

Dynamics of Mass Transfer in the Double Film Resistance

By

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(Received April 18, 1964)

The reasonability of using a constant mass transfer capacity coefficient based on the "double film theory" for the dynamic analysis of mass transfer is discussed from a point of view of diffusion equation in films, and it is concluded that for ordinary operating condition of mass transfer, the dynamics obtained in this detailed analysis may be almost identical with those which are obtained under the assumption of a constant mass transfer capacity coefficient during an unsteady state condition concerning concentration change.

1. Introduction

On studying the dynamic performances of usual stagewise mass transfer operation such as plate column for distillation process, the assumption of an ideal stage has usually been used. It is, however, a well known fact that this assumption may not generally hold for the most of practical stagewise mass transfer operations. In order to represent the discrepancies between the results of theoretical analysis under the assumption of the ideal stage mentioned above and the actual phenomena of mass transfer, there have been proposed the following two kinds of expressions with respect to the degree of mass transfer rate: the first is the use of the Murphree plate efficiency, and the second is the adoption of the mass transfer capacity coefficient, where both Murphree plate efficiency and mass transfer capacity coefficient are assumed to be always constant during an unsteady state condition. It has already been pointed out from the macroscopic dynamic analysis of mass transfer¹⁾ that it is always valid to use the mass transfer capacity coefficient as a constant parameter through an unsteady state, while the Murphree plate efficiency can not generally be assumed as constant in the dynamic analysis.

In this paper, it is discussed from the point of view of mass diffusion based on the "double film theory" whether the mass transfer capacity coefficient can be used as a constant parameter to represent the degree of mass transfer rate,

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2. Preliminary Considerations

On analyzing the steady state performances of mass transfer resistance, most familiar model is so called "double film theory". This model states that all the mass transfer resistances are attributed to the imaginary "film" and the degree of this resistance is represented by a constant parameter, that is, mass transfer capacity coefficient. In the previous paper¹⁾, this model has formally been used in the dynamic analysis of mass transfer operations under the following assumptions; mass transfer capacity coefficient is constant, or there are not any transfer lag of concentration change in the film. In other words, this assumption means that no sooner the bulk concentration of fluid changes than a new equilibrium steady state of concentration gradient in the film is attained. Under this assumption, the basic equations for the dynamic

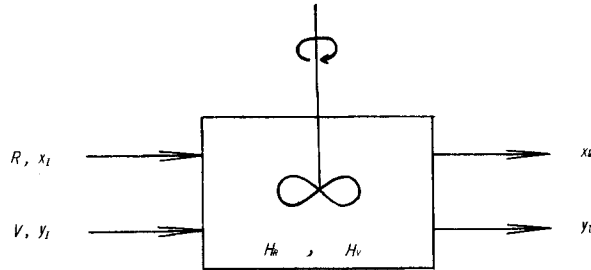


Fig. 1. Mass balance in a perfectly mixed vessel.

analysis of mass transfer operation in a perfectly mixed vessel as shown in Fig. 1 are given by the following equations,

$$H_R \frac{dx_{II}}{dt} = R(x_{I}(t) - x_{II}(t)) + K_R a(x_{I1}^*(t) - x_{II}(t)) \quad (1)$$

$$H_V \frac{dy_{II}}{dt} = V(y_{I}(t) - y_{II}(t)) + K_V a(y_{I1}^*(t) - y_{II}(t)) \quad (2)$$

where both flow rates R , V , both holdups in the vessel H_R , H_V are always constant.

However, it does not strictly hold that there is no transfer lag of concentration change in the film, and it is more reasonable to consider that there is more or less a transient state of concentration gradient in the film according to a variation of bulk concentration, as long as there is any transfer resistance in the film. The difference between the results obtained by using Eqs. (1) and (2) and by taking into consideration of transfer lag of concentration change in the film is considered in this paper.

