representing the flow rate of water vapor in the free-molecule flow regime is given by

$$N_w = \frac{4r_c\Gamma\bar{v}_w\sigma\,[\bar{P}_{w0} - \bar{P}_{wX}]}{3\tau XR\,[T_0 + T_X]}. \tag{10}$$

Continuum flow regime. The momentum equation for the gaseous mixture is derived from Darcy's Law (see Carman [11]) for flow through a porous material. Thus

$$N = -\frac{\rho}{\eta}\varepsilon_D\frac{\partial P}{\partial x}. \tag{11}$$

The proportionality constant ε_D is called permeability and is usually experimentally determined for the material under study. If the equation is integrated, again assuming isothermal flow, the mass rate of flow of water vapor is

$$N_w = \frac{\rho\varepsilon_D\,[P_0 - P_X]\,g_c}{\mu X}. \tag{12}$$

It should be noted that the actual density variation in the dried region is such that under the most severe conditions, the local values will not deviate from the density calculated at the average region temperature by more than 10 per cent.

In the analytical model, the pressure quantities that are assumed known are the total chamber pressure, P_0, partial pressure of the water vapor in the chamber, $\bar{P}_{w0}$, and the partial pressure of the water vapor at the interface, $\bar{P}_{wX}$. Under actual drying conditions, P_0, and $\bar{P}_{w0}$ can be controlled by properly regulating the flow of air and water vapor in the chamber. The last quantity is assumed to be the equilibrium vapor pressure of the frozen solid at the temperature that exists at the interface. This relationship was determined for several frozen meats by Hill and Sunderland [12]. Note that the total pressure at the interface appears in equation (12) and is therefore an unknown quantity. It must be determined by use of an additional momentum equation for this regime.

Johnson [13] and [14] suggests that the steady diffusion equation (Fick's law) for continuous transport can be interpreted as an equation of motion of one of the constituent gases. Thus

$$\bar{N}_w = y_w(\bar{N}_w + \bar{N}_a) - \frac{PD_{aw}}{\bar{R}T}\frac{\mathrm{d}y_w}{\mathrm{d}x}. \tag{13}$$

Since D_{aw} is inversely proportional to pressure (from kinetic theory) and $\bar{N}_a = 0$ (from continuity), the equation can be integrated directly to give:

$$N_w = \frac{PD_{aw}}{RTX} \ln \left\{ \frac{1 - y_{wX}}{1 - y_{w0}} \right\}. \tag{14}$$

Equation (14) represents the flow if D_{aw} is the effective diffusion coefficient for flow in a porous medium $[D_{aw}]_e$. In applying the theory, a value for $[D_{aw}]_e$ of $\frac{1}{3}$ the value for free diffusion in air at atmospheric pressure, as suggested by Harper and Chichester [15] will be used.

Equations (12) and (14) can be combined to eliminate the total pressure at the interface:

$$N_w = \frac{\rho[D_{aw}]_e}{X} \ln \left\{ \frac{1 - \dfrac{\bar{P}_{wX}}{P_0 - [\mu X N_w / \rho \varepsilon_D g_c]}}{1 - \dfrac{\bar{P}_{w0}}{P_0}} \right\}. \tag{15}$$

Transition flow regime. The momentum equation for the gaseous mixture is:

$$N_w = \frac{\rho\varepsilon[P_0 - P_X]\, g_c}{\mu X}. \tag{16}$$

pressure difference terms, as shown by Dyer and Sunderland [7].

As in the continuum regime, the total pressure at the interface can be eliminated by using an applicable diffusion equation. Dyer and Sunderland [16] presented and solved numerically the diffusion equation for the transition regime. More recently, Hill [17] solved the equation in closed form using an approximate integral technique to give:

$$N_w = \frac{\rho}{X} \frac{y_{wX} - y_{w0}}{\dfrac{1}{D_{aw}} \left\{ \dfrac{y_{w0} + y_{wX}}{2} - 1 \right\} - \dfrac{8}{3\pi D_{kw}}}. \tag{17}$$

As in the continuum regime, equation (17) can be applied if D_{aw} and D_{kw} are effective coefficients. Again, a value for $[D_{aw}]_e$ of $\frac{1}{3}$ the value for free diffusion in air at atmospheric pressure will be used. The effective value of the Knudsen diffusion coefficient will be obtained by a formula suggested by Scott and Dullien [18]

$$\frac{[D_{aw}]_e}{[D_{kw}]_e} = \frac{D_{aw}}{D_{kw}}. \tag{18}$$

Equations (16) and (17) can be combined to eliminate the total pressure at the interface.

