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Researches on Heat and Mass Transfer by Sublimation of Ice*

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The rate of sublimation of ice was investigated by experiment. The pressure range was from 10 to 10^{-3} mmHg.

The following three processes were shown to determine the rate in the mass transfer of sublimation of ice.

(1) In the pressure range ($P > 1$ mmHg), the rate of mass transfer is governed by the diffusion velocity of vapor in vapor phase, and the maximum rate is reached when the vapor supersaturates and recondensates on the ice surface.

(2) Under 10^{-2} mmHg, the velocity of molecular flow, known in the kinetic theory of gases, governs the rate of mass transfer.

(3) In the pressure range 1 to 10^{-2} mmHg, the rate is governed by the velocity of phase transition from ice to vapor on the ice surface. In this range, the ice surface becomes very rough.

Maximum rate is reached when the surface area of ice increases to the maximum.

(4) For finding the correlation between heat and mass transfer from these experimental results, use of the following relation is recommended.

$$\alpha/h = \rho C_p (a/D) (\bar{P}_g/P)$$

α : coefficient of heat transfer, h : coefficient of mass transfer.

1. Introduction

Recently vacuum freeze-drying has been developed remarkably in many fields. It is one of the typical industrial processes which utilize the phenomena of sublimation. To continue sublimation, it is necessary to keep the partial pressure of water vapor in gas phase below the triple point (for instance, 4.6 mmHg for pure ice) and to supply latent heat of sublimation. The rate of phase change from solid to gas, and the rate of heat and mass transfer in gas phase influence the whole process of sublimation.

In the low pressure region, heat and mass transfer are greatly influenced by pressure. Dickens⁽¹⁾ showed that the rate of heat transfer depended on pressure under about 10 mmHg, which did not coincide with theoretical results of the kinetic theory of gases. Concerning the mass transfer in this region, other research projects have been investigated; sublimation of naphthalene by Sherwood and

Cooke⁽²⁾, molecular distillation by Nagai⁽³⁾ and phenomena of vacuum freeze-drying by Kawamura⁽⁴⁾.

In the intermediate pressure region, where the mechanism of mass flow consists of molecular and viscous flow, Ueha introduced the boundary layer theory and discussed the thickness of the layer as the function of pressure⁽⁵⁾.

As the accommodation coefficient of ice in the molecular flow region, which is the correction factor for theoretical mass transfer rate, Sherwood and K. Tschudin⁽⁶⁾ got 1 to 10^{-2} and 0.96 ± 0.06 respectively.

In the viscous flow region the thermal diffusivity (a) is equal to the diffusion coefficient (D) as shown by the kinetic theory of gases: therefore $P_r = S_g$, and in the systems of heat and mass transfer Lewis' equation $\alpha/h = \rho C_p$ is valid if R_e numbers are equal. Among the studies of processes of sublimation, few were found to cover all pressure ranges of sublimation phenomena from the viscous range to the free molecular range.

In this paper, we report experimental results about the sublimation of ice in these pressure ranges and show the following points:

- (1) The rate determinant processes in mass transfer in each pressure range.

* Received 26th December, 1967.

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- (2) Relation between rate of mass transfer and supplied heat flux.
- (3) The value of accommodation coefficient.
- (4) The correction factor between heat and mass transfer in each pressure range.

2. Nomenclature

A : area	m^2
a : thermal diffusivity	m^2/hr
C_p : specific heat	$kcal/kg^\circ C$
D : diffusion coefficient	m^2/hr
h : coefficient of mass transfer	m/hr
L : latent heat for sublimation	$kcal/kg$
L_m : mean free path	m
M : molecular weight	$kg/kmol$
P : total pressure	$kg/m \cdot hr^2$
q : heat flux	$kcal/m^2 hr$
R : gas constant	$kg \cdot m^2 / ^\circ K \cdot kmol \cdot hr^2$
W : weight of transferred mass	kg
α : coefficient of heat transfer	$kcal/m^2 hr^\circ C$
ϵ : accommodation coefficient	
ζ : slip distance	m
λ : thermal conductivity	$kcal/mhr^\circ C$
ρ : density	kg/m^3
σ : activation grade	

