

Unsteady-state mass transfer by fluid particles of changing volume†

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(Received 22 September 1988 and in final form 12 January 1989)

Abstract—Time-dependent concentration patterns have been calculated as well as Sherwood numbers for two-phase processes employing bubbles and droplets. Results are reported for the cases of shrinking and growing particles, and for particles of constant volume. The influences of solubility, resistance to mass transfer, and first-order homogeneous reaction are taken into consideration.

1. INTRODUCTION

UNSTEADY-STATE mass exchange between disperse spherical particles like droplets, bubbles, and solid particles and their surroundings may be observed in many processes that take place in nature [1]. Also many processes of technical importance are based upon such mass exchange, often combined with a chemical reaction.

Mass transfer across the interface of particles is a time-dependent process due to the small volume of the particles. The size of particles can be considered to be constant as a first approach as long as the amount of mass transferred is small in comparison with the volume of the particle [2]. This simplification is not permissible when considering processes in which relatively large amounts of mass are exchanged between the disperse phase and the continuous phase. The radial motion of the particle interface—depending on the direction of mass transfer—becomes the predominating influence on the process.

Examples of practical importance are the dissolution of air bubbles in biosuspension during biological waste water treatment, the evaporation of fuel droplets in the reaction chamber of internal combustion engines, the dissolution of residual monomeric bubbles in plastic melts, and the growth of cavities during the production of polymeric foams.

Most of the previous work on this topic considered the change of volume for particles of pure substances or dealt with the change of concentration in particles of constant volume. In this paper the change in concentration inside and around a particle will be investigated while its volume changes due to mass transfer. The investigation is carried out by means of theoretical-numerical methods. A single particle is considered the volume of which changes with time according to the intensity of mass transfer. The particle is

located in continuous surroundings of infinite dimension; the surroundings are assumed to be quiescent. Brauer [2] proved there is only little influence of fluid motion on unsteady-state mass transfer.

Three cases are distinguished concerning the resistance to mass transfer. In the general case, resistance occurs in both phases; the limiting case of primary resistance inside the particle describes a system droplet/gas while the limiting case of primary resistance in the surrounding phase corresponds to the system bubble/liquid. Mass transfer is either directed into the particle or out of it. The distance of the particle to other particles as well as to system boundaries like vessel walls, and to regions where fluid motion occurs should be large enough that interactions between them are excluded.

The particle and its surroundings are treated each as a binary system. Only one of the compounds of the system, i.e. substance A, is assumed to be capable of being transferred across the interface. All other compounds are assumed to be inert concerning mass transfer and chemical reaction and therefore treated as one homogeneous substance B.

2. MATHEMATICAL DESCRIPTION OF MASS TRANSPORT

2.1. Differential equation for the concentration field

Using symbols as shown in Fig. 1, one obtains a differential equation for the description of the concentration pattern inside the particle as follows:

$$\frac{\partial \rho_{A1}}{\partial t} = D_1 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \rho_{A1}}{\partial r} \right) \quad (1)$$

and for the concentration pattern in the surrounding phase

$$\frac{\partial \rho_{A2}}{\partial t} + \frac{dR}{dt} \frac{R^2}{r^2} \frac{\partial \rho_{A2}}{\partial r} = D_2 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \rho_{A2}}{\partial r} \right) + k_v \rho_{A2} \quad (2)$$

† Dedicated to O. Professor Dr. h. c. Dr.-Ing. Heinz Brauer on the occasion of his 65th birthday.