$$N_w = \frac{\rho}{X} \frac{\dfrac{\bar{P}_{wX}}{P_0 - \mu X N_w / \rho \varepsilon g_c} - \dfrac{\bar{P}_{w0}}{P_0}}{\dfrac{1}{[D_{aw}]_e} \left\{ \dfrac{\dfrac{\bar{P}_{w0}}{P_0} + \dfrac{\bar{P}_{wX}}{P_0 - \mu X N_w / \rho \varepsilon g_c}}{2} - 1 \right\} - \dfrac{8}{3\,\pi[D_{kw}]_e}}. \tag{19}$$

This equation takes the same form as that of the continuum regime with the exception that ε is now the permeability of the porous solid filled with gases at a pressure in the transition regime. From molecular theory it can be shown that the flow rate in the transition regime will not be directly proportional to the pressure difference as seems to be indicated by equation (16). However, this is consistent with the present analysis since the permeability itself contains

It is important to note the significance of equations (15) and (19). If there is no concentration or partial pressure gradient in the dried region, the flow rate of water vapor will be zero. The reason for this has been noted previously by Dyer [19]. Whenever there is a binary mixture flowing under steady state conditions away from an interface where one of the components is insoluble, the concentration gradient and total pressure gradient are not independent. One cannot occur without the other. This is not to say that drying cannot take place when $dy_w/dx = 0$ and $dP/dX \neq 0$. In fact, it has recently been noted by Massey [20] that under some freeze-drying conditions, the water vapor moves out of the dried region so fast that all residual air is swept away and only hydrodynamic flow takes place; diffusional flow is negligible. In that case equations (15) and (19) are not applicable since there is no longer a flow of two species. Equations (12) and (16) are then the governing momentum equations for the water vapor flow. The remainder of this work will be applicable to the conditions of two species bulk and diffusional flow. The special case of one species hydrodynamic drying will be discussed in a later paper.

Interface temperature

An energy balance over the dried region is used to couple the energy and momentum equations to get the interface temperature relations.

$$k_{II}\left.\frac{dT_{II}}{dx}\right|_{x=X^+} - k_I\left.\frac{dT_I}{dx}\right|_{x=0^+} - C_pN_w[T_0 - T_X] = [-N_w\Delta H]. \tag{20}$$

If the temperature gradients are obtained from equations (6) and (7) and if equation (20) is slightly rearranged, the result is:

$$\frac{\dfrac{k_{II}[T_X - T_L]}{X - L} + \dfrac{k_I[T_0 - T_X]}{X}}{\Delta H + \dfrac{C_p}{2}[T_0 - T_X]} = -N_w. \tag{21}$$

After substitution of the appropriate flow equation [equation (10) for the free-molecule regime, equation (15) for the continuum regime and equation (19) for the transition regime] into equation (21), it is found that the following relationship for the interface position had the same form for all three regimes:

$$\frac{X}{X - L} = \frac{k_I[T_X - T_0] + \left\{\Delta H + \dfrac{C_p}{2}[T_0 - T_X]\right\}Q}{k_{II}[T_X - T_L]}. \tag{22}$$

Expressions for Q are given below for the three flow regimes. For the free-molecule flow regime,

$$Q = [\bar{P}_{wX} - \bar{P}_{w0}]\tfrac{2}{3}r_c\frac{\Gamma}{\tau}\bar{v}_w\frac{\sigma}{R}\frac{2}{T_0 + T_X}. \tag{23}$$

In the transition flow regime,

$$Q = \frac{R_3 - [4C_2R_2 + R_3^2]^{\frac{1}{2}}}{2C_2} \tag{24}$$

where

$$C_2 = \frac{\bar{P}_{w0}\mu}{P_0\rho\varepsilon 2[D_{aw}]_e} - \frac{\mu}{\rho\varepsilon[D_{aw}]_e} - \frac{8\mu}{3\pi\rho\varepsilon[D_{kw}]_e}, \tag{25}$$

$$R_2 = \rho[\bar{P}_{w0} - \bar{P}_{wX}]g_c, \tag{26}$$

and

$$R_3 = g_c\left\{\frac{P_0}{[D_{aw}]_e} + \frac{8P_0}{3\pi[D_{kw}]_e} + \frac{\bar{P}_{w0}\mu}{P_0\varepsilon g_c} - \frac{\bar{P}_{w0} + \bar{P}_{wX}}{2[D_{aw}]_e}\right\}. \tag{27}$$

