STUDIES ON SUBLIMATION COEFFICIENT OF ICE

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Sublimation rate of ice into rarefied gases is studied experimentally between two concentric spheres in the range of sublimating surface temperature of $-50^{\circ}\text{C} \sim -30^{\circ}\text{C}$, and the range of stagnant gas pressure at the condensing surface of $0 \sim 1$ mmHg.

The results are compared with the analytical results obtained with the two-sided Maxwellian distribution functions. Applying the theoretical results to mass transfer through the gaseous phase, a sublimation coefficient of ice of about 0.3 is obtained near -30°C and 0.7 near -50°C . The effect of the partial pressure of stagnant gas on experimental measurements of the sublimation coefficients is also discussed.

1. Introduction

The study of sublimation rate of ice under vacuum is interesting as a basic study of freeze-drying as well as of mass transfer through rarefied gases. As is well known, the equation of diffusion which holds under atmospheric pressure cannot be applied to mass transfer through rarefied stagnant gases or under pressure so decreased that the mean free path of molecules is comparable with the characteristic length of the diffusion space. Under these conditions the assumption of quasi-equilibrium between the gas phase and the evaporating surface no longer holds and, therefore, new boundary conditions concerned with the rate of phase change must be taken into account as well as the rate of diffusion through stagnant gas. Under such conditions the rate of phase change can be expressed by the well-known Hertz-Knudsen equation,

$$G = a \left(\frac{M}{2\pi RT_s} \right)^{1/2} (P_s - P) \quad (1)$$

where a is the evaporation (sublimation) coefficient. This evaporation (sublimation) coefficient becomes an important controlling factor for mass transfer with evaporation, especially when the diffusional resistance of the gaseous phase is so small that the mass transfer rate approaches its maximum rate. And if the evaporation coefficient is very small, evaporation resistance cannot be neglected even when the diffusional resistance is relatively large.

Theoretical studies of these evaporation (sublimation) coefficients of liquids and solids have been made by many investigators^{8,10,11,13,15,19,29)} considering various models of evaporating surface. The most successful theory for the evaporation coefficients of liquids is that of Eyring *et al.*¹³⁾, who proposed the free angle ratio of liquids, which was found to be

equal to the evaporation coefficient^{19,29)}. As for the sublimation coefficient of solids, none of them can be used to estimate successfully the sublimation coefficients for practical use.

There are also a number of experimental investigations of the evaporation (sublimation) coefficients^{2,7,9,14,20,23,26)} of various kinds of substances, some of which are listed in Table 1. In Table 2 are shown the experimental results of the sublimation coefficient of ice. As shown in this table, some of them are nearly equal to 1.0 at temperatures below -60°C , and the coefficient seems to decrease as the temperature increases. But this is not clear from these data. The scattering of these values may be considered to be due to the unsuitable estimation of mass transfer in the gaseous phase (effect of stagnant gas which might exist and the uncertainty of the diffusing space)

Table 1 Examples of evaporation (sublimation) coefficients of liquids and solids

Material	Value of evaporation coefficient
Ethanol	0.02 at 0°C ²⁾ , 0.036 at 25°C ¹⁶⁾ , 0.25 ⁴⁾
Methanol	0.045 at 0°C ²⁾ , 0.022 at -10°C and 0.03 at -27°C ⁷⁾
Water	0.036~0.04 at $10 \sim 30^{\circ}\text{C}$ ¹⁾ 0.25~1.0 at $2 \sim 5^{\circ}\text{C}$ ⁹⁾ 0.042 at 0°C and 0.026 at 43°C ⁶⁾ 0.35~1.0 at $10 \sim 50^{\circ}\text{C}$ (condens.) ²¹⁾
Cadmium	0.388~0.65 at $417.6 \sim 507.6^{\circ}\text{C}$ ³⁾
Iodine	0.055~0.208 at $40 \sim 70^{\circ}\text{C}$ ¹⁸⁾ 0.005~0.023 at $35 \sim -28^{\circ}\text{C}$ ²⁵⁾
Mercury	0.85~0.94 at $-64 \sim 70^{\circ}\text{C}$ ²⁹⁾
Naphthalene	0.036~0.135 at $40 \sim 70^{\circ}\text{C}$ ¹⁸⁾ 0.88 at 0°C ⁵⁾ , 0.9 at $-10 \sim -20^{\circ}\text{C}$ ²⁶⁾

Table 2 Sublimation coefficient of ice

0.94±0.06	at $-58 \sim -60^{\circ}\text{C}$ ²⁸⁾
nearly unity	at $-60 \sim -40^{\circ}\text{C}$ ¹⁷⁾
0.67	at $-80 \sim -60^{\circ}\text{C}$ ²²⁾
0.6~0.4	at $-80 \sim -60^{\circ}\text{C}$ (condensation ²²⁾)
0.83±0.12	at -128°C ²²⁾
0.0144	at $-13 \sim -2^{\circ}\text{C}$ ⁶⁾
0.0009~0.6	at $0 \sim -50^{\circ}\text{C}$ ¹²⁾

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Fig. 1 Schematic diagram of apparatus

Fig. 2 Details of sample sphere of ice

in addition to the difficulty of temperature measurement of the sublimating surface.