NOMENCLATURE

D_1, D_2	diffusivity [$\text{m}^2 \text{s}^{-1}$]	ξ_1, ξ_2	reduced concentration, equations (6) and (7)
k_v	volumetric reaction rate constant [s^{-1}]	ρ_0^*	reduced initial concentration, equation (18)
\dot{m}_A	mass flux density [$\text{kg m}^{-2} \text{s}^{-1}$]	ρ_∞^*	reduced final concentration, equation (19)
r	radial local coordinate [m]	Φ	enhancement factor, equation (23)
R	particle radius [m]	ΔV_∞^*	volume change number, equation (20).
t	time [s]		
V	particle volume [m^3]		
β	mass transfer coefficient [m s^{-1}]		
ρ_{A1}, ρ_{A2}	partial mass density (concentration) of A [kg m^{-3}]		
ρ'_A	mass density of A [kg m^{-3}].		
Dimensionless quantities		Subscripts	
D^*	diffusivity number, equation (13)	A	substance A
Da_v	volumetric Damköhler number, equation (14)	p	at the interface
Fo_{m1}, Fo_{m2}	Fourier number, equations (8) and (9)	ph	physical transport
H^*	Henry number, equation (11)	t	instantaneous; at time t
r^*	reduced radial coordinate, equation (10)	v	volumetric
R^*	reduced particle radius, equation (12)	0	at time 0; initial value
Sh_{1t}, Sh_1, Sh_2	Sherwood number	1	in phase 1 (particle)
		2	in phase 2 (surroundings)
		∞	at time ∞ ; final value.
		Superscript	
		-	mean value.

A dimensionless formulation of equations (1) and (2) will be used in order to reduce the number of parameters that determine the problem considered

$$\frac{\partial \xi_1}{\partial Fo_{m1}} = \frac{1}{r^{*2}} \frac{\partial}{\partial r^*} \left(r^{*2} \frac{\partial \xi_1}{\partial r^*} \right) \quad (3)$$

$$\begin{aligned} \frac{\partial \xi_2}{\partial Fo_{m2}} + \frac{dR^*}{dFo_{m2}} \frac{R^{*2}}{r^{*2}} \frac{\partial \xi_2}{\partial r^*} \\ = \frac{1}{r^{*2}} \frac{\partial}{\partial r^*} \left(r^{*2} \frac{\partial \xi_2}{\partial r^*} \right) - Da_v \xi_2. \end{aligned} \quad (4)$$

To apply equations (3) and (4) simultaneously, equation (3) will be transformed by introducing the Fourier number Fo_{m2} . This leads to

$$\frac{1}{D^*} \frac{\partial \xi_1}{\partial Fo_{m1}} = \frac{1}{r^{*2}} \frac{\partial}{\partial r^*} \left(r^{*2} \frac{\partial \xi_1}{\partial r^*} \right). \quad (5)$$

Equations (3)–(5) contain the following dimensionless parameters:

dimensionless concentration inside the particle

$$\xi_1 \equiv \frac{\rho_{A1} - H^* \rho_{A2\infty}}{\rho_{A10} - H^* \rho_{A2\infty}}; \quad (6)$$

dimensionless concentration outside the particle

$$\xi_2 \equiv \frac{\rho_{A2} - \rho_{A2\infty}}{\rho_{A10}/H^* - \rho_{A2\infty}}; \quad (7)$$

Fourier numbers

$$Fo_{m1} \equiv t/(R_0^2/D_1) \quad (8)$$

$$Fo_{m2} \equiv t/(R_0^2/D_2); \quad (9)$$

dimensionless radial coordinate

$$r^* \equiv r/R_0; \quad (10)$$

Henry number

$$H^* \equiv \rho_{A1p}/\rho_{A2p}; \quad (11)$$

dimensionless particle radius

$$R^* \equiv R/R_0; \quad (12)$$

diffusivity number

$$D^* \equiv D_1/D_2; \quad (13)$$

volumetric Damköhler number

$$Da_v \equiv k_v R_0^2/D_2. \quad (14)$$

Depending on the location of the primary resistance to mass transport, the following equations are to be applied:

(a) equations (4) and (5) if the resistance occurs in both phases;

(b) equation (3) for resistance prevailing in the particle;

(c) equation (4) for resistance prevailing in the surrounding phase.