For the continuum flow regime,

$$Q = \frac{-B + [B^2 - 4AC]^{\frac{1}{2}}}{2A} \tag{28}$$

where

$$A = \frac{2P_0\mu}{\rho\varepsilon_D g_c} - \frac{\bar{P}_{w0}\mu}{\rho\varepsilon_D g_c}, \tag{29}$$

$$B = 2P_0^2 - \bar{P}_{w0}P_0 - \bar{P}_{wX}P_0 + \frac{\bar{P}_{w0}\mu}{\rho\varepsilon_D g_c}2\rho[D_{aw}]_e, \tag{30}$$

and

$$C = 2\rho[D_{aw}]_e[\bar{P}_{w0}P_0 - \bar{P}_{wX}P_0]. \tag{31}$$

For the special case where the back face is perfectly insulated or there is equal drying from both sides, equation (21) takes the form:

$$\frac{k_I[T_0 - T_X]}{\Delta H + (C_p/2)[T_0 - T_X]} = - N_w X. \quad (32)$$

By substituting the appropriate equation for N_w, it can be shown that T_X is a constant throughout the process, regardless of the flow regime.

Drying time equations

The differential equation describing the interface movement is obtained by combining equation (20) with the following mass balance at the interface:

$$- N_w = \rho_i \sigma \frac{\mathrm{d}X}{\mathrm{d}t} \quad (33)$$

The resulting differential equation takes the form:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{\dfrac{k_{II}[T_X - T_L]}{X - L} + \dfrac{k_I[T_0 - T_X]}{X}}{\rho_i \sigma \{\Delta H + (C_p/2)[T_0 - T_X]\}} \quad (34)$$

with boundary condition $X = 0$ at $t = 0$.

Before equation (34) can be solved, a relationship for T_X as a function of X must be obtained from equation (22). This can be accomplished by plotting T_X as a function of X and then using the least squares method for expressing T_X as a polynomial function of X. If the following linear relation between T_X and X is used,

$$T_X = r_0 + r_1 X \quad (35)$$

then the differential equation can be solved in closed form to give

$$t = \frac{C_8}{C_5}\frac{X^2}{2} + \frac{C_6}{C_5} X + \frac{C_7 C_5 - C_6 C_4}{2 C_5^2} \ln\left\{\frac{C_5}{C_3} X^2 + \frac{C_4}{C_3} X + 1\right\} + \frac{C_6 C_4^2 - 2 C_6 C_3 C_5 - C_7 C_4 C_5}{2 C_5^2[C_4^2 - 2 C_3 C_5]^{\frac{1}{2}}} \ln\left\{\frac{\dfrac{2 C_5 X + C_4 - [C_4^2 - 4 C_3 C_5]^{\frac{1}{2}}}{2 C_5 X + C_4 + [C_4^2 - 4 C_3 C_5]^{\frac{1}{2}}}}{\dfrac{C_4 - [C_4^2 - 4 C_3 C_5]^{\frac{1}{2}}}{C_4 + [C_4^2 - 4 C_3 C_5]^{\frac{1}{2}}}}\right\} \quad (36)$$

where

$$C_3 = L k_I[r_0 - T_0], \quad (37)$$

$$C_4 = k_{II}[r_0 - T_L) + k_1 r_1 L - k_1[r_0 - T_0], \quad (38)$$

$$C_5 = r_1[k_{II} - k_I], \quad (39)$$

$$C_6 = \frac{\rho_i \sigma}{2}\left\{2 \Delta H + C_p r_1 L - C_p[r_0 - T_0] + \frac{C_p k_{II}[r_0 - T_L]}{[k_{II} - k_I]} + \frac{C_p k_I r_1 L}{[k_{II} - k_I]} - \frac{C_p k_I[r_0 - T_0]}{[k_{II} - k_I]}\right\}, \quad (40)$$

$$C_7 = \frac{\rho_i \sigma}{2} L\left\{C_p[r_0 - T_0] - 2 \Delta H + \frac{C_p k_I[r_0 - T_0]}{[k_{II} - k_I]}\right\}, \quad (41)$$

and

$$C_8 = - \frac{\rho_i \sigma}{2} C_p r_1. \quad (42)$$

The total time can be determined by substitution of $X = L$ into equation (36).