Suffix

- c: condenser surface, s: sublime surface
 g: non-condensable gas, w: water vapor
 -: logarithmic mean
 *: equilibrium state
 +: activated state

3. Heat and mass transfer by sublimation of ice

3.1 The mechanism of sublimation phenomena of ice

The process under consideration is illustrated schematically in Fig. 1. Water vapor is sublimated from the ice surface in a vacuum, and heat and mass are transferred one-dimensionally from the ice to the condenser where the vapor condenses on the low temperature surface of the condenser. Assuming a large capacity of the condenser, the basic mechanisms of these phenomena consist of:

Fig. 1 Schematic drawing of experimental device

- (1) Supply of latent heat for sublimation to keep the temperature of ice surface constant.
- (2) Phase change from ice to water vapor on ice surface
- (3) Heat and mass transfer in gas phase

3.2 Mass transfer in gas phase

The range of our experiment was $10^{-3} \sim 10^{-2}$ mmHg in total pressure to keep the partial pressure of water vapor below the triple point of water (4.6 mmHg). In this pressure range, the process of mass transfer changes from the viscous flow region to the free molecular flow region. For this process, the possible driving forces for mass transfer are:

- (1) Partial pressure difference of water vapor between evaporator and condenser
- (2) Bulk flow of gas due to pumping
- (3) Natural convection
- (4) Entrainment of ice particles within the gas stream
- (5) Thermal diffusion

The effects of (3), (4), (5) have a minor role in the mass transfer and may be neglected. When the rate of mass transfer in the gas phase governs the rate of the whole processes, partial pressure of water vapor on the surfaces of ice and condenser could be assumed to be saturated, because the surfaces are not superheated.

3.2.1 Viscous flow region

The rate of mass transfer in the atmospheric pressure region is governed by Stephan's equation of diffusion, Eq. (1) and Fig. 2. In vacuum, Eq. (2) for constant partial pressure of the air may be valid, (Fig. 3). But when mass flow of the air exists between evaporator and condenser by leakage of apparatus or by release of dissolved air from the subliming ice cake, the rate equation is governed by Eq. (3).

Fig. 2 The relation of total pressure P , vapor pressure P_w and the gas pressure P_g in Stephan's flow in constant P

Fig. 3 Relation P , P_g , P_g^* and P_c by constant P_g in vacuum

$$dW/d\theta = A(DM/RT_s X)(P/\bar{P}_g)(P_s^* - P_e^*) \dots (1)$$

$$dW/d\theta = A(D_0 P_0 M/RT_s X)(P_s^* - P_e^*)/P_g \dots (2)$$

$$dW/d\theta = A(DM/RT_s X)(P/\bar{P}_g)(P_s^* - P_e^*) - \{M_w(S-Q)/RT_s\}P \dots (3)$$

S : the speed of vacuum pump m^3/hr

Q : leak rate m^3/hr

3.2.2 Molecular flow region

Assuming the molecules of water vapor to have a Maxwell velocity distribution both on the ice and the condenser surfaces, the rate of mass transfer is simply represented by Eq. (4) as the sum of the absolute rate of vaporization and condensation. At the surface of the condenser, the above assumption of an equilibrium velocity distribution may be disturbed by the net mass flow⁽⁷⁾. But this disturbance could be neglected by keeping partial pressure of water vapor very small with a liquid nitrogen condenser in the present experiments

$$dW/d\theta = A(M/2\pi RT_s^*)^{1/2} P_s^* - A(M/2\pi RT_e^*)^{1/2} P_e^* \dots (4)$$

3.2.3 Intermediate region

The mechanism of mass flow in the semi-viscous region is illustrated schematically in Fig. 4⁽⁸⁾. In this region, the flow near the surfaces of the ice and the condenser are assumed to be molecular and the flow between them is assumed to be viscous. From Eqs. (1), (4) the rate of mass transfer is given by Eqs. (5), (6), (7) in the regions (S)~(1), (1)~(2), (2)~(c) respectively where ϵ_1 , ϵ_2 are the accommodation coefficients.