3. Theoretical and Numerical Analyses

Mass transfer in the film is associated with molecular diffusion, bulk flow, chemical reaction, etc., but it is considered here only on mass transfer without chemical reaction. Supposing the cases of equimolar counter-diffusion or of diffusion through a stationary fluid phase with low concentration, and assuming that the diffusion coefficient is independent of concentration which changes by

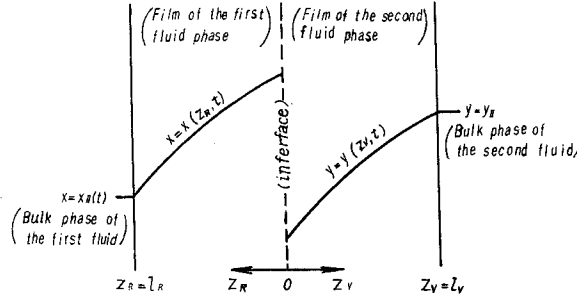


Fig. 2. Schematic diagram of the "film" based on the double-film theory.

position in the film and time, the Fick's second law of diffusion holds for the mass transfer in the film. Under the situations mentioned above, the diffusion equations are given for the first and the second fluids' films as follows ;

$$\frac{\partial x(z_R, t)}{\partial t} = D_R \frac{\partial^2 x(z_R, t)}{\partial z_R^2}, \quad 0 \leq z_R \leq l_R \quad (3)$$

$$\frac{\partial y(z_V, t)}{\partial t} = D_V \frac{\partial^2 y(z_V, t)}{\partial z_V^2}, \quad 0 \leq z_V \leq l_V \quad (4)$$

where $x(z_R, t)$, $y(z_V, t)$ are concentrations in both films (see Fig. 2). At the interface between both films, there is no accumulation of mass, and then the following equation of continuity is obtained.

$$D_R \frac{\partial x(z_R, t)}{\partial z_R} \Big|_{z_R=0} + D_V \frac{\partial y(z_V, t)}{\partial z_V} \Big|_{z_V=0} = 0 \quad (5)$$

It is assumed here that an equilibrium state is always attained at the interface between both films and its equilibrium relation is represented by the following equation.

$$y(z_V, t) \Big|_{z_V=0} = mx(z_R, t) \Big|_{z_R=0} + c \quad (m, c : \text{const.}) \quad (6)$$

From the assumption of perfect mixing of both fluids in the vessel (Fig. 1), the bulk concentrations of both fluids x_{II} , y_{II} are uniform through the whole vessel, and these values are equal to the concentrations at both boundary planes between bulk phase and film, $x(l_R, t)$ and $y(l_V, t)$, respectively, from the assumption

of double film theory. That is to say, the boundary conditions describing the relation between the concentrations of bulk phase and film are given as follows.

$$x(z_R, t)_{z_R=l_R} = x_{II}(t) \quad (7)$$

$$y(z_V, t)_{z_V=l_V} = y_{II}(t) \quad (8)$$

On the other hand, mass balances in the bulk phases are expressed by the following equations,

$$H_R \frac{\partial x_{II}(t)}{\partial t} = R(x_I(t) - x_{II}(t)) + \left(-a_{OR} D_R \frac{\partial x(z_R, t)}{\partial z_R} \right) \Big|_{z_R=l_R} \quad (9)$$

$$H_V \frac{\partial y_{II}(t)}{\partial t} = V(y_I(t) - y_{II}(t)) + \left(-a_{OV} D_V \frac{\partial y(z_V, t)}{\partial z_V} \right) \Big|_{z_V=l_V} \quad (10)$$

assuming that both fluids are completely mixed in the vessel and the holdups of both fluids are always constant. These two equations (9) and (10) are corresponding to Eqs. (1) and (2) which are derived without taking into consideration of the transfer lag of concentration change in the film. Using the basic equations given above, it can be expressed how the bulk concentrations of both fluids in the vessel x_{II} , y_{II} are affected by the variations of the inlet concentrations x_I , y_I . The inlet concentration x_I and y_I at any time are expressed by the inlet concentration changes Δx_I , Δy_I and the steady state values x_I^0 , y_I^0 , as follows,

$$\begin{aligned} x_I(t) &= x_I^0 + \Delta x_I(t) \\ y_I(t) &= y_I^0 + \Delta y_I(t) \end{aligned} \quad (11)$$

and also the concentrations at any time in the vessel x_{II} , y_{II} are

$$\begin{aligned} x_{II}(t) &= x_{II}^0 + \Delta x_{II}(t) \\ y_{II}(t) &= y_{II}^0 + \Delta y_{II}(t) \end{aligned} \quad (12)$$