For the case where equation (35) does not adequately describe the interface relation, an equation of higher order must be used, and the differential equation must be integrated numerically. The numerical technique used in this paper is similar to that suggested by Dyer and Sunderland [7].

For the special case where the back face is perfectly insulated or there is equal drying from both sides, $T_X = T_L$ and the interface temperature remains constant. Therefore, equation (34) is easily integrated to give:

$$t = \frac{\rho_i \sigma \{\Delta H + (C_p/2)[T_0 - T_X]\}}{k_I[T_0 - T_X]} \cdot \frac{X^2}{2}. \tag{43}$$

The total drying time is obtained by setting $X = L$.

DISCUSSION OF THEORETICAL RESULTS

Numerical calculations have been carried out for the freeze-drying of beef using the theoretical analysis. Beef was chosen because of available property data and also because experimental drying times were available for comparison.

Values of the mean radius of the capillary channels r_c and the tortuosity factor τ for beef were taken from the work of Harper [21] and were 0·000164 ft and 4·4 respectively. The thermal conductivity of the dried region was calculated by a formula suggested by Massey and Sunderland [22]. The thermal conductivity of the frozen region was taken from the work of Hill, Leitman and Sunderland [23]. The latent heat of sublimation and the equilibrium vapor pressure of frozen beef was taken from the experimental data of Dyer *et al.* [24]. The porosity of freeze-dried beef was taken to be 0·70 as suggested by Harper and Tappel [1]. The diffusion coefficients for air and water vapor were calculated by methods outlined by Reid and Sherwood [25]. The permeability of freeze-dried beef to the flow of water vapor in the transition regime was calculated according to the work of Dyer [9], and the permeability in the continuum regime was calculated according to Carman [11]. In addition, Carman suggested the correction factor for nonroundness of the capillary tubes in the freeze-dried region to be $\Gamma = 0·8$.

Theoretical interface temperatures

The interface temperature as a function of the

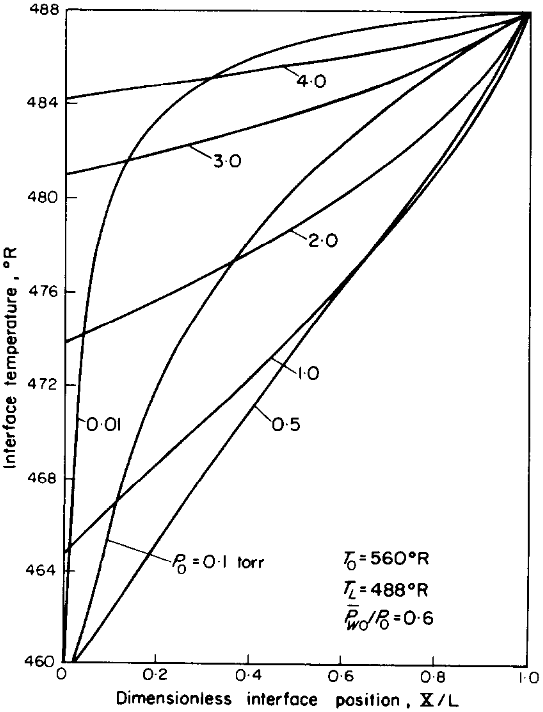

FIG. 2. Interface temperature as a function of dimensionless interface position for unidirectional drying of beef.

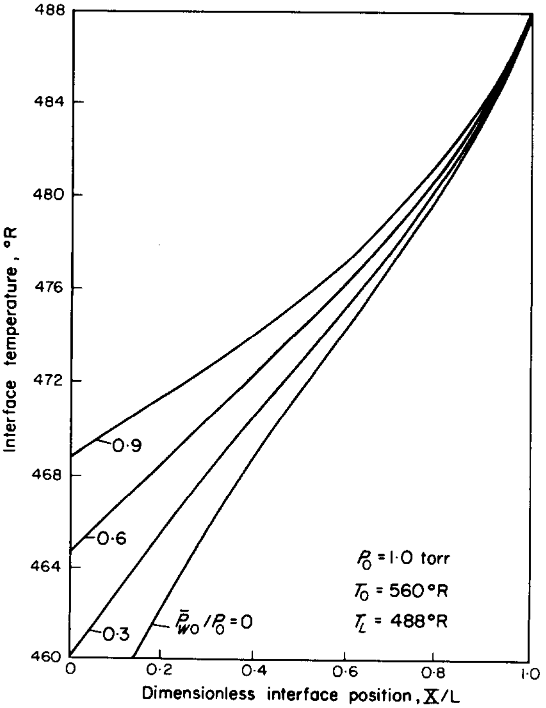

FIG. 3. Interface temperature as a function of dimensionless interface position for unidirectional drying of beef at 1 torr and several chamber concentrations.