2.2. Differential equation for the particle radius

As a result of mass balances one obtains for the instantaneous particle radius

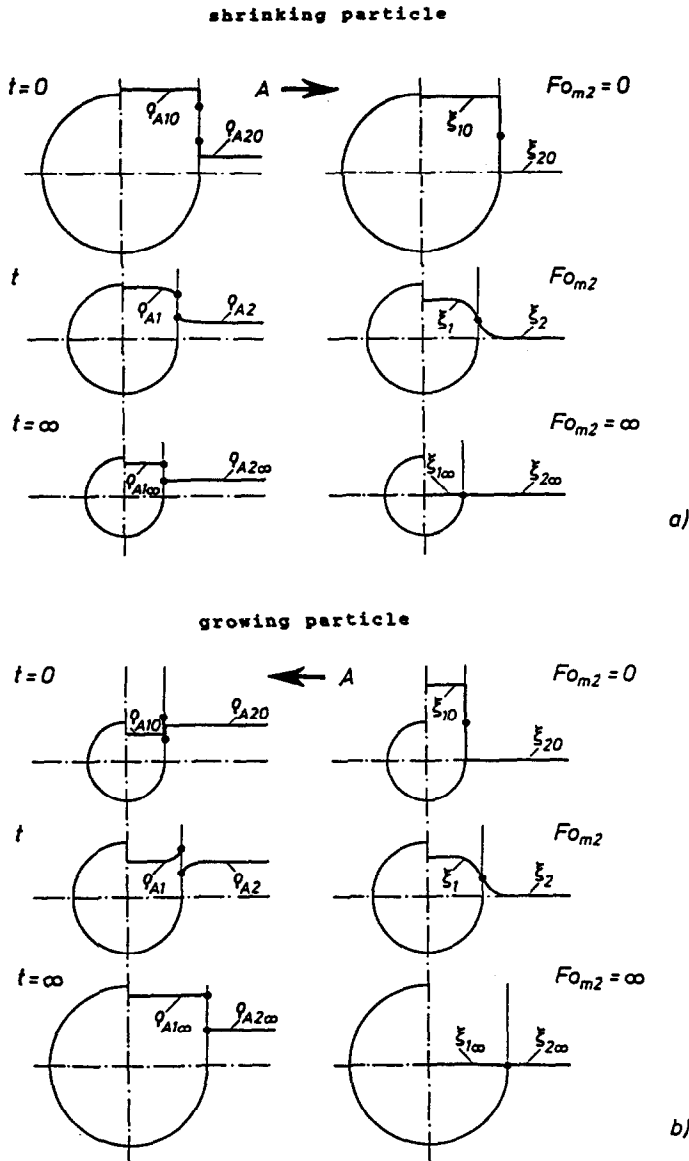


FIG. 1. Schematic plot for explanation of concentration profiles and symbols.

$$R = \left(\frac{1 - \rho_{A10}/\rho'_A}{1 - \rho_{A1}/\rho'_A} \right)^{1/3} \quad (15)$$

and in dimensionless form

$$R^*(t) = \left(\frac{1 - \rho_0^*}{1 - \rho_\infty^* - \xi_1(\rho_0^* - \rho_\infty^*)} \right)^{1/3} \quad (16)$$

The time derivation of equation (16) leads to a differential equation that describes the velocity of the moving interface

$$\frac{dR^*}{dFo_{m2}} = \frac{1}{3}(\rho_0^* - \rho_\infty^*)(1 - \rho_0^*)^{1/3} \times [(1 - \rho_\infty^*) - \xi_1(\rho_0^* - \rho_\infty^*)]^{-4/3} \frac{\partial \xi_1}{\partial Fo_{m2}} \quad (17)$$

In addition to the dimensionless groups previously mentioned, the following quantities are introduced:

dimensionless initial concentration

$$\rho_0^* \equiv \rho_{A10}/\rho'_A; \quad (18)$$

dimensionless final concentration

$$\rho_\infty^* \equiv H^* \rho_{A2\infty}/\rho'_A. \quad (19)$$

For the description of the volume change it is useful to introduce the volume change number

$$\Delta V_\infty^* \equiv (V_\infty - V_0)/V_0 = (\rho_\infty^* - \rho_0^*)(1 - \rho_\infty^*). \quad (20)$$

