# Mass Transfer Through a Rarefied Gas Between Two Concentric Spheres 

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(Received Aug. 31, 1967)


#### Abstract

The present work was undertaken to derive a theoretical formula of mass transfer under a reduced pressure, especially the transition regime, through the gas kinetic-theory and compare it with the experimental results. The Maxwell moment method utilizing the two-sided Maxwellian distribution function having been proposed by Lees et al. was applied to the mass transfer between two concentric spheres. In the process of analysis, the accomodation coefficient for mass transfer was taken into account. The analytical solution in which the value of accomodation coefficient was evaluated as 0.9 showed in good agreement with the experimental results of sublimation of naphthalene.


## 1. Introduction

Mass transfer operations under reduced pressure, such as freezing drying, molecular distillation, metallizing under vacuum and so on, are accompanied with a phase change in all cases and play a very important roll in chemical engineering. Considering the mass transfer phenomena with phase change, for example, sublimation, condensation and evaporation, two kinds of resistance for transfer rate should be evaluated. One is the resistance for mass transfer through the surrounding space which may also be called a gaseous diffusion under an ordinary pressure, and the other is the resistance for phase change at the interface which is concerned in accomodation, condensation or evaporation coefficient.

The mechanism of mass transfer through the surrounding space has been classified into three regimes by Knudsen number ( $K n$ ). Those are the free molecular regime at highly rarefied condition, $K n>10$, the continuum regime at an ordinary condition, $K n<0.01$, and the transition regime between them. The mass transfer in this transition regime has been given a great interest by investigators of physics and technology. Especially its applications are very important for chemical engineering but few theoretical and experimental works ${ }^{3,4,8,11)}$ have been done because of its complexity.

It has been generally accepted apriori by the previous investigators that the

[^0]Stefan relation with the pressure-jump boundary condition which is analogous to the Maxwell-Smoluchowski temperature-jump boundary condition for heat transfer would be correct. There has been no theoretical basis on applying the Stefan relation to the mass transfer with a large degree of rarefaction, high mass flux and large pressure gradient between evaporation or sublimation and condensation surface.

The present work was undertaken to derive a theoretical formula of mass transfer under a reduced pressure, especially transition regime, through the gas kinetic-theory and compare with the experimental results.

The Maxwell moment method utilizing the two-sided Maxwellian distribution function ${ }^{2,6,7)}$ was applied to the mass transfer between two concentric spheres. The analytical solution obtained was compared with the experimental results obtained in the sublimation of naphthalene under reduced pressure $\left(10^{-1} \sim 10^{-3} \mathrm{~mm}\right.$ Hg in total pressure).

## 2. Theoretical Works

## 2-1. Distribution Function and Mean Quantities

Let us consider a sphere of radius $R_{I}$ placed at the center of a concentric sphere of radius $R_{I I}$, with $R_{I}<R_{I I}$ (Fig. 1).

Sublimation or evaporation of molecule, A, occurs at the outer surface of the inner sphere and condensation at the inner surface of the outer sphere. The annular region ( $R_{I}<R<R_{I I}$ ) is filled with inert gas, B , at an arbitrary density level and diffusion gas, A.


Fig. 1. Spherical polar coordinates.

By applying Lees's model"), the "two-sided Maxwellian" velocity distribution functions are defined at an arbitrary point in the annular space as follows (Fig. 1); all outwardly directed molecules with velocity vector $\xi$,

$$
\begin{align*}
\xi & =\left(\xi_{R}{ }^{2}+\xi_{\theta}{ }^{2}+\xi_{\phi}{ }^{2}\right)^{1 / 2},  \tag{1}\\
\psi & =\tan ^{-1}\left\{\left(\xi_{\theta}^{2}+\xi_{\phi}{ }^{2}\right)^{1 / 2} / \xi_{R}\right\}, \tag{2}
\end{align*}
$$

lying inside "the wedge of influence" ${ }^{2}$, (region 1 in Fig. 1) are characterized by one Maxwellian $f_{1}$,
for

$$
\begin{aligned}
f=f_{1}= & n_{1}(m / 2 \pi k T)^{3 / 2} \exp \left(-m \xi^{2} / 2 k T\right), \\
& -(\pi / 2)+\alpha<\psi<(\pi / 2)-\alpha
\end{aligned}
$$

in which

$$
\begin{equation*}
\alpha=\cos ^{-1}\left(R_{I} / R\right) \tag{4}
\end{equation*}
$$

Then, all molecules with velocity vector $\leqslant$ lying outside of region 1 are characterized by $f_{2}$,
i.e.,

$$
\begin{equation*}
f=f_{2}=n_{2}(m / 2 \pi k T)^{3 / 2} \exp \left(-m \xi^{2} / 2 k T\right), \tag{5}
\end{equation*}
$$

for

$$
(\pi / 2)-\alpha<\psi<(3 \pi / 2)-\alpha
$$

where $n_{1}(R)$ and $n_{2}(R)$ are the two unknown functions of radial distance.
In the above definitions, as we consider the case of the temperature difference between the two spheres is small so that each temperature of the two spheres can be shown as the same $T$ in the absolute temperature [ ${ }^{\circ} \mathrm{K}$ ] and also it is assumed that the Maxwellian velocity distribution function for being at rest could be approximately applicable when the net flow of molecule A between the concentric spheres is relatively small.