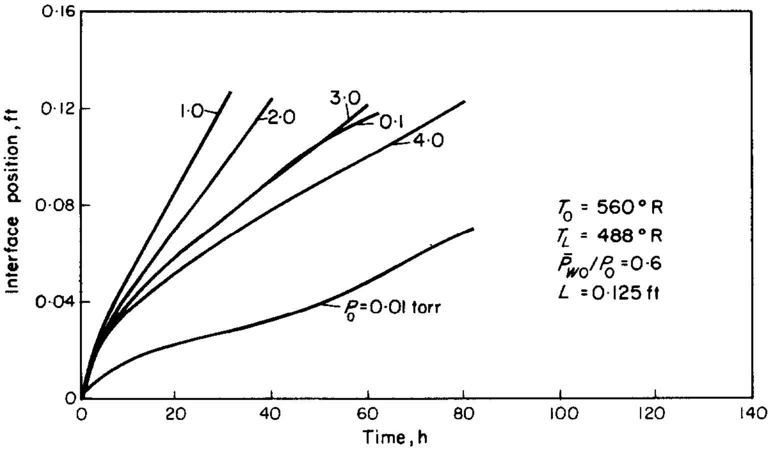

FIG. 4. Interface position as a function of time for unidirectional drying of beef.

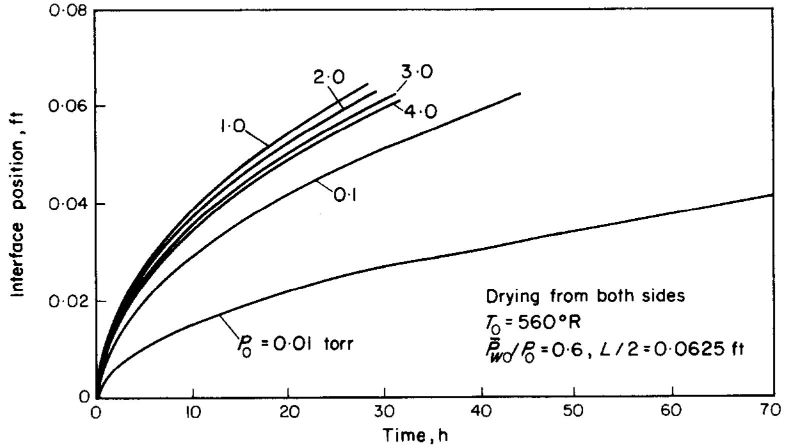

FIG. 5. Interface position as a function of time for drying beef from both sides.

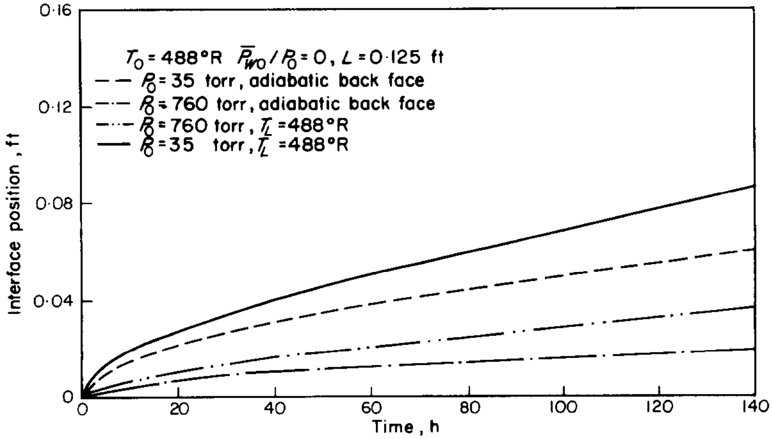

FIG. 6. Interface position as a function of time for drying beef in the continuum regime.

