

AN ANALYTIC STUDY OF THE INTERNAL MASS TRANSFER
DURING VACUUM-SUBLIMATION DRYING

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An equation for the drying rate during the ice sublimation stage of the process is derived on the basis of the molecular-kinetic theory of gases, with the vapor (gas) permeability of materials of various structures taken into account.

During the main stage of the sublimation drying process, namely during the sublimation of ice, a large portion of the moisture in the material remains frozen and, therefore, its transport in liquid form is practically impossible. The sublimation zone, which expands deeper into the material, becomes an interface between the region containing frozen stationary moisture and the relatively dry region through which water vapor and small quantities of noncondensing gases trapped in pores migrate. All three flow modes occur here at the same time: molecular (Knudsenian), transitional (sliding), and viscous.

For the case of mutual diffusion in a binary mixture through a porous medium, the velocity of each component (1 or 2) can be expressed in terms of the following equation [1]:

$$G_1 = - \frac{cD_{12}^0 K_1 P}{(cD_{12}^0 + K_m P) RT} \frac{dy_1}{dx} - \left[\frac{K_1 (cD_{12}^0 + K_2 P)}{cD_{12}^0 + K_m P} + \frac{c_0 P}{\mu} \right] \frac{y_1}{RT} \frac{dP}{dx} \quad (1)$$

Equation (1) contains two interdependent variables $y_1(x)$ and $P(x)$. No solution to it in quadratures has been found yet. A numerical solution is possible, however, by integrating this equation by parts over narrow intervals of the variables.

As a result of such a procedure, the molar fraction of a component in a binary mixture is expressed as a function of the total pressure in the linear steady mode:

$$\frac{F - (F + 1)y_1}{F - (F + 1)y_{10}} = \frac{P^{-a_0} e^{-a_1 P - a_2 P^2}}{a_3 [F - (F + 1)y_{10}] \int_{P_0}^P P^{1-a_0} e^{-a_1 P - a_2 P^2} dP + P_0^{-a_0} e^{-a_1 P_0 - a_2 P_0^2}} \quad (2)$$

Equation (2) has been obtained on the basis of the following assumptions:

- 1) the viscosity μ does not vary when the composition of the mixture varies, and
- 2) the quantity $k_0 = (Fm - (Fm + 1)y_1) / (F - (F + 1)y_1)$ is constant.

The first of these assumptions is most essential and limiting. It is to be noted that the viscosity does vary when the composition of the mixture varies and, in that case, Eq. (2) is valid only for a limited range of composition variation.

The second assumption, which involves diffusion under pressure, is usually of little significance. The factor k_0 varies from $k_0 = 1$ when $y_1 = 1$ to $k_0 = m$ when $y_1 = 0$. Therefore, its average value may be used with little error.

As has been mentioned at the beginning of this article, during vacuum-sublimation drying the water vapor diffuses through very small amounts of inert gases, mainly in the air, along the capillaries and the pores.

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In this case $F = 0$, $k_0 = 1$, and $a_0 = 1$. Then Eq. (2) becomes

$$\frac{P_1}{P_{10}} = \left(e^{-a_1 P - a_2 P^2} \right) \left\{ e^{-a_1 P_0 - a_2 P_0^2} - a_3 P_{10} \sqrt{\frac{\pi}{4a_2}} e^{a_1^2/4a_2} \left[\operatorname{erf} \left(a_2^{1/2} P_0 + \frac{a_1}{2a_2^{1/2}} \right) - \operatorname{erf} \left(a_2^{1/2} P + \frac{a_1}{2a_2^{1/2}} \right) \right] \right\}^{-1}$$

The process of mutual diffusion during sublimation drying, which we consider here, is complicated by the prevailing temperature and pressure gradients in the dried material. Gunn has derived an equation for G_1 [1] taking these factors into account.

This equation contains a coefficient K_1 , however, which is determined indirectly according to the formula $K_1 = c' \sqrt{RT/M}$ with c' denoting the permeability constant for a molecular (Knudsenian) gas flow. This precludes an application of the proposed equation to real processes, although it is well known that sublimation drying of materials occurs in most cases under pressures which correspond to a transitional (molecular-viscous) flow of moisture through it. Various materials for drying have different structural properties. Under such circumstances it is almost impossible to derive theoretically a single permeability characteristic for all materials.

It seems more expedient to replace K_1 by a coefficient which would quantitatively reflect the coexistence of all three flow modes in a porous material during sublimation drying. For structurally heterogeneous real materials, most appropriate here appears to us the vapor permeability coefficient K_V determined experimentally for each material of a group of structurally similar materials. If the quantity of vapor passing through a unit length of the porous body per unit time under a unit pressure drop is expressed in units of mass (or weight), then the dimension of the vapor permeability coefficient will be $\text{kg/m} \cdot \text{sec} \cdot \text{mm(Hg)}$, but, with the quantity of passing vapor expressed in units of volume, the dimension of the vapor permeability coefficient will be m^2/sec — which corresponds to the dimension of the standard diffusion coefficients in the theory of transfer processes.

In view of all this, the authors have transformed the Gunn equation into

$$S = \frac{D_{12}^0 K_V \Delta P}{(K_V P + D_{12}^0) RT \xi}$$

The quantities in formula (4) are defined as follows:

$$D_{12}^0 = D_{12} P_s,$$

where D_{12} is the coefficient of mutual diffusion for the vapor-air system under atmospheric pressure, P_s is the sublimation pressure, $\Delta P = P_s - P_c$, P is the total sublimator pressure, R is the universal gas constant, T is the temperature in the sublimation zone, $\xi = b\tau^n$, K_V is the vapor permeability coefficient determined from tests under conditions simulating vacuum-sublimation drying.

Formula (4), which has been derived by a physical analysis of the process mechanism, is proper for calculating the rate of sublimation drying.

NOTATION

G_1, G_2	are the flow intensity of components 1 and 2 respectively, $\text{kg/m}^2 \cdot \text{sec}$;
c	is the geometrical factor affecting the diffusion, dimensionless;
D_{12}	is the coefficient of mutual diffusion, m^2/sec ;
K_1, K_2	are the coefficients of Knudsenian diffusion, m^2/sec ;
R	is the universal gas constant;
T	is the temperature, $^\circ\text{K}$;
P	is the pressure, N/m^2 ;
y	is the molar fraction;
x	is the thickness of dry layer, m ;
$D_{12}^0 = D_{12} P$	N/sec ;
c_0	is the Darcy diffusion constant, m^2 ;
c'	is the Knudsen permeability coefficient, m ;
$K_m = y_1 K_2 + y_2 K_1$	m^2/sec ;
$F = G_1/G_2$;	
$m = \sqrt{M_1/M_2}$;	
M	is the molecular weight;
$a_0 = (F + 1)k_0/(F_m + 1)$;	

$$a_1 = ((F + 1)/(F_m + 1))$$

$$\cdot (K/cD_{12}^0 + c_0/\mu K_1);$$

$$a_2 = c_0/2\mu cD_{12}^0;$$

$$a_3 = c_0(1-m)/(Fm + 1)\mu cD_{12}^0;$$

μ

is the dynamic viscosity of gaseous mixture, N·sec/m²;

ξ

is the distance from the material surface to the sublimation zone.

LITERATURE CITED

1. R. D. Gunn, J. P. Clark, and C. J. King, Recent Developments in Freeze-Drying, Vol. 1: Thermodynamic Aspects (Heat and Mass Transfer), Suppl. to Bull. of Internatl. Inst. of Refrig., Paris (1969).