Knowing the distribution function $f$, one can evaluate all mean quantities $\langle Q\rangle$ by averaging over the all velocity space,

$$
\begin{align*}
& n\langle Q\rangle=\int Q f d \boldsymbol{\xi}=\int_{I} Q f_{1} d \boldsymbol{\xi}+\int_{I I} Q f_{2} d \boldsymbol{\xi},  \tag{6}\\
& \int f d \boldsymbol{\xi}=\langle n\rangle=(1 / 2)\left\{n_{1}(1-\sin \alpha)+n_{2}(1+\sin \alpha)\right\},  \tag{7}\\
& \int f \xi_{R} d \boldsymbol{\xi}=\left\langle u_{R}\right\rangle=(1 / 4)(2 k / m \pi)^{1 / 2}(1+\cos 2 \alpha)\left(n_{1}-n_{2}\right) T^{1 / 2},  \tag{8}\\
& -\int f m \xi_{R}^{2} d \xi=\left\langle P_{R R}\right\rangle=-(k / 2)\left\{n_{1}\left(1-\sin ^{3} \alpha\right)+n_{2}\left(1+\sin ^{3} \alpha\right)\right\} T,  \tag{9}\\
& \langle p\rangle=-(1 / 3)\left\{\left\langle P_{R R}\right\rangle+\left\langle P_{\theta \theta}\right\rangle+\left\langle P_{\phi \phi}\right\rangle\right\}=(k / 2)\left\{n_{1}(1-\sin \alpha)+n_{2}(1+\sin \alpha)\right\} T . \tag{10}
\end{align*}
$$

## 2-2. Maxwell Integral Equation of Transfer

In spherical co-ordinates the Maxwell integral equation of transfer being spherical symmetric is as follows:

$$
\begin{align*}
& \frac{1}{R^{2}} \frac{\partial}{\partial R} R^{2} \int f \xi_{R} Q d \boldsymbol{\xi}+\frac{1}{R \tan \theta} \int f \xi_{\theta} Q d \xi-\int f\left(\frac{\xi_{\theta}^{2}}{R}+\frac{\xi_{\phi}^{2}}{R}\right) \frac{\partial Q}{\partial \xi_{R}} d \boldsymbol{\xi} \\
& \quad+\int f\left(\frac{\xi_{R} \xi_{\theta}}{R}-\frac{\xi_{\phi}^{2}}{R \tan \theta}\right) \frac{\partial Q}{\partial \xi_{\theta}} d \boldsymbol{\xi}+\int f\left(\frac{\xi_{R} \xi_{\phi}}{R}+\frac{\xi_{\theta} \xi_{\phi}}{R \tan \theta}\right) \frac{\partial Q}{\partial \xi_{\phi}} d \boldsymbol{\xi}  \tag{11}\\
& =\Delta Q
\end{align*}
$$

where $\Delta Q$ is the collision integral.
There are the two kinds of molecule, diffusing molecule A and non-diffusing molecule B , and one should take the distribution functions for each molecule into account. Therefore there are four unknown parameters, $n_{A_{1}}, n_{A 2}, n_{B_{1}}$ and $n_{B 2}$, and they could be evaluated by utilizing the four Maxwell integral equations as follows.
(a) Mass Conservation for A Molecule

Setting $Q=m_{A}$, we find $\Delta Q=0$ because the mass is invariant during collisions, and obtain the ordinary continuity equation as follows;

$$
\begin{equation*}
\frac{1}{R^{2}} \frac{\partial}{\partial R} R^{2} \int f_{A} m_{A} \xi_{A R} d \xi_{A}=0 \tag{12}
\end{equation*}
$$

From eqs. (8) and (12), we obtain the following relation;

$$
\begin{equation*}
(1 / 4)\left(2 m_{A} k / \pi\right)^{1 / 2} \frac{1}{R^{2}} \frac{\partial}{\partial R} R^{2}(1+\cos 2 \alpha)\left(n_{A_{1}}-n_{A_{2}}\right) T^{1 / 2}=0 . \tag{13}
\end{equation*}
$$

On the other hand;

$$
R^{2}(1+\cos 2 \alpha)=2 R_{I}^{2}=\text { const. }
$$

then the following equation is obtained,

$$
\begin{equation*}
n_{A_{1}}-n_{A 2}=r^{\prime}=\text { const. } \tag{14}
\end{equation*}
$$

where $\gamma^{\prime}$ is an integral constant.
(b) Mass Conservation for $\mathbf{B}$ Molecule

Setting $Q=m_{B}$,

$$
\begin{equation*}
(1 / 4)\left(2 m_{B} k / \pi\right)^{1 / 2} \frac{1}{R^{2}} \frac{\partial}{\partial R} R^{2}(1+\cos 2 \alpha)\left(n_{B 1}-n_{B 2}\right) T^{1 / 2}=0 \tag{15}
\end{equation*}
$$

