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Researches on Vacuum Freeze-Drying*

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The rate of sublimation dehydration by the process of Vacuum freeze-drying was investigated after our former reports^{(1) (2)} on the researches of sublimation of ice. Analyses of the temperature distribution in the sublimating materials by numerical methods and of the ideal drying-characteristics were presented. In the above analysis, the rate-determining steps considered were the rate of phase change from ice to vapor, the rate of heat supply to the sublimating surface and the rate of mass transfer of vapor through porous sublimated materials by the Darcy's and the Knudsen's flow. The analytical results were compared with experiments using homogeneous beds of sands and beef in pressure range $1-10^{-2}$ mmHg.

1. Preface

1.1 Introduction

Vacuum freeze-drying is the method of drying by dehydrated sublimation at a low temperature and a low pressure; below the triple point (for H_2O , $0.0075^\circ C$ and 4.6 mmHg). By this method, few materials change in quality in the process of drying treatment, and therefore its applications to food stuffs are increasing.

As for the basic researches on vacuum freeze-drying, D. F. Dyer and J. E. Sunderland⁽³⁾ analyzed it, supposing that the dried porous medium is a bundle of capillary tubes, under a constant temperature on the surface, considering that the mass transfer is governed by the heat flux which gets to the sublimating surface. On the other hand, the rate of drying is compared with the results of J. D. Hatcher's⁽⁴⁾ experiments on beef. Kawamura⁽⁵⁾ got the drying-characteristics of vacuum freeze-drying by the experiments on drying milk. J. C. Harper⁽⁶⁾ experimentally got the permeability, thermal conductivity and porosity of porous materials.

In the former reports^{(1) (2)}, we experimented the phenomena of sublimation on pure ice, and reported the following; The rate of mass transfer, the reciprocity of heat and mass transfer in the gas phase, the rate of mass transfer in the molecular flow region in consideration of the effect of mass flow and the accommodation coefficient for ice.

In this paper, the freeze-drying is investigated

through experiments, using a homogenous bed of sand and beef. The following matters were examined as the rate-determinant factors of the process.

(1) The mechanism of mass transfer in the dried porous bed is clarified.

(2) The rate of drying in vacuum freeze-drying and the temperature distribution in the sublimating materials are analyzed as a problem of heat conduction with phase change in consideration of the rate-determining steps of mass transfer.

(3) Clarifying the characteristics of vacuum freeze-drying, the ideal drying characteristics which is obtained theoretically and the ideal process of drying are suggested.

(4) On the basis of the ideal drying characteristics, the most appropriate conditions of drying are investigated about the supplied heat, and the sizes of the sublimating materials.

1.2 The mass transfer

1.2.1 The mechanism of the rate-determination of mass transfer

An ideal model of mass transfer mechanism is shown in Fig. 1. In vacuum freeze-drying the vapor sublimated from the frozen surface flows through the dried bed and the gas phase and condenses on the condenser surface, and the mechanism of mass transfer (a) of Fig. 1 differs from that of free surface shown in (b) of Fig. 1. As to the rate of phase change (sublimation) and the vapor transfer in the gas phase in vacuum freeze-drying (a), just like the sublimation from the free surface of ice (b), the former is determined by the temperature of the sublimating surface and the supplied heat and the latter has different transfer mechanisms according to the pressure. The mass

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transfer mechanism in the porous dried bed is complex and is considered in one case as the diffusion or the Darcy' flow in consideration of Knudsen's number based upon the diameter of pore, in the other case as the Knudsen's flow or the Molecular Streaming.

From above mentioned, the rate-determining factors of mass transfer to be considered in this research are as follows.

(1) The rate of phase change determined by the rate process.

(2) The rate of phase change depending upon the supplied heat.

(3) The rate of vapor transfer in the dried bed and in the gas phase.

The third rate-determining factor must be specially considered, as the thickness of the dried bed increases with time.