Taking into consideration that the deviational quantities of concentrations, $\Delta x_{II}(t)$, $\Delta y_{II}(t)$, $\Delta x(z_R, t)$, $\Delta y(z_V, t)$ should be equal to zero at $t=0$ and taking Laplace transformation of these quantities with respect to time, the following two relations are obtained,

$$X_{II}(s) = G_1(s)X_I(s) + G_3(s)(Y_I(s)/m) \quad (13)$$

$$Y_{II}(s) = G_2(s)(mX_I(s)) + G_4(s)Y_I(s) \quad (14)$$

$$X(s) = \int_0^{\infty} \Delta x(t)e^{-st} dt, \quad Y(s) = \int_0^{\infty} \Delta y(t)e^{-st} dt$$

where $G(s)$ is the transfer functions which describe how the bulk concentrations of both fluids in the vessel are affected by the variations of concentrations of the inlet fluids, and these are expressed by the following equations,

$$G_1(s) = \frac{X_{II}(s)}{X_I(s)} = \frac{1}{H_1(s)} \left(1 + \tau_V s - \frac{N_{0R}}{\lambda} (\eta \nu_R + \nu_V) \frac{B(s)}{A(s)} \right) \quad (15)$$

$$G_2(s) = \frac{Y_{II}(s)}{mX_I(s)} = -\frac{2N_{0R}/\lambda \cdot \eta \nu_R + \nu_V}{H_1(s) \cdot A(s)} \quad (16)$$

$$G_3(s) = \frac{mX_{II}(s)}{Y_I(s)} = -\frac{2N_{0R} \cdot \eta \nu_R + \nu_V}{H_1(s) \cdot A(s)} \quad (17)$$

$$G_4(s) = \frac{Y_{II}(s)}{Y_I(s)} = \frac{1}{H_1(s)} \left(1 + \tau_R s + \frac{N_{0R}}{\eta} (\eta \nu_R + \nu_V) \frac{C(s)}{A(s)} \right) \quad (18)$$

where

$$H_1(s) = \left\{ 1 + \tau_R s + \frac{N_{0R}}{\eta} (\eta \nu_R + \nu_V) \frac{C(s)}{A(s)} \right\} \left\{ 1 + \tau_V s - \frac{N_{0R}}{\lambda} (\eta \nu_R + \nu_V) \frac{B(s)}{A(s)} \right\} - \frac{4}{\lambda} \left\{ \frac{N_{0R} (\eta \nu_R + \nu_V)}{A(s)} \right\}^2$$

$$A(s) = (1 - \eta) \sinh(\nu_R - \nu_V) - (1 + \lambda) \sin(\nu_R + \nu_V)$$

$$B(s) = (1 - \eta) \cosh(\nu_R - \nu_V) + (1 + \lambda) \cosh(\nu_R + \nu_V)$$

$$C(s) = (1 - \eta) \cosh(\nu_R - \nu_V) - (1 + \lambda) \cosh(\nu_R + \nu_V)$$

$$\nu_R = \sqrt{\frac{l_{RS}^2}{D_R}}, \quad \nu_V = \sqrt{\frac{l_{VS}^2}{D_V}}, \quad \eta = m \sqrt{\frac{D_V}{D_R}}$$

$$\lambda = \frac{mV}{R}, \quad \tau_R = \frac{H_R}{R}, \quad \tau_V = \frac{H_V}{V}$$

and N_{0R} is defined as follows,

$$\frac{1}{N_{0R}} = \frac{1}{N_R} + \frac{1}{\lambda N_V}, \quad N_R = \frac{a \left(\frac{D_R}{l_R} \right) \rho_R}{R}, \quad N_V = \frac{a \left(\frac{D_V}{l_V} \right) \rho_V}{V}$$

This is equivalent to $K_R a/R$ which is the (N.T.U.) based on the first fluid phase that has been defined in the previous paper¹⁾. In the above transfer functions, the new additional parameters ν_R, ν_V, η except N_{0R}, λ are appeared from taking into consideration the transfer lag of concentration change in the film. In fact, setting $\nu_R, \nu_V \rightarrow 0$ (this means to neglect the transfer lag of concentration change in the film), the transfer functions expressed by Eqs. (15) to (18) are rewritten by the following expressions, being independent of the value of η .