$$dW/d\theta = A\epsilon_1(M/2\pi RT_s^*)^{1/2}(P_s^* - P_1) \dots (5)$$

$$dW/d\theta = A\{(DMP)/RT_s(X - L_{m1} - L_{m2})\} \times (P_1 - P_2)\bar{P}_g \dots (6)$$

$$dW/d\theta = A\epsilon_2(M/2\pi RT_e^*)^{1/2}(P_2 - P_e^*) \dots (7)$$

Assuming the slip flow, the slip pressure differences, $(P_s^* - P_1)$ and $(P_2 - P_e^*)$ exist at the ice and condenser surfaces, the rate of mass transfer is represented by Eq. (8).

$$dW/d\theta = A\{(DMP)/RT_s(X - \zeta_1 - \zeta_2)\} \times (P_s^* - P_e^*)/P_g \dots (8)$$

$$\zeta = \zeta_1 + \zeta_2 = L_{m1} + L_{m2} - (DMP)/(RT_s \bar{P}_g) \times \{(1/\epsilon_1)(M/2\pi RT_s^*)^{-1/2} + (1/\epsilon_2)(M/2\pi RT_e^*)^{-1/2}\} \dots (9)$$

Fig. 4 Mechanism of mass transfer in semi-viscous region

In Eq. (8), if the slip distance is assumed to be equal to the distance of transport, the mass flow may be considered to be molecular.

3.3 The rate of phase change

When the rate of mass transfer of whole processes is determined by the rate of phase change from ice to water vapor on the ice surface, i.e. the conductance of mass transfer in the gas phase is sufficiently larger than the rate of phase change on the ice surface, the temperature and partial pressure of water vapor on the ice surface are not at the equilibrium state.

Here we assume that only a small part of the ice surface is activated and that the local activated points could be considered as a cluster of ice molecules. If we note the number of activated molecules, surface area of activated ice, that of the molecules and activation energy by n^+ , A^+ , A_n and E respectively, the rate equation of phase change is represented as follows.

$$\begin{aligned} dW/d\theta &= A^+(M/2\pi RT_s^*)^{1/2} P_s^* \\ &= n^+ A_n (M/2\pi RT_s^*)^{1/2} P_s^* \\ &= n e^{-E/RT_s^*} A_n (M/2\pi RT_s^*)^{1/2} P_s^* \\ &= A e^{-E/RT_s^*} (M/2\pi RT_s^*)^{1/2} P_s^* \\ &= A \sigma (M/2\pi RT_s^*)^{1/2} P_s^* = A \kappa P_s^* \dots (10) \end{aligned}$$

$$\kappa = \sigma (M/2\pi RT_s^*)^{1/2} \dots (11)$$

where K , n and σ are mass transfer coefficient, number of ice molecules at ice surface and the activated-portion of ice surface. Differentiating $\log \sigma$ with $1/T_s^*$, we obtain activation energy E by Eq. (12) and from Eqs. (11) and (12) the relation between mass transfer coefficient K and temperature T_s^* is obtained as Eq. (13).

$$d(\log \sigma)/d(1/T_s^*) = -E/2.303 R \dots (12)$$

$$\begin{aligned} \log \sigma &= \log \kappa - (1/2) \{ \log M + \log 2\pi R + \log T_s^* \} \\ d(\log \kappa)/d(1/T_s^*) &= -E/2.303 R - 1/2 T_s^* \dots (13) \end{aligned}$$

3.4 Correlation between heat and mass transfer

Mass transfer due to the partial pressure difference of water vapor is represented by Eq. (14).

Fig. 5 Reaction process in sublimation of ice

Equation (14) is the fundamental relation in every process of mass transfer. Heat transfer due to the temperature difference between the ice and the condenser surfaces is given by Eq. (15).