1.2.2 The equation of the rate of mass transfer

The equation of the rate in each rate determining step, as it was clarified in the former report, is represented as follows,

(1) The rate of phase change

$$\dot{w}_1 = \varepsilon (M/2\pi RT_s)^{1/2} p_s$$

$$\varepsilon = \exp(2.81 \times 10^3/T_s - 13.55), \quad q \geq \dot{w}_1 L \quad (1)$$

$$\dot{w}_2 = q/L, \quad q \leq \dot{w}_1 L \quad (2)$$

(2) The rate of vapor transfer in the dried bed

$$\dot{w} = \frac{MK}{RT} \text{grad } p_w \quad (3)$$

K in Eq. (3) is represented in three forms, according to the pressure of the vapor:

(i) In the viscous flow region

$$K = B_0 p / \mu$$

(ii) In the slip flow region

$$K = B_s p / \mu$$

(iii) In the molecular flow region

$$K = 4/3 K_0 (8RT/\pi M)^{1/2}$$

(3) The rate of vapor transfer in the gas phase.

(i) In the viscous flow region

$$\dot{w} = (D_0 M p_0 / RT X) (p_i - p_c) / \bar{p}_g \quad (4)$$

(ii) In the slip flow region

$$\dot{w} = \{D_0 M p_0 / RT (X - \xi)\} (p_i - p_c) / \bar{p}_g \quad (5)$$

(iii) In the molecular flow region

$$\dot{w} = (M/2\pi RT_i)^{1/2} p_i \{1 - (p_c/p_i)(T_i/T_c)^{1/2}\} \quad (6)$$

where $\Gamma = \sqrt{\pi} \text{ierfc}[(1/2\sqrt{\pi})\{1 - (p_c/p_i)\Gamma\}]$

$$D_0 p_0 = 92.3 [\text{mmHg} \cdot \text{m}^2/\text{hr}]$$

2. Nomenclature

c_p : specific heat kcal/kg°C

D : diffusion coefficient m^2/hr

d : diameter of pore m

K : permeability

L : latent heat for sublimation kcal/kg

M : molecular weight kg/kmol

p : pressure mmHg

q : heat flux kcal/ m^2 hr

R : gas constant kg-m/kmol°C

T : absolute temperature °K

$\dot{w}$: rate of mass transfer kg/ m^2 hr

X : distance m

Γ : correction factor of mass transfer for molecular flow

ε : accommodation coefficient

ϕ : porosity

θ : temperature °C

λ : thermal conductivity kcal/mhr°C

ρ : density kg/m^3

Suffixes

c : condenser

g : non-condensable gas

i : surface of material

s : sublimating surface

w : water vapor

3. Experimental procedure

The main part of the experimental apparatus in this research is shown in Fig. 2. The pressure range in the experiments is $4 \sim 10^{-2}$ mmHg. A rotary pump and a diffusion pump are used to exhaust and the pressure is controlled by a variable leak valve. The heat of sublimation is supplied either by radiation heating from the upper surface of a specimen or by a conductive heating from the bottom of the specimen. The following are measured; the pressure in the gas phase, the temperature distribution in the sublimating materials and the rate of mass transfer. The partial pressure of the noncondensable gas is measured by the

Fig. 1 Model mechanism of mass transfer

Macleod's gauge and the partial pressure of vapor is read from the calibration of values by means of Macleod's and Piranny's gauge.

The temperature distribution in the sublimating materials is measured by 0.1 mm ϕ Copper-Constantan thermo-couples, and the temperature of the surface of sublimation is measured from the temperature distribution by extrapolation. As the position of the surface of sublimation needs special precision, the weight by the spring balance is compared with the value calculated by the measured temperature. Beef or homogenous bed of sand (80~100 mesh) with its pore saturated with water, is set on a tray and is frozen. The surface of the material is covered with a wire netting, so that the condition of the dried bed may not be changed by the vapor flow, and an evaporator is set in the vacuum chamber parallel to the condenser (kept at -196°C by liquified nitrogen).