Here B molecule is the non-diffusing component, then

$$
\begin{equation*}
n_{B_{1}}-n_{B 2}=0 . \tag{16}
\end{equation*}
$$

(c) $R$-momentum Conservation

The collision integral is equal to zero when taking the sum of the transfer equations for A and B molecules, because the R -momentum is conservative as a whole.
Substituting $Q=m_{A} \xi_{A R}$ or $Q=m_{B} \xi_{B R}$ into eq. (11),

$$
\begin{align*}
& \frac{\partial}{\partial R} \int f_{A} m_{A} \xi_{A R}^{2} d \xi+\frac{3}{R} \int\left\{-\frac{1}{3}\left(f_{A} m_{A} \xi_{A R}^{2}+f_{A} m_{A} \xi_{A \theta}^{2}+f_{A} m_{A} \xi_{A \phi}^{2}\right)\right. \\
& \left.+f_{A} m_{A} \xi_{A R}^{2}\right\} d \xi=\Delta Q_{A B} \tag{17}
\end{align*}
$$

Then we obtain the next equation,

$$
\begin{equation*}
\sin ^{3} \alpha \frac{d}{d R}\left(n_{A_{1}}-n_{A 2}\right) T-\frac{d}{d R}\left(n_{A_{1}}+n_{A 2}\right) T=-\left(\frac{2}{k}\right) \Delta Q_{A B}, \tag{18}
\end{equation*}
$$

likewise

$$
\begin{equation*}
\sin ^{3} \alpha \frac{d}{d R}\left(n_{B_{1}}-n_{B_{2}}\right) T-\frac{d}{d R}\left(n_{B_{1}}+n_{B_{2}}\right) T=-\left(\frac{2}{k}\right) \Delta Q_{B A} . \tag{19}
\end{equation*}
$$

Summing up eqs. (18) and (19),

$$
\begin{align*}
& \frac{d}{d R}\left(n_{A 1}+n_{A 2}+n_{B 1}+n_{B 2}\right)=0  \tag{20}\\
& n_{A 1}+n_{A 2}+n_{B 1}+n_{B 2}=\delta^{\prime}=\text { const. } \tag{21}
\end{align*}
$$

where $\delta^{\prime}$ is an integral constant.

## (d) Mass Flux for A Molecule ${ }^{5}$

Since we are primarily interested in radial mass transfer, the mass flux equation is given by taking $Q=m_{A} \xi_{A R}$. In the mass flux equation, the collision integral $\Delta Q_{A B}$, for simplicity, is evaluated with Maxwell's inverse-fifth-power force law $F=\widehat{K}_{A B} / r^{55}$. Then it should be noted that mass flux is influenced only by the collision integral $\Delta Q_{A B}$ involving the collisions between A and B molecules.

Assuming that an A molecule is collided by a B molecule from the P direction (see Fig. 2), the collision integral $\Delta Q_{A B}$ is expressed as follows:

$$
\begin{equation*}
\Delta Q_{A B}=\iiint \int\left(Q^{\prime}-Q\right) f_{A} f_{B} V d \xi_{A} d \xi_{B} b d b d \varepsilon \tag{22}
\end{equation*}
$$

and by Maxwell ${ }^{5}$,

$$
\begin{align*}
\int_{0}^{2 \pi}\left(Q^{\prime}-Q\right) d \varepsilon & =\int_{0}^{2 \pi} m_{A}\left(\xi_{A R}^{\prime}-\xi_{A R}\right) d \varepsilon \\
& =\left\{m_{A} m_{B} /\left(m_{A}+m_{B}\right)\right\}\left(\xi_{B R}-\xi_{A R}\right) 4 \pi \sin ^{2} \theta^{\prime} \tag{23}
\end{align*},
$$



Fig. 2. Binary encounter.

$$
\begin{equation*}
A_{1}=\int_{0}^{\infty} 4 \pi \beta \sin ^{2} \theta^{\prime} d \beta=2.6595 \tag{25}
\end{equation*}
$$

Therefore,

$$
\begin{align*}
\Delta Q_{A B} & =A_{1}\left\{\tilde{K}_{A B} m_{A} m_{B} /\left(m_{A}+m_{B}\right)\right\}^{1 / 2} \int f_{A} f_{B}\left(\xi_{B R}-\xi_{A R}\right) d \xi_{A} d \xi_{B} \\
& =A_{1}\left\{\widetilde{K}_{A B} m_{A} m_{B} /\left(m_{A}+m_{B}\right)\right\}^{1 / 2}\left\{\left\langle n_{A}\right\rangle\left\langle u_{B R}\right\rangle-\left\langle n_{B}\right\rangle\left\langle u_{A R}\right\rangle\right\} \tag{26}
\end{align*}
$$

Taking B molecule being at rest into account:

$$
\begin{align*}
\Delta Q_{A B} & =-A_{1}\left\{\tilde{K}_{A B} m_{A} m_{B} /\left(m_{A}+m_{B}\right)\right\}^{1 / 2}\left\langle n_{B}\right\rangle\left\langle u_{A R}\right\rangle \\
& =-\left(A_{1} / 2\right)\left\{\tilde{K}_{A B} m_{A} m_{B} /\left(m_{A}+m_{B}\right)\right\}^{1 / 2}\left(2 k T / m_{A} \pi\right)^{1 / 2} \gamma^{\prime} n_{B 1}\left(R_{I} / R\right)^{2} . \tag{27}
\end{align*}
$$