This parameter will not be applied to mathematically solve the problem but to simplify the discussion of

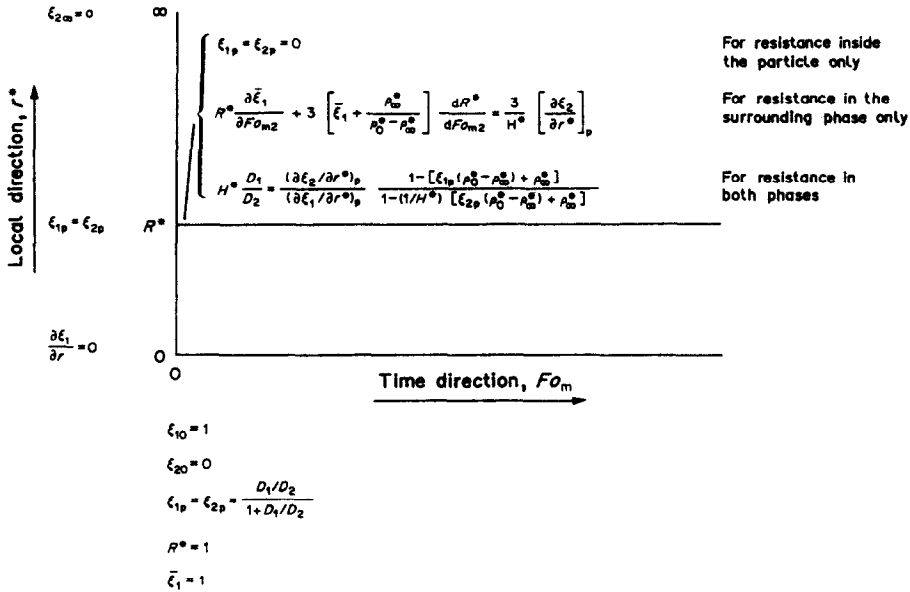


FIG. 2. Initial, boundary, and interfacial conditions.

results. For a growing particle one obtains positive volume change numbers in the range

$$0 \leq \Delta V_{\infty}^* \leq \infty \tag{21}$$

and for a shrinking particle negative values in the range

$$-1 \leq \Delta V_{\infty}^* \leq 0. \tag{22}$$

The volume change number $\Delta V_{\infty}^* = 0$ indicates the case of equimolar mass transfer without any change in the particle volume.

2.3. Initial, boundary, and interfacial conditions

The initial, boundary, and interfacial conditions are synoptically shown in Fig. 2.

2.4. Numerical solution

The differential equations for the concentration pattern, i.e. equations (3)–(5), together with the differential equation for the particle size, i.e. equation (17), build a coupled system of parabolic partial differential equations. The numerical solution of the equations has to take into consideration the so-called moving boundary problem [3] with steadily changing locations of the interfacial conditions. The solution was obtained by using a modified finite difference method [4, 5].

3. PRESENTATION AND DISCUSSION OF RESULTS

As a solution of the differential equations (3)–(5), and (17), and their initial and boundary conditions, concentration patterns as well as derived quantities for the description of mass transfer will be discussed. In particular, the influence of the following par-

ameters is regarded: volume change number, Henry number, diffusivity number, and Damköhler number.

3.1. Influence of the volume change number

3.1.1. General description. The volume change number is defined by equation (20) using the concentrations inside the particle at the beginning, ρ_{A10} , and at the end of the mass transfer process, $\rho_{A1\infty}$. This dimensionless group may be interpreted as the ratio of the maximum change in volume $V_{\infty} - V_0$, to the initial volume of the particle V_0 . Thus, a positive volume change number describes an absorption process where the particle volume increases. A negative volume change number occurs at evaporation processes where the particle volume decreases. The volume change number $\Delta V_{\infty}^* = 0$ represents the special case of equimolar mass transfer where the particle volume remains unchanged. This special case approximately occurs by transferring only small amounts of mass with a negligible change in volume.