4. The mass transfer in dried bed

4.1 The mechanism of pressure distribution in the dried bed

Several small glass pipes for measuring the pressure shown in Fig. 2 are arranged between the specimen and the condenser. The distributions of the partial vapor pressure and the partial non-condensable gas, are measured by the Macleod's and the Piranny's vacuum gauge. The pressure distribution on the dried bed is calculated from the vapor pressure assuming equilibrium to be established between the pressure and the temperature on the surface of sublimation, and from the pressure distribution in the gas phase.

Fig. 2 Main part of the experimental apparatus

Examples of experimental results of the distribution mechanisms of the partial pressure of vapor p_w and the total pressure p are shown in Fig. 3 (in case of sublimation from the free surface of ice), and in Fig. 4 (in case of vacuum freeze-drying with a dried bed on the surface of sublimation). Figure 3 shows that in the region governed by diffusion, the total pressure is con-

Fig. 3 Pressure distribution in case of sublimation from free surface

Fig. 4 Pressure distribution in case of vacuum freeze-drying

stant (a), and in the phase change, the partial pressure of non-condensable gas is constant (b).

$$\frac{D_0 p_0 M}{RT_s X} \frac{0.88 p_s}{\bar{p}_g} = e^{(2.81 \times 10^3 / T_s - 13.55)} \left(\frac{M}{2\pi RT_s} \right)^{1/2} \bar{p}_g \dots \dots \dots (7)$$

$$\bar{p}_g = \frac{0.88 D_0 p_0 M}{RT_s X} e^{-(2.81 \times 10^3 / T_s - 13.55)} \left(\frac{M}{2\pi RT_s} \right)^{-1/2} \dots \dots \dots (8)$$

Under the pressure $\bar{p}_g$ determined by Eqs. (7) and (8), there is a transition point from diffusion to phase change for the free surface of ice.

In freeze-drying as the thickness of the dried bed increases with time, and the position of the surface of sublimation moves inside, the temperature of the sublimating surface gradually loses its relation to the pressure of the gas phase and then it comes to be affected by the supplied heat. That is to say a stable pressure distribution is not maintained, as shown in Fig. 4(a) and the mechanism of mass transfer in the gas phase is diffusion under constant pressure, while the mechanism in the dried bed has a hydrodynamic flow due to the pressure difference. At the same time, the non-condensable gas in the dried bed is exhausted by the vapor flow and the water vapor becomes the chief ingredient. In the region of comparatively low pressure Fig. 4(b), in which the rate of phase change is small in comparison with the rate of diffusion in the gas phase, the distribution of the partial pressure of the noncondensable gas p_g in the gas phase is constant, while in the dried bed, the distribution of it is the same as that of (a). From above mentioned, the pressure distribution in the dried bed in freeze-drying is not constant and the mass transfer is caused by the hydrodynamic flow due to differences in the vapor pressure.

4.2 The mechanism of mass transfer in the dried bed

The vapor transfer in the dried bed, as stated above, is considered as a hydrodynamic flow, that is to say a Darcy's or a Knudsen's flow. The rela-

tion between the permeability and the pressure shown in Fig. 5 is indicated by our data on a homogenous bed of sand and beef and by J. C. Harper's.

Therefore in the usual process of vacuum freeze-drying (in the pressure region of about $1 \sim 10^{-2}$ mmHg), the rate of mass transfer is governed by the Knudsen's flow and the value of permeability is assumed to be constant. Figure 6 shows a diagram of the measuring device for permeability in the region of the low pressure.

5. The analysis of the drying process and the drying characteristics

5.1 The analysis of the process of drying by the balance of heat

In this paper, the rate of drying and the temperature distribution are analyzed in only the first period of drying, not considering the second period. The heat conduction in the drying process is a two-phase problem about dried and frozen bed, as shown in the model Fig. 7. Considering the energy transfer by mass flow, the energy balance in the dried bed is treated. For the analysis, the following are assumed.