The diffusion coefficient for the Maxwell molecule is evaluated by the following formula ${ }^{1)}$,

$$
\begin{equation*}
\left[D_{A B}\right]=6 \pi / 8 n A_{1} \Gamma(2.5)\left\{k T\left(m_{A}+m_{B}\right) / 2 \pi m_{A} m_{B}\right\}^{1 / 2}\left(2 k T / \tilde{K}_{A B}\right)^{1 / 2} \tag{28}
\end{equation*}
$$

Eliminating $\widehat{K}_{A B}$ of eq. (27) using eq. (28), we obtain

$$
\begin{align*}
& \Delta Q_{A B}=-\left(n_{B 1} r^{\prime} / n\left[D_{A B}\right]\right)\left(2 k T / m_{A} \pi\right)^{2 / 2}\left(R_{I} / R\right)^{2}(k T / 2),  \tag{29}\\
& \frac{d}{d \bar{R}}\left(n_{A 1}+n_{A 2}\right)=-\left(R_{I} n_{B 1} r^{\prime} / n\left[D_{A B}\right]\right)\left(2 k T / m_{A} \pi\right)^{1 / 2}(1 / \bar{R})^{2}, \tag{30}
\end{align*}
$$

where $\bar{R}=R / R_{I}$.
Converting $n$ to $p$ by utilizing the relation $p=n k T$, we obtain the following set of equations;

$$
\begin{align*}
& p_{A 1}-p_{A 2}=\gamma=\text { const. }  \tag{31}\\
& p_{B 1}-p_{B 2}=0  \tag{32}\\
& p_{A 1}+p_{A 2}+p_{B 1}+p_{B 2}=\delta=\text { const. }  \tag{33}\\
& \frac{d}{d \bar{R}}\left\{\left(p_{A 1}+p_{A 2}\right) / 2\right\}=-\zeta \gamma p_{B_{1}}(1 / \bar{R})^{2} \tag{34}
\end{align*}
$$

where

$$
\begin{equation*}
\zeta=\left(R_{I} / 2 p_{t}\left[D_{A B}\right]\right)\left(2 k T / m_{A} \pi\right)^{1 / 2}=\text { const. . } \tag{35}
\end{equation*}
$$

Then the following equations are obtained from eqs. (31) $\sim(34)$,

$$
\begin{align*}
& p_{A_{1}}=(1 / 2)\{r+\delta+M \exp (-\zeta r / \bar{R})\}  \tag{36}\\
& p_{A 2}=(1 / 2)\{-r+\delta+M \exp (-\zeta r / \bar{R})\} \tag{37}
\end{align*}
$$

and

$$
\begin{equation*}
p_{B 1}=p_{B 2}=-(M / 2) \exp (-\zeta r / \bar{R}), \tag{38}
\end{equation*}
$$

where $M$ is an integral constant.
The set of equations, eqs. $(36) \sim(38)$, can be solved by using the boundary conditions in 2-3.

## $2-3$. Boundary Conditions and Solutions

On defining the accomodation coefficient for mass transfer, it was assumed that when a number of molecules are impinging a surface, the fraction $a$ of them sticks and condenses, and the fraction ( $1-a$ ) reflects diffusely.
Then

$$
\begin{align*}
\text { at } & \bar{R}=R_{I} / R_{I}=1 ; p_{A 1}=p_{A 1 I}=(1-a) p_{A 2 I}+a p_{A I},  \tag{39}\\
\text { at } & \bar{R}=R_{I I} / R_{I}=R^{*} ; \\
& p_{A 2}=p_{A 2 I I}=\{(1-a) / 2\}\left\{\left(1+\cos 2 \alpha_{I I}\right) p_{A 1 I I}+\left(1-\cos 2 \alpha_{I I}\right) p_{A 2 I I}\right\}+a p_{A I I},  \tag{40}\\
& p_{B 1}=p_{B 2}=p_{B 1 I I}=p_{B 2 I I}, \tag{41}
\end{align*}
$$

where $a$ denotes the accomodation coefficient for mass transfer, and $p_{A I}$ and $p_{A I I}$ are equal to the saturated vapor pressures of substance $A$ at the surfaces of the inner and outer spheres, respectively. Eqs. (36) $\sim(38)$ yield by using eqs. (39) $\sim$ (41),

$$
\begin{align*}
p_{A I}-p_{A I I}=[(1 / a) & \left.+\{(1-a) / a\}\left(1 / R^{*}\right)^{2}\right] r \\
& +p_{B_{1 I I}\left[1-\exp \left\{-\zeta r\left(1-1 / R^{*}\right)\right\}\right]} \tag{42}
\end{align*}
$$