$$\begin{aligned} dW/d\theta = & A\{(DMP)/RT(X-\zeta_1-\zeta_2)\} \\ & \times (P_s^*-P_c^*)/\bar{P}_g \\ & \times (h/RT)(P_s^*-P_c^*) \dots\dots\dots(14) \end{aligned}$$

$$\begin{aligned} dQ/d\theta = & A\{\lambda/(X-\zeta_1-\zeta_2)\}(T_s^*-T_c^*) \\ = & \alpha(T_s^*-T_c^*) \dots\dots\dots(15) \end{aligned}$$

where slip ζ_1 and ζ_2 could be considered to be equal both in heat transfer and in mass transfer by kinetic theory of gases. Using S_h and N_u , Eqs. (14) and (15) are expressed dimensionlessly

$$\begin{aligned} S_h = hl/D = & \{X/(X-\zeta_1-\zeta_2)\}(P/\bar{P}_g) \\ N_u = \alpha l/\lambda = & X/(X-\zeta_1-\zeta_2) \\ \therefore S_h/N_u = & (a/D)(h/\alpha)C_p\rho = P/\bar{P}_g \dots\dots\dots(16) \\ \therefore \alpha/h = & C_p\rho(a/D)(\bar{P}_g/P) \\ = & (\lambda/D)(\bar{P}_g/P) \dots\dots\dots(17) \end{aligned}$$

Partial pressure P_g of noncondensing gases acts as a resistance in mass transfer but acts as a conducting medium in heat transfer process.

Fig. 6 Experimental installation

Fig. 7 Diagram of temperature measurement

4. Experimental procedure

The experimental apparatus is composed of a vacuum chamber, measuring devices and evacuating systems as shown in Fig. 6. An evaporator, a 10×10 cm rectangular tray, is set in the vacuum chamber parallel to the condenser (kept at -196°C by liquified Nitrogen) whose surface area (about 300 cm^2) is sufficiently larger than the ice surface (100 cm^2) in the evaporator so that the resistance of condensation could be neglected. Experimental procedures to attain steady state sublimation are as follows: The vacuum chamber is evacuated down to a fixed pressure by vacuum pumps 15, 16 and the pressure is adjusted by leak valves 10, 12. The partial pressure of the air is measured by a McLeod gauge 4 and the total pressure is measured by a Pirani gauge 5. The pressure range in this experiment is $10 \sim 10^{-3}$ mmHg. Latent heat of sublimation is supplied either by an electric heater at the bottom of the ice sample, or by radiation heating

from the upper surface of the ice. The temperature and heat flux in the ice is measured by 0.2 mm copper-constantan thermo-couples buried at fixed points in the ice, as shown in Fig. 7. The surface temperature of the ice is determined by the extrapolation of ice temperature. The heat flux (q) is determined from the temperature gradient and the thermal conductivity of ice. The thermal conductivity of the ice is assumed not to change with pressure. The rate of mass transfer is determined from the time rate of change of weight of ice measured by the spring balance 3. The measurement is started after attaining steady state temperature distribution of the ice and the rate of mass transfer, and the temperature distribution is measured to a constant energy supply at a constant total pressure.

5. Experimental results

Experimental results are shown in Fig. 8 ~ Fig. 12. Change of the rate of mass transfer ($\dot{W}/A$) with total pressure ($10 \sim 10^3$ mmHg) at constant heat fluxes is shown in Fig. 8. The process clearly consists of three ranges of pressure. In the range ($P > 1$ mmHg), designated as A range, the mass transfer at constant heat flux is increased linearly with a decreasing $\log P$. In the range ($1 \text{ mmHg} > P > 10^{-2}$ mmHg), designated as B range, the mass transfer by constant heat flux

does not change with pressure, but is increased with an increase in the supplied heat flux. In the range ($P < 10^{-2}$ mmHg) the mass transfer rate decreases linearly with a decreasing $\log P$ and is independent of supplied heat flux. In each range, maximum rates of mass transfer are observed.

The change of heat transfer between ice and condenser surfaces with pressure is shown in Fig. 9.

Fig. 8 Mass transfer rate against total pressure in various heater input

Fig. 9 The rate of heat conduction between ice and condenser surface

Fig. 10 Mass transfer rate against heat flux in phase change region

The transferred heat is observed to decrease linearly with a decreasing $\log P$ in the A range. Figure 10 shows the relation between the rate of mass transfer

Fig. 11 $P_g-t_g^*$ diagram for various heater inputs

Fig. 12 $P_g-t_g^*$ diagram for heater input 15 W

$\dot{W}/A$ and the heat q supplied to the surface of the ice in B range. The result shows that if $q < 1000$ kcal/m²hr, $\dot{W}/A$ increases linearly with q and that if $q > 1000$ kcal/m²hr, $\dot{W}/A$ does not change with q . In the latter range, line ① shows an unstable result in the early stage of the experiment and finally $\dot{W}/A$ increases to line ②, which is the maximum mass transfer rate. Figures 11 and 12 show the relationship between the temperature of the ice surface (t_s^*) and the partial pressure of noncondensing gases ($\log P$). From Fig. 12, corresponding to a heater input of 15 watts; it is understood that there is not a stable relation between them.