- (1) The one dimensional heat and mass flow are assumed.
- (2) The temperature of the dried bed is equal to that of the vapor flowing through it. (The Reynold's number is small enough.)
- (3) The thickness of dried bed does not vary in the drying process. (It is proper to consolidate

Fig. 6 Simplified measuring device for permeability at a low pressure

Fig. 5 Permeability

Fig. 7 Model figure of drying process

substance.)

(4) The vapor pressure and the temperature on the surface of the sublimation are in equilibrium.

(5) The real rate of phase change, the rate of phase change depending on the supplied heat and the rate of vapor transfer through the dried bed and the gas phase are considered, the rate-determining factors of mass transfer.

5.1.1 Considering the rate-determining factors of mass transfer

A coordinate system is shown in Fig. 7. In this case the latent heat of sublimation is supplied by radiation heating from the upper surface of the specimen. The temperature on the surface of material is represented by a function of time $f(t)$ in Eq. (13).

The basic equation

$$\lambda_1 \frac{\partial^2 \theta_1}{\partial x^2} + c_{pw} \dot{w} \frac{\partial \theta_1}{\partial x} = (c_p \rho)_1 \frac{\partial \theta_1}{\partial t} \quad 0 \leq x \leq X(t) \quad (9)$$

$$\lambda_2 \frac{\partial^2 \theta_2}{\partial x^2} = (c_p \rho)_2 \frac{\partial \theta_2}{\partial t}, \quad X(t) \leq x \leq l \quad (10)$$

The initial condition

$$\theta_2 = 0, \quad t = 0 \quad (11)$$

$$X(t) = 0, \quad t = 0 \quad (12)$$

The boundary condition

$$\theta_1 = f(t), \quad x = 0 \quad (13)$$

$$\frac{\partial \theta_2}{\partial x} = 0, \quad x = l \quad (14)$$

$$\theta_1 = \theta_2, \quad x = X(t) \quad (15)$$

$$\lambda_1 \frac{\partial \theta_1}{\partial x} - \lambda_2 \frac{\partial \theta_2}{\partial x} = \dot{w} L \quad (16)$$

The rate of mass transfer

$$\dot{w} = \min(\dot{w}_1, \dot{w}_2, \dot{w}_3) \quad (17)$$

$$\dot{w}_1 = e^{(2.81 \times 10^3 / T_s - 13.55)} (M / 2\pi RT_s)^{1/2} p_s \quad (18)$$

$$\dot{w}_2 = -\lambda_1 \left(\frac{\partial \theta_1}{\partial x} \right)_{x=X} \frac{1}{L} \quad (19)$$

$$\dot{w}_3 = -\frac{MK}{RT_s} \text{grad} p_w \quad (20)$$

The conductance K is represented as follows, by considering a series model of the dried bed and the gas phase.

$$1/K = 1/K_1 + 1/K_2$$

$$K_1 = (4\pi d p^3 / 3) (8RT / \pi M)^{1/2}$$

$$K_2 = (D_0 p_0) / \{ \bar{p}_g (X - \xi) \}$$

5.1.2 The numerical method

The above problems are analyzed numerically. As in Fig. 8 space and time are divided by Δx and Δt . In order to calculate precisely the rate of phase change depending on the supplied heat, the element about the surface of sublimation is subdivided more closely, (cf. Fig. 9). The temperature at: $x = n\Delta x$ and at time: $t = p\Delta t$ is represented as θ_n^p . The rate of mass transfer at time; $t = p\Delta t$ of the element ($n=m$) of proceeding sublimation is represented as W_m^p . The fraction of drying of the element is represented as r_m^p .