$$G_1(s) = \frac{X_{II}(s)}{X_I(s)} = \frac{1 + \frac{N_{0R}}{\lambda} + \tau_V s}{H_2(s)} \quad (19)$$

$$G_2(s) = \frac{Y_{II}(s)}{mX_I(s)} = \frac{N_{0R}/\lambda}{H_2(s)} \quad (20)$$

$$G_3(s) = \frac{mX_{II}(s)}{Y_I(s)} = \frac{N_{0R}}{H_2(s)} \quad (21)$$

$$G_4(s) = \frac{Y_{II}(s)}{Y_I(s)} = \frac{1 + N_{0R} + \tau_R s}{H_2(s)} \quad (22)$$

$$H_2(s) = (1 + \tau_R s)(1 + \tau_V s) + N_{0R}(1 + \tau_V s) + \frac{N_{0R}}{\lambda}(1 + \tau_R s)$$

It is, of course, easily shown that the above transfer functions for a limiting case of $\nu_R = \nu_V = 0$ are completely the same as those that are obtained by using Eqs. (1), (2) which assume to neglect any transfer lag of concentration change in the film. Thus, for the purpose of investigating how much the dynamic performance of mass transfer is influenced by the degree of the transfer lag of concentration change in the film, it is sufficient to analyze the effects of ν_R, ν_V, η on the transfer functions expressed by Eqs. (15) to (18). Here, the performances of the transfer functions are analyzed by the frequency response of these transfer functions. For this purpose, it is convenient to introduce the following new parameters in stead of ν_R, ν_V .

$$\gamma_R = \frac{l_R^2}{D_R \tau_R} W, \quad \gamma_V = \frac{\kappa \cdot l_V^2}{D_V \tau_V} W, \quad W = \omega \tau_R, \quad \kappa = \tau_V / \tau_R$$

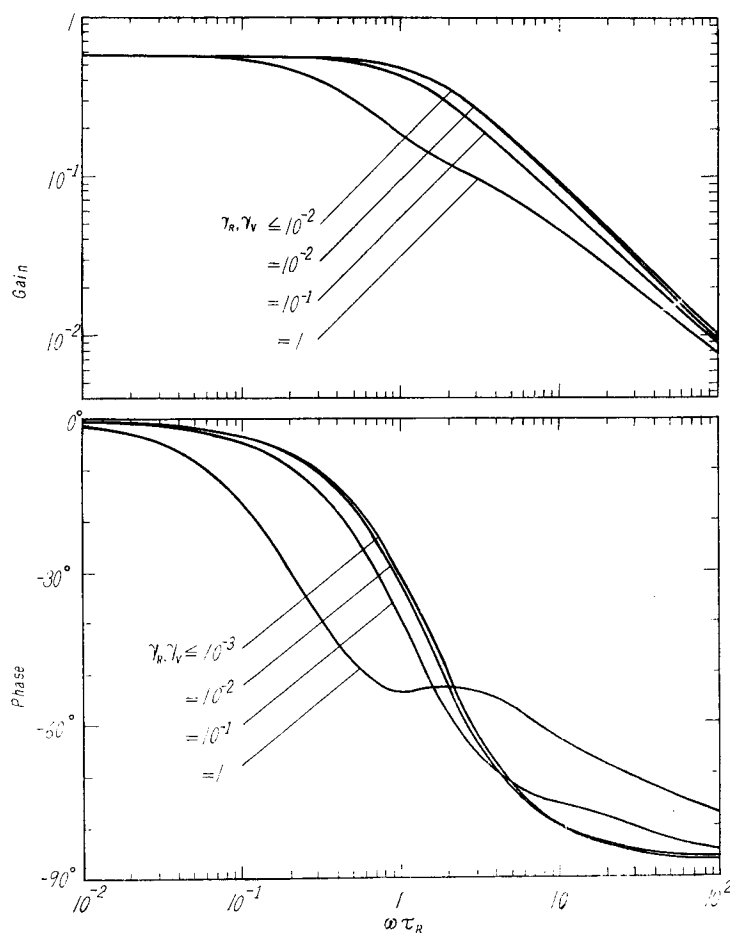


Fig. 3. Effect of γ_R, γ_V on $G_1(j\omega)$ for $\lambda=1, N_{0R}=3, \kappa=0.1, \eta=1$.