6. Discussion

6.1 The rate determinant process

From the experimental results, it is observed that the rate of mass transfer consists of three pressure ranges. We shall examine the rate determining processes for each region.

6.1.1 A-Region ($P=10 \sim 1$ mmHg, $\kappa_n=10^{-5} \sim 10^{-4}$)

In this pressure range, Knudsen number κ_n is $10^{-5} \sim 10^{-4}$, and the mechanism of flow is predominated by viscous flow. Therefore mass transfer is supposed to be determined by diffusion. In Fig. 13, experimental results are plotted in $\ln P$ and $\ln D$ coordinates. The linear relation in Fig. 13 shows the well known diffusion relation of water vapor in the air, $DP/T^{1.75} = \text{const.}$ The process in this region is determined by the rate of diffusion of water vapor

Fig. 13 D - P diagram in viscous flow region

in the gas phase. The value of diffusion coefficient at 0°C and 1 mmHg is about 93.8 m²/hr.

6.1.2 B-Region ($P=1 \sim 10^{-2}$ mmHg, $\kappa_n=10^{-4} \sim 10^{-2}$)

This region does not satisfy the relation $DP/T^{1.75} = \text{const.}$ in spite of the viscous flow region (See Fig. 13). It is clear that the rate is not controlled by the diffusion process in gas phase. Experimental results of mass transfer coefficient κ by Eq. (14) are plotted against inverse absolute temperature ($1/T_s^*$) in Fig. 14. From the linear relation in κ - $1/T_s^*$ diagram and Eq. (13), it is clear that the process is determined by the rate of phase change. By Eqs. (13) and (18) the activation energy (E) of sublimation of ice can be calculated to be $E = -12.9$ kcal/mole = -719 kcal/kg.

$$d(\log \kappa)/d(1/T) = 2.81 \times 10^3 \dots\dots\dots (18)$$

The activated portion of the ice surface is calculated by Eq. (11). Figure 15 shows experimental results plotted in $\log \sigma$ and $1/T_s^*$ coordinates. At $t_s^* = -65.75^\circ\text{C}$, the extrapolated line in Fig. 15 crosses abscissa $\sigma = 1.00$, which means the whole ice surface is activated, namely the rate of phase change is equal to the rate of molecular transfer in gases when the surface temperature of the ice attains this temperature.

Fig. 14 Coefficient of mass transfer κ against inverse absolute temperature $1/T_s^*$

6.1.3 C-Region

Lines C and D in Fig. 8 are the experimental results of ours and K. Tschudin's and they agree with the rate of molecular flow calculated by Eq. (4). The transition temperature from region B to C can be obtained from the transition pressure in Fig. 8 to be about -65°C , which agrees with the prescribed $t_s^* = -65.75^{\circ}\text{C}$ for $\sigma=1$. In region C, the rate of the process is determined by the rate of molecular flow in the gas phase.

6.2 Discussion on the accommodation coefficient

From our experiments, the value of the accommodation coefficient of molecular mass transfer $\epsilon = 0.96 \pm 0.06$, obtained by K. Tschudin is recommended. The other experimental values of ϵ proposed by T. K. Sherwood and S. Kawamura are about $1 \sim 10^{-2}$. The difference from K. Tschudin's value is considered to be because they regard the region of phase change (region B in this paper) as that of molecular flow (region C) and obtained a low value corresponding to the activation grade σ in our papers.