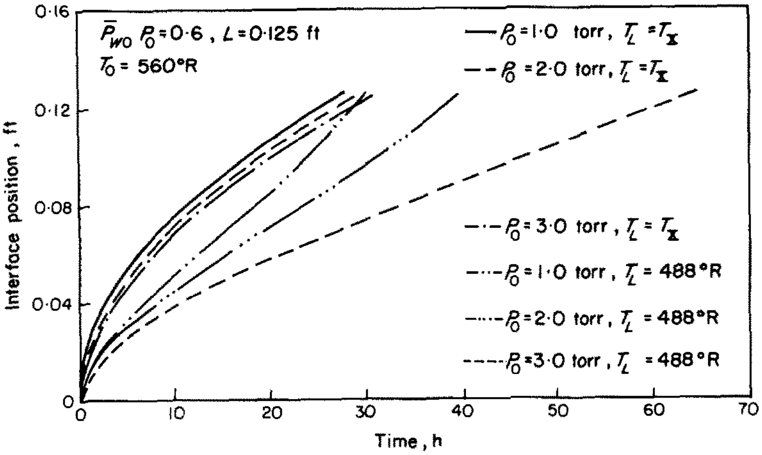

FIG. 7. Interface position as a function of time for drying beef at 1, 2 and 3 torr.

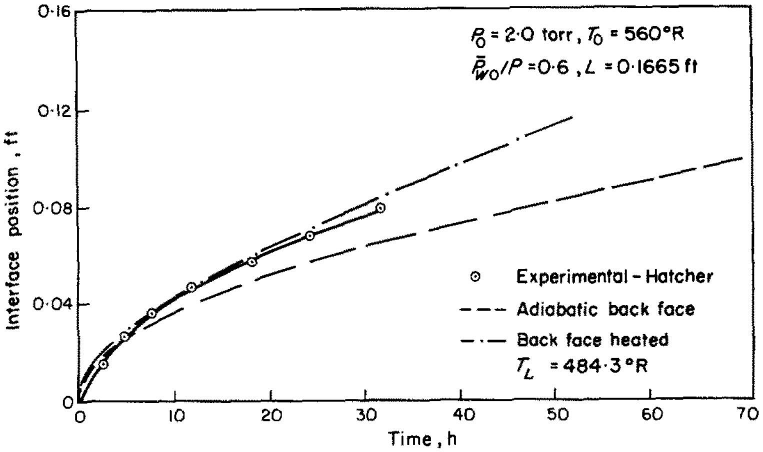

FIG. 8. Comparison of theoretical and experimental drying times at 2 torr.

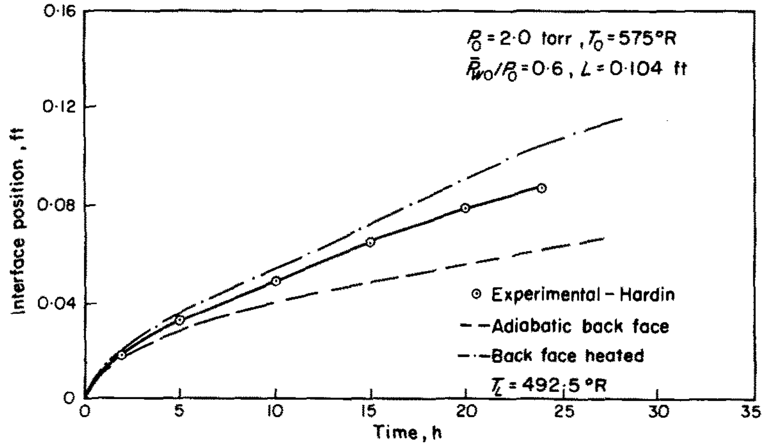

FIG. 9. Comparison of theoretical and experimental drying times at 2 torr.

dimensionless interface position, X/L, for "unidirectional" drying was calculated using equation (22) and is plotted in Fig. 2 for several different pressures. The boundary temperatures and the chamber concentration are fixed. As can be seen, for all pressures between 0·5 and 4·0 torr, the interface temperature is approximately a linear function of interface position. The closed form drying equation, equation (36), is therefore valid in this pressure range.

Figure 3 shows the dependence of interface temperature on the chamber concentration. It can be seen that a lower chamber concentration causes a decrease in the interface temperature. This can be explained from an analysis of the vapor flow. If the partial pressure at the exit is decreased, the vapor flow rate will increase as can be seen from equation (17). This in turn will result in a decrease in the partial pressure of the water vapor at the interface and consequently a decrease in the interface temperature.