In the present work the sublimation rate of ice under vacuum is studied experimentally under various partial pressures of inert gas (air). From the experimental results the sublimation coefficient of ice is obtained by applying the theoretical results of the two-sided Maxwellian distribution functions to mass transfer in the gaseous phase. The effect of the partial pressure of stagnant gas on the experimental estimation of evaporation coefficients is also discussed.

2. Experimental Apparatus and Procedures

A schematic diagram of the apparatus is shown in Fig. 1. Sublimation occurs at the surface of the inner sphere (about 31 mm diam.) of ice and the vapor diffuses through the stagnant gas (air) and then condenses on the inner surface of the outer sphere (150 mm I.D.) of glass, the temperature of which is kept constant during the measurements. These two spheres are made concentric before the experiments. The details of the heater in the sample of ice sphere are shown in Fig. 2. The heater consists of a heating wire (0.1 mm diam.) coiled around a glass sphere.

The wire is fixed with a thin layer of cohesive agent. A stainless steel pipe (1 mm O.D.) is attached as shown in this figure to support the heater in the center of the ice sphere when the sample sphere of ice is made. The heater is set in a pair of hemispherical cups (31 mm I.D.) of brass so as to coincide with the centers of these spheres. Two pairs of copper-constantan thermocouples (0.06 mm diam.) are fixed near the inner surface of the brass cups (depth from inner surface of the cup is less than 1 mm) before the pair of cups are put together. Distilled water is poured into the space between these two spheres from a small hole in the top of the brass sphere, shown in Fig. 2, and then cooled slowly to make an ice sphere. The sublimation rates of the ice sphere are measured by the weighing mechanism, shown in Fig. 1, which consists of a spring, an electric transformer and a displacement meter. The temperature of the condensing surface is measured by two pairs of thermocouples (0.29 mm diam.) attached to the inner surface of the outer sphere, where a small amount of ice is condensed before the experiments. The temperature of this surface is kept constant (within $\pm 0.05^\circ\text{C}$) during each measurement by circulating a coolant. The temperature of the sublimating surface is also measured by two pairs of thermocouples mounted near the surface of the ice sphere as described above.

After the sample of ice sphere frozen as described above was cooled further by coolant from a refrigerator the temperature of which was kept constant, evacuation was carried out until a definite pressure was attained. Then the glass cock was closed and heating was started. After a quasi-steady state was attained, measurements of surface temperature, rate of sublimation and pressure were made. After the measurements the ice sphere was taken out of the chamber to measure its diameter and to check if the junctions of the thermocouples were just at the surface or not.

Embedment of the thermocouple in the ice sphere will cause a direct error in readings of the surface temperature. For example, if the junction is at a depth of 0.1 mm from the surface the temperature reading will be higher than the temperature of the sublimating surface by about 0.1°C for the worst case. Accordingly, it was strictly checked if the junction was just on the surface of the ice sphere or not. And the temperature distribution of the sublimating surface was checked by mounting two thermocouples in the thin layer near the surface. The maximum difference in the readings of these thermocouples was about 20% of the temperature difference between the sublimating and condensing surfaces when both thermocouples were confirmed to be just on the surface.

3. Discussion of the Results

The mechanism of mass transfer in the gaseous phase must be clearly known to determine sublimation (evaporation) coefficients. If it is not, the ambiguity of the rate of mass transfer in the gaseous phase causes uncertainty in the value of sublimation (evaporation) coefficients, because these coefficients cannot be determined experimentally without mass transfer in the gaseous phase.

Until now two models of mass transfer under vacuum have been proposed, one of which is the classical "series resistance model²³⁾", where the resistances of evaporation and diffusion are considered in series. The other is the one derived from the two-sided Maxwellian distribution functions²⁶⁾. It was found that the results of these two models completely coincided for mass transfer between two infinite parallel plates²⁷⁾, but not for the case of curved surfaces such as was the case in the present work.