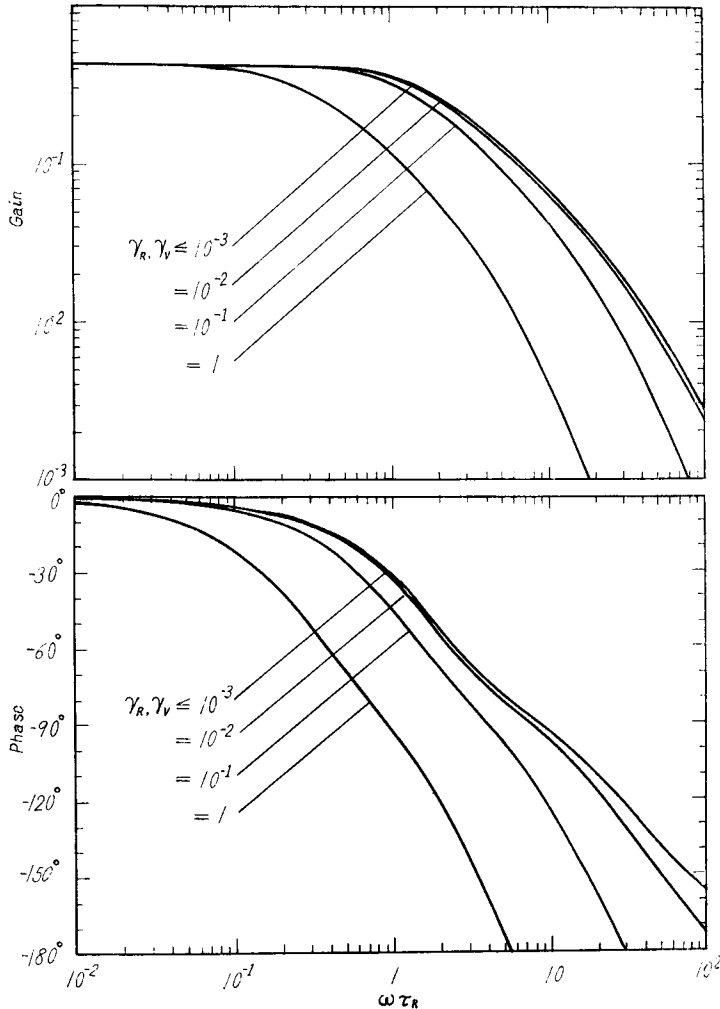


Fig. 4. Effect of γ_R, γ_V on $G_2(j\omega)$ or $G_3(j\omega)$ for $\lambda=1, N_{0R}=3, \kappa=0.1, \eta=1$.

Fig. 3, 4 and 5 show the effects of γ_R, γ_V on the transfer functions $G_1(s)$ to $G_4(s)$. It is obviously seen that the dynamic performances expressed by the transfer functions $G_1(s)$ to $G_4(s)$ are not almost influenced by the value of γ_R, γ_V when these two parameters are smaller than 10^{-3} , and of course, the transfer functions in this case are identical with those for $\gamma_R=\gamma_V=0$. Appreciable differences of the frequency properties of the transfer functions due to the values of γ_R, γ_V are found when γ_R, γ_V are larger than 10^{-2} . For the most of practical mass transfer operations, the magnitudes of $l_R^2/D_R, l_V^2/D_V$ lies approximately in the range of 10^{-1} – 10^{-2} sec. And hence, the values of γ_R, γ_V are at