The time-dependent change in particle size is connected with the motion of the interface in the radial direction. Therefore, the concentration layer in the vicinity of the interface will be influenced. During mass absorption ($\Delta V_{\infty}^* > 0$), the particle volume increases with time so that there is a motion of the interface radially outward. The thickness of the concentration layer close to the particle interface is diminished, thus the concentration gradient becomes greater, leading to an enhancement of mass transfer compared with the equimolar case. On the other hand, the particle volume decreases during evaporation of mass ($\Delta V_{\infty}^* < 0$). The interface moves towards the centre point of the particle. The thickness of the surrounding concentration layer increases, and the concentration gradient becomes smaller. In this case there

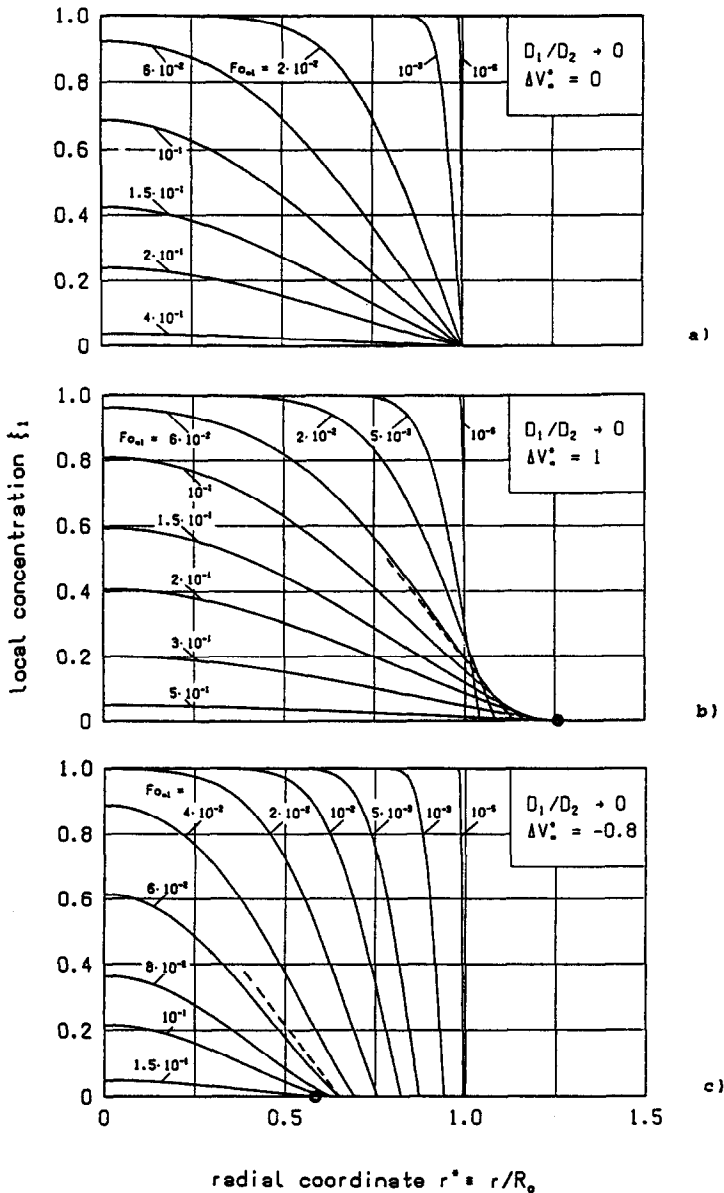


FIG. 3. Local concentration ξ_1 inside the particle plotted vs the radial coordinate r^* for several Fourier numbers Fo_{m1} : (a) equimolar transfer: volume change number $\Delta V_{\infty}^* = 0$; (b) absorption: volume change number $\Delta V_{\infty}^* = 1$; (c) evaporation: volume change number $\Delta V_{\infty}^* = -0.8$.

is less mass transfer than in the case of equimolar transport.