On the other hand, the mass flux based on the outer surface of the inner sphere is given as follows;

$$
\begin{align*}
& N_{A I}=\int m_{A} \xi_{A R} f d \xi=m_{A}\left\langle u_{A R I}\right\rangle \\
& =\left(m_{A} k T / 2 \pi\right)^{1 / 2}\left(n_{A 1}-n_{A 2}\right)=\left(m_{A} / 2 \pi k T\right)^{1 / 2} r,  \tag{43}\\
& k_{g}=N_{A I} /\left(p_{A I}-p_{A I I}\right)=\left(m_{A} / 2 \pi k T\right)^{1 / 2} r /\left(p_{A I}-p_{A I I}\right),  \tag{44}\\
& \left.\begin{array}{l}
M=-2 p_{B_{1 I I}} \exp \left(\zeta r / \bar{R}^{*}\right) \\
\delta=2 p_{A I}-(2 / a-1) r-M \exp (-\zeta \tau)
\end{array}\right\} . \tag{45}
\end{align*}
$$

when $p_{A I}, p_{A I I}$ and $p_{B_{1 I I}}$ are known, one can obtain the value of $r$ from eq. (42) and then the mass transfer rate from eq. (43) also.

It could be easily verified that eq. (43) approaches the Hertz-Kundsen equation under a highly rarefied pressure and the Stefan equation under an ordinary pressure as follows.

If $p_{B 1 I I}$ approaches to zero, eq. (42) reduces to the following equation.

$$
\begin{equation*}
r \cong\left(p_{A I}-p_{A I I}\right) / F(a) \tag{46}
\end{equation*}
$$

where

$$
\begin{align*}
& F(a)=(1 / a)+\{(1-a) / a\}\left(1 / R^{*}\right)^{2} .  \tag{47}\\
& N_{A I} \cong\left(p_{A I}-p_{A I I}\right)\left(m_{A} / 2 \pi k T\right)^{1 / 2} \mid F(a) \tag{48}
\end{align*}
$$

This is the Hertz-Knudsen equation.
If $p_{B 1 I I}$ takes so large a value that the first term in the right hand side of eq. (42) is negligibly smaller than the second,

$$
\begin{equation*}
\exp \left\{-\zeta r\left(1-1 / R^{*}\right)\right\} \cong\left(p_{A I I}+p_{B 1 I I}-p_{A I}\right) / p_{B 1 I I}, \tag{49}
\end{equation*}
$$

and

$$
\begin{align*}
& p_{A I I}+p_{B 1 I I}-p_{A I} \cong p_{t}-p_{A I} \cong p_{B 1 I}  \tag{50}\\
& r \approx-\left\{1 / \zeta\left(1-1 / R^{*}\right)\right\} \ln \left(p_{B 1 I} \mid p_{B 1 I I}\right) \tag{51}
\end{align*}
$$

because the value of $p_{t}$ is approximately constant.

$$
\begin{align*}
N_{A I} & \cong-\left(m_{A} / 2 \pi k T\right)^{1 / 2}\left(m_{A} \pi / 2 k T\right)^{1 / 2}\left\{2 p_{t}\left[D_{A B}\right] / R_{I}\left(1-1 / \bar{R}^{*}\right)\right\} \ln \left(p_{B_{1} I} / p_{B 1 I I}\right) \\
& \cong\left(m_{A} / k T\right)\left\{p_{t}\left[D_{A B}\right] / R_{I}\left(1-1 / R^{*}\right)\right\}\left(p_{A I}-p_{A I I}\right) / p_{B m} . \tag{52}
\end{align*}
$$

The above equation is the Stefan equation.
The distributions of the total pressure and the partial pressure of A component are expressed by

$$
\begin{align*}
p_{t} & =(1 / 2)\left\{(1-\sin \alpha)\left(p_{A 1}+p_{B 2}\right)+(1+\sin \alpha)\left(p_{A 2}+p_{B 2}\right)\right\} \\
& =(1 / 2)(\delta-r \sin \alpha),  \tag{53}\\
p_{A} & =(1 / 2)\{\delta+M \exp (-\zeta r / \bar{R})-\gamma \sin \alpha\} . \tag{54}
\end{align*}
$$

## 3. Experimental Apparatus and Procedures

Experimental investigation of mass transfer under the reduced pressure was based on the measurement of the sublimation rate of naphthalene coated on the inner sphere. The inner sphere was placed at the center of the outer sphere working as a condensating surface.


Fig. 3. Schematic diagram of apparatus.
The experimental apparatus used is schematically shown in Fig. 3.

The outer sphere-the sublimation chamber ( $150 \mathrm{~mm} \phi$ I.D. $\times 160 \mathrm{~mm} \phi$ O.D.) was made of bronze and jacketed by the copper cooling pipe in which the methanol cooled by a refrigerator, $0 \sim-40^{\circ} \mathrm{C}$, was circulated, therefore the inner surface was the condensating surface for the sublimated substance.

The inner sphere (about $22 \sim 30 \mathrm{~mm} \phi$ ) was the copper spherical shell having 1.5 mm thickness in which the electric heater was provided, and was coated with naphthalene about 2 mm thickness and located concentrically in the outer sphere (see Fig. 3 and Fig. 4). The coating with naphthalene was carried


Fig. 4. Inner sphere and mechanism of weighing.
out by dipping the inner sphere into a bath of molten naphthalene purified by recrystallization.