In this paper the results obtained from the model of the two-sided Maxwellian distribution functions is used to estimate the sublimation coefficient. According to this model, the mass transfer rate can be expressed as²⁶⁾

$$N_{AI} = \left(\frac{m_A}{2\pi kT} \right)^{1/2} \gamma \quad (2)$$

where γ is to be obtained from the following equation:

$$P_{AI} - P_{AII} = \left[\frac{1}{a} + \left\{ \frac{1-a}{a} \left(\frac{1}{\bar{R}^*} \right)^2 \right\} \right] \gamma + P_{BIII} \left[1 - \exp \left\{ -\zeta \gamma \left(1 - \frac{1}{\bar{R}^*} \right) \right\} \right] \quad (3)$$

where

$$P_{BIII} = P_m - P_{AII} - \frac{1}{a} \left(\frac{1}{\bar{R}^*} \right)^2, \\ \zeta = \frac{1}{2P_t D} \left(\frac{2kT}{\pi m_A} \right)^{1/2} \text{ and } \bar{R}^* = \frac{R_{II}}{R_I}$$

In the absence of stagnant gases Eq. (2) can be written as

$$N_{AI} = \frac{1}{\frac{1}{a} + \left(\frac{1-a}{a} \right) \left(\frac{1}{\bar{R}^*} \right)^2} \cdot \left(\frac{m_A}{2\pi kT} \right)^{1/2} (P_{AI} - P_{AII}) \quad (4)$$

The experimental results of the sublimation coefficient of ice calculated by Eq. (4) are shown in Table 3, which also shows the experimental results at various partial pressures of stagnant gas (air) (group B). The vapor pressure of ice was measured as shown in Fig. 3 and was used in the calculations of these values. It can be seen from the results of group (A) in Table 3 that the sublimation coefficient of ice depends on the temperature. It decreases as the temperature

Table 3 Experimental results

Group A ($P_{BIII}=0$)					
Run No.	T_I [°C]	T_{II} [°C]	ΔP [μ Hg]	$N_{AI} \times 10^5$ [g/cm ² ·sec]	a [—]
1	-40.02	-40.70	7.2	5.60	0.51
3	-39.13	-40.15	11.3	7.98	0.45
19	-39.95	-40.75	8.2	6.78	0.52
20	-39.02	-40.05	11.4	7.37	0.41
32	-49.10	-50.38	5.1	5.71	0.68
33	-36.56	-37.05	7.4	7.26	0.62
43	-33.35	-33.85	9.0	7.22	0.53
45	-27.35	-27.63	13.0	5.93	0.30
46	-28.95	-29.40	15.0	6.85	0.30

Group B						
Run No.	T_I [°C]	T_{II} [°C]	ΔP [μ Hg]	$N_{AI} \times 10^5$ [g/cm ² ·sec]	$K_g \times 10^3$ [g/cm ² ·sec·mmHg]	P_{BIII} [μ Hg]
34	-29.75	-30.50	21.0	5.04	2.40	33
35	-29.65	-30.53	26.0	4.94	1.90	26
36	-29.40	-29.80	13.0	5.24	4.03	18
37	-28.05	-28.45	14.0	5.33	3.81	4
38	-30.29	-30.88	16.0	5.47	3.42	10
39	-29.45	-30.01	20.0	7.94	3.47	16
40	-30.80	-31.47	17.0	6.90	4.07	10
41	-31.45	-31.95	12.0	7.21	6.55	7
44	-30.53	-31.20	17.0	7.19	4.23	3
2	-39.65	-40.52	9.1	7.84	8.62	3
4	-38.90	-40.75	20.1	1.68	0.836	140
5	-38.15	-40.45	26.5	1.12	0.423	332
6	-36.30	-40.60	54.9	1.41	0.357	467
7	-36.35	-40.01	58.0	1.12	0.193	607
8	-34.90	-40.01	84.8	1.33	0.157	756
9	-39.65	-40.75	11.4	7.37	6.47	6
10	-40.25	-41.40	11.3	4.31	3.81	26
11	-39.70	-41.90	21.8	2.59	1.19	82
12	-40.05	-41.85	17.4	4.31	2.48	40
13	-40.60	-41.85	11.8	6.49	5.50	9
14	-40.65	-41.65	9.6	6.48	6.75	12
15	-40.45	-41.40	9.3	6.25	6.72	10
16	-40.45	-41.00	5.4	3.07	5.69	3
17	-40.10	-40.98	8.7	2.51	2.89	43
21	-48.15	-49.80	7.1	2.75	3.87	21
22	-46.85	-49.80	13.5	2.73	2.02	62
23	-46.90	-49.80	13.3	2.47	1.86	6
24	-46.75	-49.70	13.7	3.79	2.77	19
26	-47.70	-49.85	9.5	3.79	3.99	25
27	-48.40	-49.85	6.2	4.90	7.90	6
28	-48.20	-50.23	8.7	5.10	5.86	8
29	-47.99	-50.20	9.6	5.40	5.63	13
30	-48.33	-50.38	8.5	4.52	5.23	12
31	-48.85	-50.23	5.8	5.73	9.89	5