The volume change number not only designates the direction of mass transfer but also the amount of mass transferred. For large volume change numbers there will be a large amount of mass transferred. Although the amount of mass transferred per unit time increases with larger volume change numbers, the mass transfer process will take a much longer time to reach the state of equilibrium.

The influence of the volume change number will be explained in detail by means of selected diagrams.

3.1.2. *Concentration patterns.* Figure 3 shows the

development of concentration patterns within the particle with time. In this series of figures, only the volume change number has been varied; other parameters remained unchanged. All figures are valid for the lower limiting case of the diffusivity number, i.e. $D^* \rightarrow 0$. Then the resistance to mass transfer is inside the particle. In the surroundings of the particle the concentration is constant; in dimensionless terms $\xi_2 = 0$. It has to be considered, that the dimensionless concentration ξ_1 always decreases with time according to its definition, equation (6), even if the non-normalized concentration ρ_{A1} increases during an absorption process.

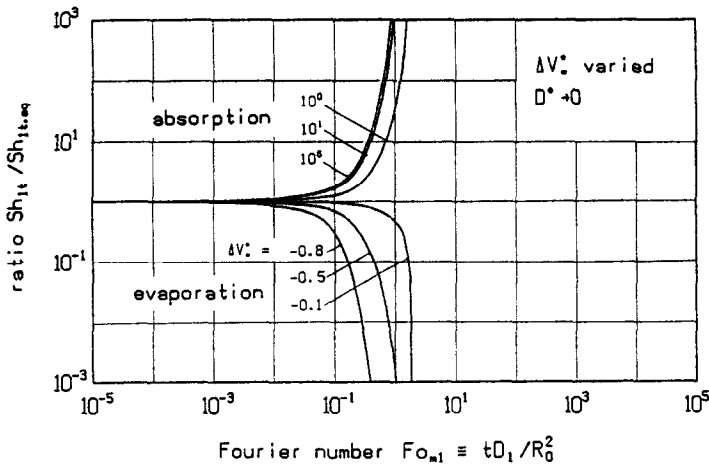


FIG. 4. Ratio of Sherwood numbers $Sh_{1t}/Sh_{1t,eq}$ plotted vs the Fourier number Fo_{m1} for several volume change numbers ΔV_∞^* .

3.1.3. *Sherwood number.* A quantitative comparison of mass transfer during absorption and evaporation with equimolar transport is shown in Fig. 4. The ratio of each instantaneous Sherwood number Sh_{1t} to the Sherwood number $Sh_{1t,eq}$ for $\Delta V_\infty^* = 0$ is plotted in this figure. Absorption always enhances mass transfer, evaporation always diminishes it. The more the volume change number differs from zero, the stronger the influence is.

Figure 5 shows the course of the mean Sherwood number Sh_1 plotted vs the Fourier number Fo_{m1} for several volume change numbers. The case of equimolar transport, i.e. $\Delta V_\infty^* = 0$, is used as reference. For small Fourier numbers, the Sherwood number is described by the limiting law. From $Fo_{m1} = 10^{-2}$ the Sherwood number decreases more rapidly and runs into a second limiting curve [2]. This second limiting curve represents the state of equilibrium. The mean Sherwood number is, similar to the instantaneous one,

larger for absorption, and smaller for evaporation compared with equimolar transport.

3.2. *Influence of the Henry number*

3.2.1. *General description.* The Henry number is defined according to equation (11) as the ratio of the partial densities, ρ_{A1p} to ρ_{A2p} , at both sides of the interface. These partial densities are equal to the saturation concentration of substance A in the state of equilibrium. Therefore, the Henry number describes the solubility of the substance transferred in the system considered. Large Henry numbers indicate low solubility, while small values indicate high solubility of the substance in the phase. The solubility decisively determines the duration of the mass transfer process. In the case of high solubility for substance A, a large amount of mass can be transferred within a short time, while low solubility represents a resistance to mass transfer and so retards the transport. For small