So naphthalene was sublimated from the surface of the inner sphere and condensated on the inside surface of the outer sphere. The inner sphere was electrically heated by supplying D.C. current and the surface temperature of the coated substance was regulated to be constant by adjusting the variohm.

The surface temperature of the coated substance was determined from the temperature of the surface of inner sphere taking account the temperature difference through the layer.

To determine the rate of sublimation, the weight loss of the coated substance on the inner sphere was measured and recorded continuously by the Displacement Meter using the differential transformer and the recorder (see Fig. 3 and Fig. 4).

For pressure measurement, Atlas-MMM Diaphragm Vacuum Gauge for a relatively low pressure and oil manometer for a relatively high pressure were used. The measured value of the total pressure using vacuum gauge, $p_{D}$, is

$$
\begin{align*}
p_{D} & =(1 / 2)\left\{\left(1+\cos 2 \alpha_{I I}\right) p_{A_{1} I I}+\left(1-\cos 2 \alpha_{I I}\right) p_{A_{2} I I}\right\}+p_{B_{1} I I} \\
& =\left(1 / R^{*}\right)^{2} p_{A_{1 I I}}+\left\{1-\left(1 / R^{*}\right)^{2}\right\} p_{A_{2 I I} I}+p_{B_{1 I I}} \tag{55}
\end{align*}
$$

From eq. (55), the value of $p_{B_{1 I I}}$ can be calculated.
In the experiments, the total pressure of the apparatus was kept constant in the range of $10^{-1} \sim 10^{-4}$ Torr. by adjusting the variable leak valve.

The procedures of the experiments were as follows; after hanging the coated inner sphere by a hook below the core of differential transformer, the sublimation chamber was evacuated for several minutes to the prescribed pressure, and the outer sphere was cooled to the prescribed temperature also.

Then the inner sphere was electrically heated for the surface temperature to be constant. The weight loss of the inner sphere and the temperature of the sublimating and condensating surface were recorded continuously by the recorder.

The measurements and regulations of the temperatures for the inner and outer spheres were carried out within $\pm 0.1^{\circ} \mathrm{C}$ and $\pm 0.4^{\circ} \mathrm{C}$ in errors, respectively.

The relative error on the determination of sublimation rate was estimated to be $\pm 2 \%$.

## 4. Experimental Results and Discussions

The mass transfer rate based on the surface of the inner sphere, $N_{A I}$, was calculated from the rate of weight loss of the substance by using the following equation.

$$
\begin{equation*}
N_{A I}=-\frac{1}{4 \pi R_{I}^{2}} \frac{d W}{d t} \tag{56}
\end{equation*}
$$

The value of $p_{B_{1 I I}}$ was calculated from the value of $p_{D}$ measured by the vacuum gauge by using eqs. (55), (31) and (37).

$$
\begin{equation*}
p_{D}=r+p_{B_{1 I I}}+(1 / 2)\left\{-\gamma+\delta+M \exp \left(-\zeta r / \bar{R}^{*}\right)\right\} \tag{57}
\end{equation*}
$$

From eqs. (45) and (57), we obtain the following equation;

$$
\begin{equation*}
p_{B 1 I I}=p_{D}-p_{A I I}-(1 / a)\left(1 / \bar{R}^{*}\right)^{2} r . \tag{58}
\end{equation*}
$$

The experimental results for naphthalene are shown in Table 1. Further the values of $p_{B_{1 I I}}$ in Table 1 were calculated from eq. (58) approximating that the value of $a$ was equal to unity, because the error produced by this approximation was negligibly small in the final value.

In Fig. 5, the observed values of the sublimation rate are compared with the values calculated from eq. (43). The observed values for naphthalene fairly agree with the calculated values from the continuum to the transition range. It can be observed that in the free molecular range the observed values are a little smaller than the calculated ones as shown in Fig. 5.

The observed values of $k_{g}$ for naphthalene are also compared with the calculated values from eq. (44) in Fig. 6. From Fig. 6 it may be said that the accomo-


Fig. 5. Comparison between analytical and experimental results.

Table 1. Experimental Data.