Finite difference equations,

(1) The dried region ($n < m$)

$$\theta_n^{p+1} = \theta_n^p + \frac{1}{(c\rho)_1} \frac{\Delta t}{(\Delta x)^2} \{ \lambda_1 + c_{pw} w_w^p \Delta x \} \times (\theta_{n-1}^p + \theta_{n+1}^p - 2\theta_n^p) \quad (21)$$

(2) The frozen region ($n > m$)

$$\theta_n^{p+1} = \theta_n^p + \frac{\lambda_2}{(c\rho)_2} \frac{\Delta t}{(\Delta x)^2} (\theta_{n+1}^p + \theta_{n-1}^p - 2\theta_n^p) \quad (22)$$

(3) The lump in which sublimation is advancing. ($n=m$)

$$\theta^{p+1} = \theta_n^p + \frac{1}{c\rho[r_m^p]} \frac{\Delta t}{\Delta x} \left\{ (\theta_{n-1}^p - \theta_n^p) \frac{\lambda_1}{\Delta x} + (\theta_{n+1}^p - \theta_n^p) \frac{\lambda_2}{\Delta x} - \dot{w}_m^p L \right\} \quad (23)$$

$$c\rho[r_m^p] = (c\rho)_1 r_m^p + (c\rho)_2 (1 - r_m^p)$$

$$r_m^p = \sum_{p'} w_m^{p'} \{ (\Delta t / \phi \rho) \Delta x \}$$

$$w_m^p = \min(w_{1m}^p, w_{2m}^p, w_{3m}^p)$$

$c\rho[r_m^p]$ is the average heat capacity in the element of advancing sublimation, considering the degree of drying, and W_m^p takes the smallest value of three rate-determining factors of mass transfer.

In calculation of w_{3m}^p , the pressure of water vapor on the surface of sublimation is obtained by the explicit way, without considering the distribution of density in the dry bed.

Fig. 8 Temperature space

Fig. 9 Subdivided element

5.1.3 On the assumption that the rate of drying is proportional to $\sqrt{t}$

The case that the frozen substance is assumed to be semi-infinite and the energy balance in the dried bed need not take account of the influence of mass flow, under a constant temperature on the surface of sublimation and on the surface of materials, the drying process is explained by the Neumann's solution.

The transition of the dried surface, the boundary between the dried bed and the frozen one is indicated as $x=b\sqrt{t}$, and an exact solution of the temperature distribution and the rate of mass transfer can be obtained under a constant temperature of the surface of the materials. The results of analysis are as follows.

$$\lambda_1 \frac{\partial^2 \theta_1}{\partial x^2} + c_{pw} \dot{w} \frac{\partial \theta_1}{\partial x} = (c_p \rho)_1 \frac{\partial \theta_1}{\partial t} \quad (24)$$

$$\dot{w} = -\phi \rho_2 \frac{dX}{dt} = \frac{b \phi \rho_2}{2t^{1/2}} \quad (25)$$

$$\theta_1 = V, \quad x=0 \quad (26)$$

$$\theta_1 = U, \quad x=X(t) \quad (27)$$

From Eqs. (24) and (25),

$$\alpha \frac{\partial^2 \theta_1}{\partial x^2} + \frac{ab}{2t^{1/2}} \frac{\partial \theta_1}{\partial x} = \frac{\partial \theta_1}{\partial t} \quad (28)$$

where

$$\alpha = \lambda_1 / (c_p \rho)_1, \quad a = \alpha c_{pw} \phi / \lambda_1$$

Using $\eta = x/2(\alpha t)^{1/2}$, Eqs. (28), (26), (27) become

$$\frac{\partial^2 \theta_1}{\partial \eta^2} + \left(\frac{ab}{\alpha^{1/2}} + 2\eta \right) \frac{\partial \theta_1}{\partial \eta} = 0 \quad (29)$$

$$\theta_1 = V, \quad \eta = 0 \quad (30)$$

$$\theta_1 = U, \quad \eta = X(t)/2(dt)^{1/2} = b/2\alpha^{1/2} \quad (31)$$

From Eqs. (29), (30), (31), θ and b are obtained as follows.