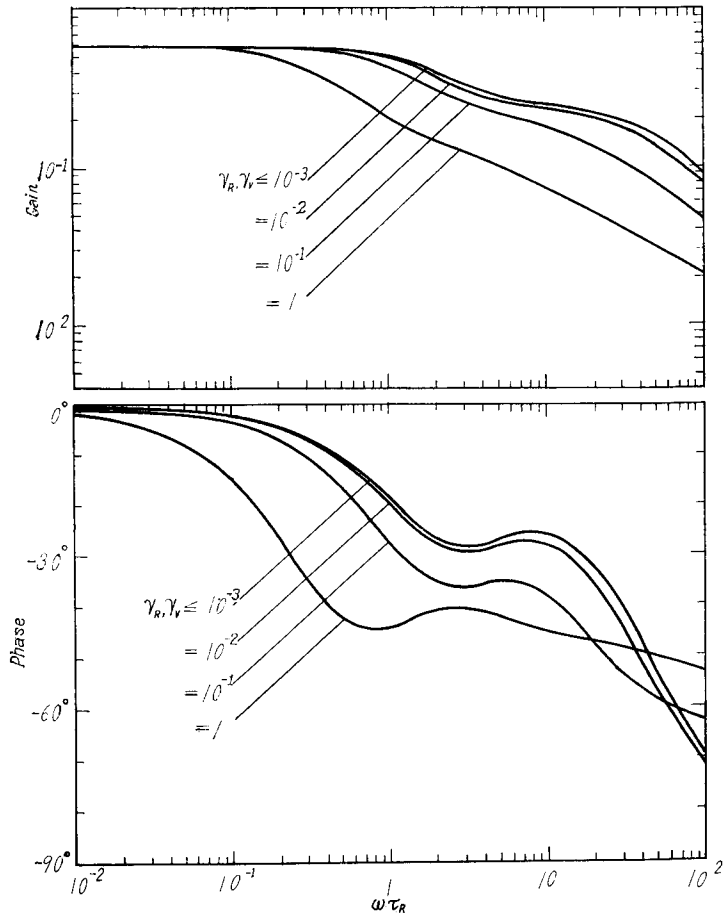


Fig. 5. Effect of τ_R, τ_V on $G_A(j\omega)$ for $\lambda=1, N_{0R}=3, \kappa=0.1, \eta=1$.

most smaller than 10^{-1} in such low range of angular frequency as $\omega \leq 1$ 1/sec, in fact, the dynamic data in the region of high frequency ($\omega \geq 1$ 1/sec) is not required for the most of practical chemical plants and processes, and hence it may be in practical sense, concluded that the assumption that there is not any transfer lag of concentration change in the film is valid for the dynamic analysis of mass transfer operation. It is also concluded from some numerical results that the parameter η does not in practice affect the properties of the transfer functions when τ_R, τ_V are comparatively small.

4. Conclusion

It has been theoretically discussed whether it is reasonable or not to analyze the dynamic performance of mass transfer by using the "double film

theory", neglecting any transfer lag of concentration change in the film. From several numerical analysis of the frequency properties of the transfer functions, it is recognized that the results deduced from Eqs. (1), (2) (those two equations mean to neglect any transfer lag of concentration change in the film) are valid when the parameters γ_R, γ_V are smaller than 10^{-3} . In most of the practical mass transfer operations, these two parameters are considered to be rather small, and hence it can be concluded that the mass transfer capacity coefficient may be treated as a constant for the dynamic analysis.

Notation

a	: effective contacting area of both fluids' phases
D_R, D_V	: diffusion coefficients in the films of both fluids' phases
H_R, H_V	: holdups of both fluids in the vessel
j	: $\sqrt{-1}$
K_{Ra}, K_{Va}	: mass transfer capacity coefficients based on the first fluid phase and the second fluid phase, respectively
l_R, l_V	: film thicknesses of both fluids' phases
N_{oR}	: overall number of transfer unit based on the first fluid phase
R	: flow rate of the first fluid
s	: complex parameter of Laplace transformation with respect to time
t	: time
V	: flow rate of the second fluid
x	: concentration of the first fluid
$X(s)$: Laplace transformation of $\Delta x(t)$ with respect to time
y	: concentration of the second fluid
$Y(s)$: Laplace transformation of $\Delta y(t)$ with respect to time
W	: $\omega\tau_R$
z_R, z_V	: abscissae in both films measured from the interface
γ_R, γ_V	: $\frac{l_R^2\omega}{D_R}, \frac{l_V^2\omega}{D_V}$
κ	: τ_V/τ_R
η	: $m\sqrt{\frac{D_V}{D_R}}$
ρ_R, ρ_V	: densities of both fluids
τ_R, τ_V	: residence times of both fluids in the vessel
ω	: angular frequency
Suffix	i) I, II mean the states of input and output, respectively
	ii) R, V mean the properties based on the first fluid and the second fluid, respectively

Superfix i) \circ denotes the steady state value

ii) $*$ denotes the equilibrium state value of concentration

Reference

- 1) Takamatsu, T. and E. Nakanishi : *This Memoirs*, Vol. XXV, part 2, pp. 233 (1963)