| Run No. | $\begin{gathered} t_{\boldsymbol{I}}{ }^{\prime} \\ {\left[{ }^{\circ} \mathrm{C}\right]} \end{gathered}$ | $\begin{gathered} \Delta t_{\boldsymbol{I}} \\ {\left[{ }^{\circ} \mathrm{C}\right]} \end{gathered}$ | $\begin{gathered} \boldsymbol{t}_{\boldsymbol{I}} \\ {\left[{ }^{\circ} \mathrm{C}\right]} \end{gathered}$ | $\begin{gathered} t_{\boldsymbol{I I}} \\ {\left[{ }^{\circ} \mathrm{C}\right]} \end{gathered}$ | $\begin{gathered} p_{A I} \\ {\left[\times 10^{-3}\right.} \\ \mathrm{mmHg}] \end{gathered}$ | $\begin{gathered} p_{A I I} \\ {\left[\times 10^{-3}\right.} \\ \mathrm{mmHg}] \end{gathered}$ | $\begin{gathered} p_{D} \\ {\left[\times 10^{-3}\right.} \\ \mathrm{mmHg}] \end{gathered}$ | $\begin{gathered} p_{B 1 I T} \\ {\left[\times 10^{-3}\right.} \\ \mathrm{mmHg}] \end{gathered}$ |  | $\begin{gathered} k_{g} \\ {\left[\times 10^{-3} \mathrm{~g} / \mathrm{cm}^{2}\right.} \\ \mathrm{sec} \mathrm{mmHg}] \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 10.4 | 0.7 | 9.7 | $-0.2$ | 18.0 | 5.90 | 84.1 | 78.1 | 3.62 | 3.00 |
| 2 | 10.4 | 0.5 | 9.9 | -0.3 | 18.2 | 5.82 | 143.0 | 137.1 | 2.32 | 1.80 |
| 3 | 0.2 | 1.2 | $-1.0$ | $-10.9$ | 5.40 | 1.65 | 10.7 | 9.00 | 5.41 | 13.7 |
| 4 | -0.3 | 0.6 | -0.9 | $-9.3$ | 5.48 | 2.01 | 28.7 | 26.7 | 2.96 | 8.54 |
| 5 | -9.7 | 0.8 | $-10.5$ | -30.6 | 1.75 | 0.118 | 2.25 | 2.10 | 3.78 | 23.2 |
| 6 | $-10.4$ | 0.9 | $-11.3$ | -30.0 | 1.58 | 0.133 | 3.78 | 3.62 | 3.50 | 24.1 |
| 7 | -9.7 | 0.7 | $-10.4$ | -30.0 | 1.75 | 0.133 | 7.56 | 7.40 | 2.98 | 18.4 |
| 8 | $-10.2$ | 0.5 | $-10.7$ | -28.3 | 1.70 | 0.169 | 2.20 | 21.8 | 1.51 | 9.84 |
| 9 | $-10.0$ | 0.4 | -10.4 | $-29.3$ | 1.75 | 0.164 | 61.6 | 61.4 | 0.621 | 3.88 |
| 10 | $-19.3$ | 0.2 | -19.5 | $-26.9$ | 0.55 | 0.205 | 2.09 | 1.88 | 0.703 | 20.1 |
| 11 | -20.2 | 0.4 | -20.6 | -29.0 | 0.485 | 0.152 | 2.90 | 2.74 | 1.10 | 33.0 |
| 12 | $-19.7$ | 0.2 | $-19.9$ | $-29.3$ | 0.530 | 0.146 | 7.25 | 7.10 | 0.700 | 18.3 |
| 13 | -20.0 | 0.2 | -20.2 | -29.0 | 0.510 | 0.153 | 23.3 | 23.2 | 0.281 | 7.87 |
| 14 | $-19.3$ | 0.2 | -19.5 | -28.1 | 0.560 | 0.174 | 24.0 | 23.8 | 0.355 | 9.20 |
| 15 | -20.2 | 0.2 | -20.4 | $-29.7$ | 0.495 | 0.139 | 72.5 | 72.4 | 0.127 | 3.58 |
| 16 | 0.0 | 0.6 | -0.6 | -9.8 | 5.60 | 1.90 | 35.2 | 33.3 | 2.50 | 6.74 |
| 17 | $-10.0$ | 0.8 | $-10.8$ | $-30.5$ | 1.67 | 0.124 | 5.14 | 4.97 | 3.69 | 23.8 |
| 18 | $-10.0$ | 0.8 | $-10.8$ | $-29.3$ | 1.67 | 0.146 | 6.32 | 6.14 | 3.67 | 24.1 |
| 19 | $-9.9$ | 0.6 | $-10.5$ | $-29.5$ | 1.74 | 0.143 | 13.2 | 13.0 | 2.43 | 15.1 |
| 20 | -9.9 | 0.6 | $-10.5$ | $-30.0$ | 1.74 | 0.133 | 1.65 | 16.3 | 2.00 | 12.4 |
| 21 | $-10.0$ | 0.9 | $-10.9$ | $-31.0$ | 1.65 | 0.115 | 3.26 | 3.10 | 4.32 | 28.1 |
| 22 | -9.9 | 0.9 | $-10.8$ | $-30.5$ | 1.67 | 0.125 | 4.31 | 4.15 | 3.94 | 25.4 |
| 23 | -9.9 | 0.5 | $-10.4$ | $-30.8$ | 1.76 | 0.119 | 24.9 | 24.8 | 1.25 | 7.62 |
| 24 | $-10.0$ | 0.7 | $-10.7$ | $-30.8$ | 1.70 | 0.119 | 8.68 | 8.53 | 3.13 | 19.8 |
| 25 | $-9.7$ | 0.4 | $-10.1$ | -29.8 | 1.83 | 0.136 | 40.5 | 40.4 | 0.965 | 5.71 |
| 26 | $-10.0$ | 0.7 | $-10.7$ | $-30.6$ | 1.70 | 0.122 | 9.33 | 9.18 | 3.21 | 20.3 |

$t_{A}^{\prime}:$ temperature of the surface of copper shell
$\Delta t_{I}:$ temperature difference through the coated layer of naphthalene
The data of vapor pressure, thermal conductivity and diffusivity of naphthalene were cited from I.C.T..