$$\theta_1 = \frac{\operatorname{erf}\left[\frac{x}{2(\alpha t)^{1/2}} + \frac{ab}{2\alpha^{1/2}}\right] - \operatorname{erf}\left(\frac{ab}{2\alpha^{1/2}}\right)}{\operatorname{erf}\left[\frac{1}{2} \frac{b}{\alpha^{1/2}} (1+a)\right] - \operatorname{erf}\left\{-\left[\frac{b(1+a)}{2\alpha^{1/2}}\right]^2\right\}} \quad (32)$$

$$b = -\frac{2\lambda_1(U-V) \exp\left\{-\left[\frac{b(1+a)}{2\alpha^{1/2}}\right]^2\right\}}{\rho \sigma L (\pi \alpha)^{1/2} \operatorname{erf}\left[\frac{b(1+a)}{2\alpha^{1/2}}\right] - \operatorname{erf}\left(\frac{ab}{2\alpha^{1/2}}\right)} \quad (33)$$

5.2 Comparison of the experimental results with the solution of analysis

As experiment of drying (the experimental apparatus is shown in Fig. 2.) is performed by means of radiation heating, using a homogenous frozen bed of sand with its pore saturated with water. One of the results of experiment, on the rate of mass transfer and the temperature distribution, is shown in Fig. 10. The solid line in Fig. 10 shows

the results obtained by the numerical method, using the measured value of the surface temperature (the number of thermocouples is 1). These results coincide considerably well with the experimental values. This implies that the conditions for the analysis by means of the energy balance and the numerical method are satisfactory.

As shown by the experimental value, the temperatures on the surface of materials and on the surface of sublimation are not constant, so the exact solution (5.1.3) can not be generally applied.

The properties of sand and packed bed in dried and frozen state are shown in Table 1. The values

Table 1 Properties of homogeneous bed of sand (80~100 mesh)

	Grain	Dried bed	Frozen bed
Porosity %		38.0	38.0
Density kg/m ³	2.60 × 10 ³	1.61 × 10 ³	1.96 × 10 ³
Specific heat kcal/kg°C	0.078	0.078	0.231
Thermal conductivity kcal/mhr°C	4.3	0.05 0.12(1mmHg)	3.23

Fig. 10 Experimental results and numerical solution of drying process

Fig. 11 Thermal conductivities of sand

of permeability are taken from Fig. 5. Thermal conductivity of sand is measured by the transient comparison method, as shown in Fig. 11. The properties of matter in the dried bed should take the value in the state with water vapor flow, but as to the conductivity, the value neighbouring the vapor pressure 1 mmHg is used and the other properties are assumed to be independent of water vapor.

5.3 The drying characteristics

The drying characteristics of vacuum freeze-drying, is generally classified into three stages. The rate of drying in the initial stage is taken to be constant according to the heat flux and is characterized by steady drying. In many cases, however, the flow resistance of the vapor changes with time and is determined as a function of permeability and the thickness of dried bed. The temperature on the surface of sublimation changes with time, for the pressure is not so dominant as on the free surface of ice. Therefore the initial stage of drying can not generally be characterized as steady drying. But in the case that the dried bed does not remain, the former theory serves the purpose.

It is clear from Fig. 10 that the rate of mass transfer is determined by the rate of phase change, the rate of phase change in turn depending on the supplied heat and the rate of vapor transfer in the dried bed, and that the characteristics of the early stage of drying is governed by the following three factors; the rate of phase change, the supplied heat and the thickness of drying and its properties; (permeability, porosity etc.).

6. The investigation of heating based upon the ideal drying-characteristics

The factors governing the rate of vacuum freeze-drying are the temperature, the pressure, the sizes of materials, the supplied heat and the way of heating.

In this paper, the supplied heat based on the ideal drying characteristics which means the most effective drying is investigated, and the way of heating or the control of the drying process under the above characteristics will be reported in the next paper.

6.1 The ideal drying characteristics

As mentioned above, the supplied heat and the vapor transfer in the dried bed govern the drying, therefore the process of drying is notably affected by them. In case that the vapor transfer in the dried bed is a molecular flow, and in the pressure condition in which the flow resistance of the vapor in the gas phase can be ignored comparing to the

resistance in the dried bed, the drying characteristics are determined by only the properties of dried materials (porosity and permeability).