Theoretical drying times

In Fig. 4, the interface position is plotted as a function of time for unidirectional drying of a slab of beef 1·5 in. thick. The fastest drying time occurred at a chamber pressure of 1·0 torr. Figure 5 shows a similar plot for drying where equal drying occurred at both exposed faces. Since two phase fronts exist, the total amount dried is twice the value of the interface position. A comparison of the two figures shows that the unidirectional drying system gives no real improvements for the particular boundary conditions chosen. Figure 5 also indicates that a chamber pressure of 1 torr is desirable for obtaining fast drying rates.

Figure 6 shows the interface movement for drying in the continuum regime. As expected, drying occurs faster at 35 torr than at atmospheric pressure, and at both pressures occurs faster with the back face heated. Unidirectional drying techniques take approximately 700 h to dry a 1·5 in. slab at atmospheric pressure as compared to 144 h at 35 torr. These drying times are very long, however, atmospheric freeze-drying could be used for thinner slabs of food. For instance, a piece of beef $\frac{1}{8}$ in. thick could be dried in approximately 15 h when allowed to dry from both sides.

The total interface movement for drying from both sides is plotted and compared with unidirectional drying in Fig. 7. Even though the total time for drying a slab 1·5 in. thick is approximately the same at 1·0 torr, in all cases the sample dries faster when allowed to dry from both sides. Dyer and Sunderland [7] show that a slab 2 in. thick, drying at 1·0 torr, will dry 40 per cent faster when heated from the back than when allowed to dry from both sides. This can be seen if the curves of Fig. 7 are extrapolated to 2 in. However, for all beef samples of 1·5 in. or less, there appears to be no advantage to unidirectional drying.

Comparison between theoretical and experimental drying times

Hatcher [8] measured the movement of the interface as a function of time during the freeze-drying of beef. His data were taken by using a gamma radiation beam and is shown in Fig. 8.

He attempted to dry 2-in. thick samples of beef unidirectionally by thermally insulating the sides and back of cylindrical-shaped samples with 2-inch thick fiberglass insulation. If perfect insulation had existed, the experimental data would be expected to follow the theoretical results for an adiabatic back face. During the initial stages of drying it can be seen that the experimental and theoretical curves compare closely, while at later stages of drying, a progressively faster experimental drying rate is achieved. A careful analysis of Hatcher's experiment shows that initially there was a negligible temperature gradient in the frozen layer but at later stages a temperature difference of 2–3°F existed. It was felt that an upper limit for the interface movement should occur if the back face is heated at the temperature experimentally measured. The results of these calculations are also shown in Fig. 8. The experimental curve lies between the two theoretical curves.

Hardin [4] presents data for the drying of beef at 2·0 torr. His results are shown in Fig. 9. Hardin also used cylindrical samples which he tried to dry unidirectionally with an insulated back face. He used an aluminum foil vapor seal and fiberglass insulation around the sides and bottom. However, the thickness of the insulation was only $\frac{1}{2}$ in. on the bottom and $\frac{3}{4}$ in. on the side. Therefore, more heat transfer should have taken place through the sides and bottom and thus the experimental data should lie closer to the theoretical case of back face heating than did in Hatcher's case. The interface movement is closer to the theoretical results for back face heating.

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SUBLIMATION-DESHYDRATATION DANS LES REGIMES D'ECOULEMENT CONTINU, DE TRANSITION OU MOLECULAIRE LIBRE

Rèsumè—On présente une analyse théorique du transfert de chaleur et de masse durant la sublimation et la déshydratation. Les équations d'énergie dans les régions sèches et gelées sont résolues. On présente des équations pour un écoulement hydrodynamique et diffusionnel dans la région sèche à des régimes d'écoulement molécule libre, de transition et continu. Les équations d'énergie et d'écoulement de vapeur sont couplées pour donner des solutions où la température de l'interface est fonction du régime d'écoulement, de la position de l'interface, des données des propriétés de transport, et des conditions limites contrôlées extérieurement. Les équations sont valables pour un écoulement simultanément hydrodynamique et diffusionnel dans les régimes d'écoulement continu et de transition, et sont valables pour une diffusion moléculaire, dans le régime moléculaire libre. On présente des équations relatives à la position de l'interface laquelle est une fonction du temps, pour des cas où la température de l'interface est soit constante soit fonction linéaire de la position de l'interface. Les résultats montrent que, si la chaleur est transférée à la fois au travers des couches sèches at gelées, la température de l'interface change ainsi que la position de l'interface. Des calculs numériques sur de la viande congelée et séchée montrent que cette dépendance est approximativement linéaire pour des pressions de chambre entre 0,5 et 4 torr. On trouve aussi que la pression entrainant la vitesse de séchage la plus rapide pour la viande se situe entre 0,5 et 1 torr. Pour tous les échantillons de viande de 3,81 cm d'épaisseur ou moins, l'assèchement est plus rapide quand il se produit sur les deux faces que lorsqu'il se produit sur une face seulement et quand la chaleur est conduite à travers la face arrière. On présente des calculs numériques montrant la bonne pratique de l'assèchement à froid d'échantillons minces dans les conditions atmosphériques.