Fig. 6. Comparison between analytical and experimental results.


Fig. 7. Distributions of pressure.
dation coefficient for naphthalene is equal to about 0.9 . It has been reported by Sherwood et al. ${ }^{9}$ ) that this value was equal to 0.88 at about $-60^{\circ} \mathrm{C}$.

The distributions of the total pressure and the partial pressure of A and B components are calculated by using eqs. (53) and (54) and a calculated example is shown in Fig. 7. The pressure-jump is observed distinctly on the surface of inner sphere, and the total pressure changes near the inner sphere.

## 5. Conclusion

The equation of mass transfer between two concentric spheres in the reduced pressure, especially in the transition regime, was derived by the gas kinetic-theory using the two-sided Maxwellian distribution function. The observed values of the sublimation of naphthalene were compared with the calculated values obtained from the equation derived in the present work and the both were in good agreement.

## Nomenclature

$A_{1} \quad: \quad$ constant defined by eq. (25)
$a$ : accomodation coefficient for mass transfer
$b$ : impact parameter, or perpendicular distance from molecule A to initial trajectory of molecule B (see Fig. 2)
[cm]
[ $D_{A B}$ ]: diffusion coefficient of molecule A through molecule B

$$
\left[\mathrm{cm}^{2} / \mathrm{sec}\right]
$$

$F \quad: \quad$ intermolecule force for the Maxwell molecule
$F(a)$ : the function of accomodation coefficient:

$$
(1 / a)+\{(1-a) / a\}\left(1 / \bar{R}^{*}\right)^{2}
$$

[-]
$f$ : velocity distribution function of molecule
[-]
$\widetilde{K}_{A B}$ : constant in expression for central force field,

$$
F=\tilde{K}_{A B} / r^{5}
$$

$k$ : Boltzman constant
$k_{g} \quad$ : mass transfer coefficient
$M \quad$ : integral constant defined in eqs. (36) $\sim(38)$
$m \quad$ : mass of a molecule
$N_{A I}$ : mass transfer rate based on the inner sphere
$n$ : number density of molecule
$P \quad:$ a component of pressure tensor
[ $\mathrm{mm} \mathrm{Hg} \cdot \mathrm{cm}^{3} /{ }^{\circ} \mathrm{K}$ ]
$\left[\mathrm{g} / \mathrm{cm}^{2} \cdot \mathrm{sec} \cdot \mathrm{mm} \mathrm{Hg}\right]$
[ mm Hg ]
[g]
$\left[\mathrm{g} / \mathrm{cm}^{2} \cdot \mathrm{sec}\right]$
[ $1 / \mathrm{cm}^{3}$ ]
[ mm Hg ]
[ mm Hg ]
$Q \quad: \quad$ a physical quantity
$\Delta Q$ : change in $Q$ produced by collisions; collision integral
$R \quad: \quad$ radial distance from the center of the inner sphere [cm]
$\bar{R} \quad$ : normalized distance from the center of the inner
sphere: $\quad R=R / R_{I}$
$\bar{R}^{*} \quad: \quad \bar{R}^{*}=R_{I I} / R_{I}$
$r$ : distance between two molecules colliding each other
$T:$ absolute temperature $\quad\left[{ }^{\circ} \mathrm{K}\right]$
$t$ : time
[sec]
$V$ : relative velocity between two interacting molecules
$W \quad$ : weight of the inner sphere
Greek letters
$\alpha \quad: \quad$ angle defined by eq. (4)
$\beta$ : variable concerned in variable $b$ (cf. literature 5)
$r \quad: \quad$ integral constant defined by eq. (31)
$r^{\prime}$ : integral constant defined by eq. (14)
[ mm Hg ]
$\delta \quad: \quad$ integral constant defined by eq. (21)
$\left[1 / \mathrm{cm}^{3}\right]$
$\left[1 / \mathrm{cm}^{3}\right]$
$\varepsilon \quad: \quad$ angle between plane of the orbit and plane containing the original relative velocity and the $x$-axis in a binary collision (see Fig. 2)
[-]
$\theta^{\prime}$ : scattering angle, or angle between relative velocity before and after collision
$\xi \quad: \quad$ velocity of molecule
[-]
$\boldsymbol{\xi} \quad$ : velocity vector of molecule
$\psi \quad: \quad$ angle defined in Fig. 1
$\zeta \quad$ : constant defined by eq. (35)
[ $1 / \mathrm{mm} \mathrm{Hg}$ ]

Suffix
$A$ : diffusing component
$B$ : stangnant component
$R \quad$ : radial direction on polar co-ordinate
$t$ : total pressure
$\theta: \theta$-direction on polar co-ordinate
$\phi \quad: \quad \phi$-direction on polar co-ordinate
1 : inside of "the wedge of influence" (cf. literature 2)
2 : outside of "the wedge of influence" (cf. literature 2)
$I$ : the inner sphere
II : the outer sphere
$\rangle$ : averaged value
, : after collision

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