We call this tentatively 'the ideal drying characteristics', and analyze this as follows.

The rate of mass transfer

$$\dot{w} = -e^{(2.81 \times 10^3/T_s - 13.55)} (M/2\pi RT_s)^{1/2} p_s \dots (34)$$

$$\dot{w} = -(MK_1/RT_s) \text{grad} p \dots (35)$$

The rate of drying

$$dX/dt = -(1/\phi\rho) dw/dt \dots (36)$$

From Eqs. (34), (35), the transition of the rate-determining step, from the diffusion to the phase change region, happens.

$$X_{(trans)} = \frac{MK_1}{RT_s} e^{-(2.81 \times 10^3/T_s - 13.55)} \times (M/2\pi RT_s)^{-1/2} \dots (37)$$

$$t_{(trans)} = \frac{MK_1\phi\rho}{RT_s p_s} e^{-2.81 \times 10^3/T_s - 13.55} \times (M/2\pi RT_s)^{-1} \dots (38)$$

Up to this point, the rate of phase change is the rate-determining step and after this it is the vapor transfer in the dried bed. From the Eqs. (34), (36) or (35), (36), the drying distance is represented as follows.

$$X(t) = \frac{e^{(2.81 \times 10^3/T_s - 13.55)}}{\phi\rho} (M/2\pi RT_s)^{1/2} p_s t = f(\phi, T_s) \cdot t, \quad (0 \leq X \leq X_{(trans)}) \dots (39)$$

$$X(t) = \left\{ \frac{2MK_1}{\phi\rho} \frac{p_s - p_c}{RT_s} (t - t_{(trans)}) + X_{(trans)}^2 \right\}^{1/2} = g\left(\frac{K_1}{\phi}, T_s\right) \sqrt{t} \quad (X \geq X_{(trans)}) \dots (40)$$

From the above mentioned, it follows that the rate of drying is characterized by the porosity ϕ in the region governed by the phase change and is characterized by the ratio of permeability to the porosity K/ϕ in the region governed by the vapor transfer in the dried bed. These rates of drying are proportional to time t and $\sqrt{t}$ respectively.

Using the permeability K_1 , and the porosity ϕ shown in Fig. 5, from Eqs. (34), (40), the ideal drying characteristics of a homogenous bed of sand, beef, apples and peaches are obtained and shown in Fig. 12. The transitions of the rate-determining step are determined by the temperature on the surface of sublimation and the permeability of the dried bed, and are represented as Fig. 13. In the region of permissible temperatures and pressures, the optimum thickness of materials is determined by increasing the pressure so far as the vapor transfer in the dried bed is defined by the molecular flow. When the values of the properties of the dried bed are already known, the ideal drying characteristics is determined, and then from the optimum size of materials and the opti-

imum supplied heat, the condition of drying can be obtained.

6.2 The investigation of heating

During drying processes, it is not easy to maintain the highest temperature on the surface of sublimation that can be permitted, and the temperature changes depending on the way of heating. Therefore as a matter of fact, for the temperature changing momentarily on the surface of sublimation, the ideal drying characteristics of each process should be obtained. The actual rate of drying and the ideal rate of drying can be obtained by knowing the temperature on the surface of sublimation in each period (as stated in Chapter 5 in the case of radiation heating, the rate of drying can be calculated from only the temperature on the surface of materials.).

Here, the ratio of the actual rate of drying to the ideal rate of drying may be called tentatively the efficiency of the rate of drying. In Figs. 14, 15, one of the experimental results of the temperature on the surface of sublimation, in case of radiation heating and an electric heater and its temporal change in the efficiency of the rate of drying is shown in Figs. 16, 17. It is clear from

Fig. 12 Ideal drying characteristics

Fig. 13 Optimum thickness of material

the figures that in the early period of drying, the supplied heat is enough and this period is governed by the rate of phase change, and that with progress

Fig. 14 Temperature of the sublimating surface (Radiation heating)

Fig. 15 Temperature of the sublimating surface (Conduction heating)

Fig. 16 Rate of drying and its efficiency (radiation heating)

in drying, the process of drying is determined by the supplied heat, and the efficiency of the rate of drying decreases.