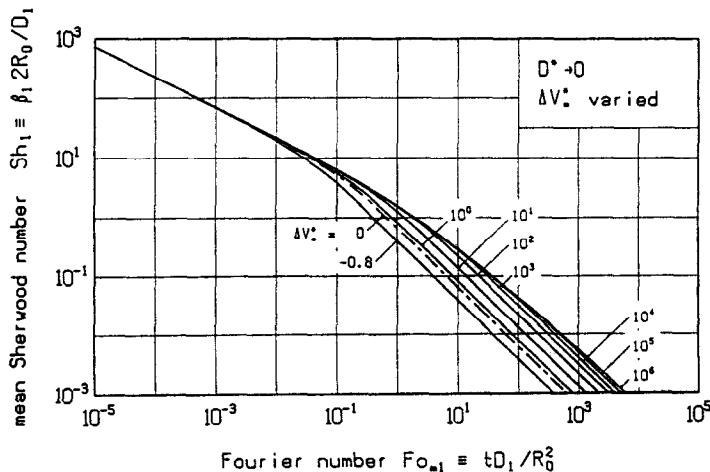


FIG. 5. Mean Sherwood number Sh_1 plotted vs the Fourier number Fo_{m1} for several volume change numbers ΔV_∞^* .

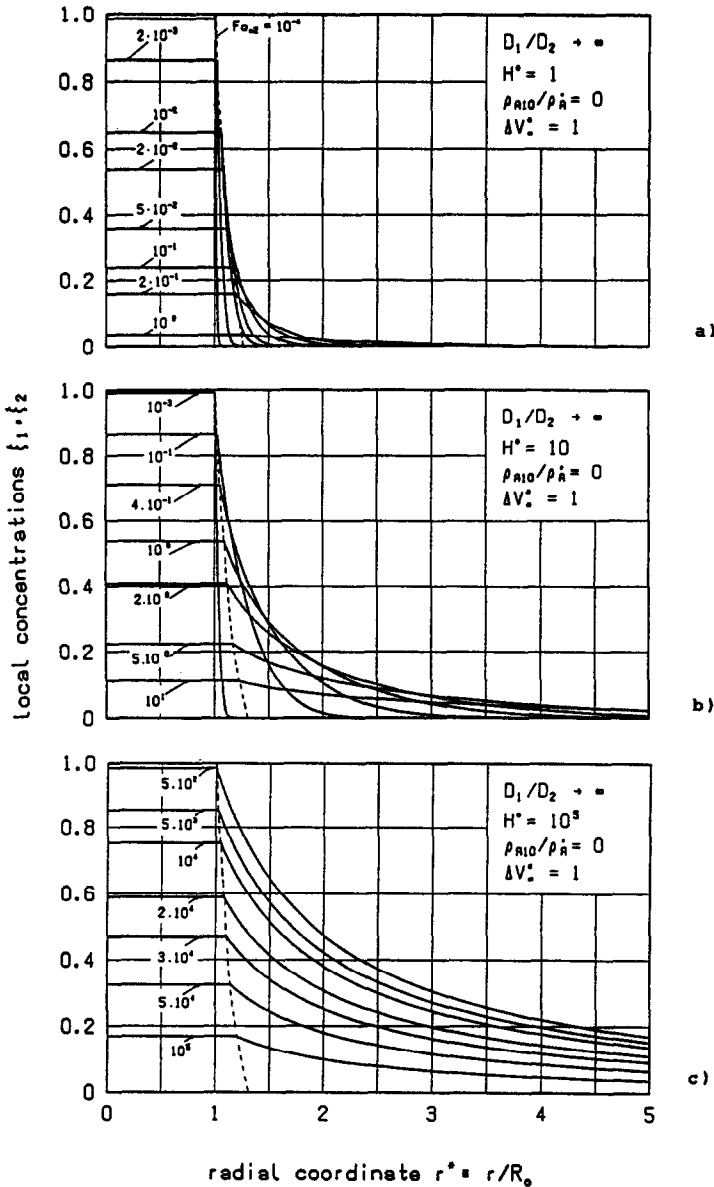


FIG. 6. Local concentrations ξ_1 and ξ_2 inside and around the particle plotted vs the radial coordinate r^* for several Fourier numbers Fo_{m2} : (a) high solubility: Henry number $H^* = 1$; (b) intermediate solubility: Henry number $H^* = 10$; (c) poor solubility: Henry number $H^* = 10^5$.