6.3 The maximum rates of mass transfer

Experimental results in Fig. 8 show that the rate of sublimation has a maximum value in spite of increased heat supply in the A and B regions, and is represented with only one line in region C. Photographs (a) and (b) in Fig. 16 show the ice surface in region B, (a) being the surface in the early stage of the experiment, and (b) the final stage where the surface becomes very rough. These surfaces correspond to the experimental results in Fig. 10, i.e. (a) to line ① and (b) to ②. When a large heat flux is supplied, the ice surface is superheated and the surface area increases by changing the initial smooth surface to a rough one until the surface area of ice reaches its maximum. The behavior of surface temperature in Figs. 11 and 12,

Fig. 15 Accommodation coefficient of ice in molecular flow region

when supplied with a large heat flux, corresponds to the above phenomena. Photograph (c) in Fig. 16 shows the ice surface in region A supplied with a large heat flux. The ice particles which can be found on the surface are supposed to be recondensed water vapor on the ice surface because of the limited rate of diffusion in gas phase.

6.4 Correlation between heat and mass transfer

The correlation equation (17) is valid when the rate of mass transfer is governed by the rate in gas phase. In our experiments, the intermediate region was not observed because of phase change phenomena, therefore we should only be concerned with this theory in the A-region. From Fig. 9 thermal conductivity of gas is represented experimentally as follows (Fig. 17).

(a) Early stage of experiment in B region

(b) Final stage of experiment in B region

(c) Recondensated ice particles in A region

Fig. 16 Photographs of the ice surface when large heat flux is supplied

$$\lambda = 0.11 \times P^{1/3} \dots\dots\dots(19)$$

From Eq. (19) and $D_0 P_0 = \text{constant}$, Eq. (17)

becomes

$$\alpha/h = C P^{1/3} P_g \dots\dots\dots(20)$$

Lewis' equation is invalid in this low pressure region.

7. Conclusions

The rate of sublimation of ice was investigated through experiments. The pressure range was from 10 to 10^{-3} mmHg. The following processes were shown to be rate-determining factors in the mass transfer of sublimation of the ice.

(1) The rate of mass transfer of ice is governed by three patterns to be determined by diffusion, molecular flow, and phase change.

(2) In the pressure range ($P > 1$ mmHg) the rate of mass transfer is governed by the diffusion velocity in gas phase, and the maximum rate is

Fig. 17 Thermal conductivity of gas in low pressure region

reached when the vapor is super-saturated and a part of it recondensates on the ice surface.

(3) Under 10^{-2} mmHg, the velocity of molecular flow, known in the kinetic theory of gases, governs the rate of mass transfer, and in our experiments, the accommodation coefficient obtained by K. Tschudin was shown to be recommendable for this region.

(4) In the pressure range ($1 \text{ mmHg} > P > 10^{-2} \text{ mmHg}$) the rate is governed by the velocity of phase transition from ice to vapor on the ice surface. In this range, the ice surface becomes very rough. The maximum rate is reached when the surface area of ice increases to the maximum.

(5) For finding the correlation between heat and mass transfer from these experimental results, use of the following relation is recommended.

$$\alpha/h = \rho C_p (a/D) (\bar{P}_g/P)$$

α : coefficient of heat transfer

h : coefficient of mass transfer

References

- (1) B. G. Dickens: *Roc. Roy. Soc. Lond.*, Ser. A, No. 143 (1934), p. 517.
- (2) T. K. Sherwood and N. E. Cooke: *A. I. Ch. E. Jour.*, Vol. 3 (1957), p. 37.
- (3) Y. Nagai et al.: *Kogyo-Kagaku-Zasshi (Jour. Chem. Soc. Japan, Indust. Chem. Sec.)*, Vol. 60 (1957), p. 856.
- (4) S. Kawamura: *Kagaku-Kogaku (Chem. Engng., Japan)*, Vol. 26 (1962), p. 438.
- (5) H. Ueha et al.: *Kagaku-Kogaku (Chem. Engng., Japan)*, Vol. 24 (1960), p. 274.
- (6) K. Tschudin: *Helv. Physic. Aca.*, Vol. 19 (1946), p. 91.
- (7) R. W. Schrage: *Interphase Mass Transfer*, (1953), Columbia.
- (8) M. Smoluchowsky: *Anu. Physik.*, Vol. 35 (1911), p. 984.