Especially in the experiment by the radiation heating, the drying is early governed by the supplied heat, without no occurrence of the rate-determining steps by the transfer in the dried materials. A heat supply which makes the efficiency of drying 100 %, is necessary. The optimum way of drying should be determined considering the efficiency of drying. From above mentioned, from a view point of heat controlling of vacuum freeze-drying, the ideal characteristics is considered a universal basis with generality.

7. Conclusions

Experiments on vacuum freeze-drying are made, using a homogenous bed of sand as the frozen material, and the following conclusions are obtained.

(1) The mechanism of mass transfer in the

dried bed is governed by Darcy's or Knudsen's flow.

(2) As the factors governing the rate of drying, the rate of phase change of ice, the supplied heat and the vapor transfer both in the gas phase and in the dried bed are confirmed, and the drying characteristics of vacuum freeze-drying is clarified.

(3) The drying process is analyzed as a problem of heat conduction with phase change, and the rate of drying and the temperature distribution of materials coincide with the experimental results in case of the radiation heating.

(4) It is proposed that the optimum heat supply and the way of heating be determined and the efficiency of the rate of drying based on the ideal drying-characteristics be defined. This gives the possibility of proper control of vacuum freeze-drying process. In case of the radiation heating, only by measuring the temperature on the surface of materials, the drying process can be controlled.

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Fig. 17 Rate of drying and its efficiency (conduction heating)

Discussion

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It is said that the mechanism of drying is governed by the influence of capillarity, and this is shown in Fig. 5 (the Harper's experiment). Therefore in the pressure region, $1 \sim 10^{-2}$ mmHg, is it proper that both sand and beef should have a constant μK and they have the same drying mechanism?

Especially thermal conductivity is influenced by the surrounding fluid, as is shown in Fig. 11, and the curve of sand in Fig. 13 seems to be

peculiar.

It seems inadequate that the problem of drying, which has many complicated factors as above mentioned, should be analyzed only as a conduction problem.

Authors' closure

(1) In many cases the drying mechanism is governed by the vapor transfer through the capillary tube, so the influence on the rate of drying is complex. The permeability, as you pointed out,

Append.-Fig. 1 Thermal conductivity of sand

is influenced by the capillarity, but as shown by Fig. 5, it has no relation to the porosity. This only means that each material has its own value for the conductance of mass transfer. In vacuum freeze-drying, the mechanism of mass transfer in the dried bed differs from that of ordinary drying, and is characterized with the vapor flow owing to the pressure difference (cf. Fig. 4). Therefore it is reasonable that using the experimental result shown in Fig. 5, μK should be constant.

(2) In analyzing the rate of drying and the temperature distribution in a specimen, the follow-

ing are assumed as stated in 5.1.1.

(a) The rate of mass transfer takes the smallest value of the following rate-determinate factors.

- (i) the rate of phase change of ice (by the rate process)
- (ii) the supplied heat
- (iii) the rate of vapor transfer in the dried bed.

(b) The enthalpy transport due to the vapor transfer exists in the dried bed.

(c) The vapor pressure and the temperature on the sublimating surface are in equilibrium.

(3) As you pointed out, the conductivity in the dried bed is greatly influenced by the surrounding fluid. In our experiments, using air as the surrounding fluid, it is ascertained that the measured value well coincides with the value calculated in Kunii-Smith' equation, and the thermal conductivity of the sand with water vapor is to be obtained by this equation (cf. Append.-Fig. 1). Then it is assumed to be proper that the thermal conductivity of the dried bed is constant in vacuum freeze-drying.