SUBLIMATIONSTROCKNUNG KONTINUIERLICHER, ANLAUFENDER UND FREIER MOLEKÜLSTRÖMUNG

Zusammenfassung—Der Wärme- und Stoffaustausch während des Trocknens durch Sublimation wird thermisch untersucht. Die Energiegleichungen werden für den trockenen und den gefrorenen Bereich gelöst. Die Gleichungen werden für hydrodynamische Strömung und Diffusionsströmung im trockenen Bereich aufgestellt, bei freier Molekularbewegung für Anlauf- und kontinuierliche Strömungszustände. Die Gleichungen für die Energie und den Dampfstrom werden gekoppelt, um strenge Lösungen für die Temperatur der Grenzfläche zu erhalten als Funktion der herrschenden Strömung, der Lage der Grenzfläche, der Transporteigenschaften und der von aussen regelbaren Randbedigungen. Die Gleichungen gelten für hydrodynamische Strömungen mit Diffusion bei kontinuierlicher Strömung im Anlauf und für molekulare Diffusion, bei freier Molekülbewegung. Eine geschlossene Form der Gleichungen wird für die Lage der Grenzfläche gegeben als Funktion der Zeit für Fälle, in denen die Temperatur der Grenzfläche entweder konstant oder eine lineare Funktion der Lage der Grenzfläche ist.

Die Ergebnisse zeigen, dass sich die Grenzflächentemperatur mit der Lage der Grenzfläche ändert, wenn die Wärme durch die trockene und die gefrorene Schicht übertragen wird. Numerische Berechnungen für die Trocknung von Gefrierfleisch zeigen, dass diese Beziehung bei Kammerdrücken zwischen 0,5 und 4,0 Torr angenähert linear ist. Ein Druck von 0,5 bis 1,0 Torr ergibt die besten Trocknungsverhältnisse. Bei allen Fleischproben mit einer Dicke von 3,81 cm oder weniger geht das Trocknen schneller, gleichzeitig an beiden Fleischseiten, als nur an einer, mit Wärmeabfuhr an der anderen. Numerische Berechnungen zeigen die Möglichkeit, dünne gefrorene Probestücke bei Atmosphärendruck zu trocknen.

СУБЛИМАЦИЯ-ДЕГИДРАЦИЯ В РЕЖИМАХ НЕПРЕРЫВНОГО НЕСТАЦИОНАРНОГО И МОЛЕКУЛЯРНОГО ТЕЧЕНИЙ

Аннотация—Проводится теоретический анализ тепло-и массообмена при сублимации-дегидрации. Решаются уравнения энергии для сухих и замороженных участков. Представлены уравнения для гидродинамического и диффузионного потока в сухом участке при молекулярном, нестационарном и непрерывном режимах течения. Уравнения энергии и гидродинамики пара спариваются с целью полчения в замкнутом виде решений для температуры границы пара раздела фаз в зависимости от режима течения, а также для молекулярной диффузии при молекулярном режиме. В замкнутом виде приводятся уравнения для положения границы раздела фаз, зависящего от времени для случаев, когда температура границы раздела фаз либо постоянна, либо является линейной фуикцией положения границы раздела фаз.

Результаты показывают, что, если теплообмен происходит как в сухом, так и в замороженноймм слое, то температура границы раздела фаз будет меняться при изменении ее положения. Численные расчеты для сублимационной сушки говяжьего мяса показывают, что эта зависимость является приблизительно линеэной при давлении в камере в диапазоне от 0,5 до 1,0 мм рт. ст. Найдено также, что при давлении от 0,5 до 1,0 мм рт. ст. получается самая высокая скорость сушки. Для всех образцов говяжьего мяса толщиной 1,5 дюйма или менее сушка происходит быстрее с обеих поверхностей образца, чем в случае односторонней сушки, когда тепло переносится теплопроводностью сзади. Представлены численные расчеты, которые показывают возмзжность сублимационной сушки тонких образцов при атмосферном давлении.