Fig. 3 Observed vapor pressure

(calculated from Eqs. (2) and (3) for $a=1.0$)

Fig. 4 Effects of partial pressure of stagnant gas (air) and driving force on mass transfer (ice)

increases, as reported by Stern *et al.*²⁵⁾ for iodine. And it can be guessed from the authors' results that the sublimation coefficient of ice approaches the results of Tschudin²⁸⁾ and others²²⁾, or 1.0 as the temperature decreases. At rather high temperatures Delany *et al.*⁶⁾ and Kawamura¹²⁾ reported sublimation coefficients of the order of $10^{-2} \sim 10^{-3}$, which seems too small judging from the relatively slight dependency of the coefficient on temperature found by the authors.

In general it is very difficult to obtain the evaporation (sublimation) coefficients of materials such as ice the vapor pressure of which sharply changes with temperature, because the temperature difference between condensing and evaporating surfaces is very small at moderate evaporation rates. And at the moderate evaporation rates even a small partial pressure of inert gas makes a large error in evaporation rate or in experimental estimation of the evaporation (sublimation) coefficient as shown in Fig. 4 (calculated from Eqs. (2) and (3) by putting a to be 1.0), where the mass transfer rate is shown with a parameter of the partial pressure of the inert gas. It can be seen from this figure that the mass transfer rate approaches the maximum evaporation rate as the driving force ΔP increases and the effect of the partial pressure of the inert gas on mass transfer rate decreases. At the moderate evaporation rates near $N_{AI} = 10^{-5} \sim 10^{-4}$ g/cm²·sec, however, the effect of partial pressure on mass transfer is large and cannot be neglected. If the effect of partial pressure of the stagnant gas of 0.005 mmHg were neglected, for example, then the apparent evaporation coefficient might be smaller than 0.7 (in spite of the real value of

Fig. 5 Comparison of experimental results of mass transfer rate with theoretical ones in the presence of stagnant gas (air)

the coefficient a of 1.0) when the mass flux is of the order of 10^{-5} g/cm²·sec. Therefore the partial pressure of stagnant gas must be precisely measured to obtain the evaporation coefficient experimentally. The effect of the partial pressure of stagnant gas and the evaporation coefficient on mass transfer is more clearly shown in Fig. 5 with the parameter of the evaporation coefficient. The ordinate is the mass transfer coefficient K_g , defined here as $K_g = N_{AI} / (P_{AI} - P_{BII})$ for convenience. In the same figure the experimental results are shown. The values of group (A) in Table 3 are plotted on $P_{BII} = 0.001$ mmHg for reference. The solid lines are the theoretical curves corresponding to the values of the sublimation coefficient of 0.7, 0.5 and 0.3. It can be seen from this figure that the sublimation coefficient plays an important role in mass transfer through a highly rarefied stagnant gas, but it does not do so at relatively large partial pressure of stagnant gas (larger than about 0.1 mmHg, for example) if the sublimation coefficient is relatively large (larger than about 0.5 in the present case).

Judging from the finding that the experimental results near the temperatures -50°C , -40°C and -30°C are in relatively good accord with the theoretical results for the sublimation coefficients of 0.7, 0.5 and 0.3 respectively, the values of sublimation coefficient of ice obtained here are considered to be reliable.

4. Conclusion

Mass transfer rates through a rarefied stagnant gas were measured between two concentric spheres. The sublimation coefficient of ice was obtained from experimental results to be about 0.3 near -30°C and 0.7 near -50°C . Using these results of the sublimation coefficient, the experimental results were in relatively good accordance with the theoretical results

in the presence of the stagnant gas. It was also found that the partial pressure of the stagnant gas significantly affects the mass transfer rate, and it cannot be neglected in the experimental estimation of the evaporation (sublimation) coefficient, even if the partial pressure is of the order of 10^{-3} mmHg.

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Nomenclature

a	= evaporation (sublimation) coefficient
D	= diffusion coefficient
G	= evaporation rate
k	= Boltzmann constant
M	= molecular weight
m_A	= mass of a molecule
N_{AI}	= mass flux per unit area of evaporating surface
P	= (partial) pressure just above evaporating surface
P_{AI}	= saturated vapor pressure at temperature T_I of evaporating surface
P_{AII}	= saturated vapor pressure at temperature T_{II} of condensing surface
P_{BIII}	= partial pressure of stagnant gas at condensing surface
P_m	= pressure measured by manometer
P_t	= total pressure
R	= gas constant
R_I	= radius of evaporating sphere
R_{II}	= radius of sphere of condensing surface
T	= temperature

(C.G.S. units are used.)

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