Henry numbers the concentration step at the interface becomes smaller, and so both the concentration difference and the concentration gradient at the interface become greater. This results in larger mass fluxes and a faster approach towards equilibrium.

3.2.2. *Concentration patterns.* Figure 6 shows the change in the concentration patterns inside the particle and in its surroundings with time. In this series of figures only the Henry number has been varied; all other parameters remained constant. All figures are valid for very large diffusivity numbers, $D^* \rightarrow \infty$. Thus, the resistance to mass transfer lies in the surrounding phase; in the particle itself the concentration is constant locally but changes with time. For Fig. 6

the case of absorption with $\Delta V_0^* = 1$ was chosen. The location of the interface is marked by a dotted line in all figures.

3.2.3. *Sherwood number.* The mean Sherwood number is plotted vs the Fourier number by varying the Henry number in Fig. 7. First the volume change number $\Delta V_0^* = 0$, marked by a dash-dotted line, should be noted. In the range of short times all the curves follow an analytically based limiting law [2]. Here the intensity of mass transfer depends only on time and the Henry number, because of nearly infinitely large concentration gradients. For extremely large times all the lines run into an upper limiting curve. In this case, the Henry number has no influence

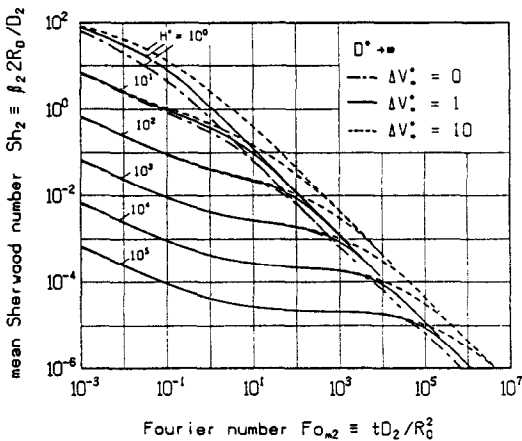


FIG. 7. Mean Sherwood number Sh_2 plotted vs the Fourier number $Fo_{m,2}$ for several Henry numbers H^* .

any more, and the mean Sherwood number is proportional only to the Fourier number. The transition range between the limiting cases is characterized by a more or less marked period in which the Sherwood number is nearly independent of time. This is also due to insufficient absorption capability caused by poor solubility. In spite of relatively large concentration gradients, less mass can be transferred. For extremely high Henry numbers, i.e. $H^* \rightarrow \infty$, a state will be reached in which mass transfer is completely suppressed.

3.2.4. Interaction of the influences of the Henry number and the volume change number. If resistance to mass transfer occurs in the continuous phase, both Henry number and volume change number jointly control transport processes. Then there are interactions between the parameters which will be discussed shortly.

The previous sections explained the fact that the volume change number becomes of importance for mass transfer only in the range of large times, while Henry number controls mass transfer in the range of small and intermediate times. Therefore, there are three distinct regions in the interaction of the two parameters.

(1) For small times the concentration gradients at the interface are so large that an increase is impossible by any means. Mass transfer then is determined by solubility. In this range the Henry number predominates.

(2) For intermediate times, concentration gradients of finite amount generally exist. They can be enhanced by an increase in the particle volume. In this range an interaction between the Henry number and the volume change number occurs.

(3) For large times mass transfer gradually comes to an end. Because the concentration gradients are already relatively small, mass flux cannot be substantially reduced by poor solubility. The amount of mass yet to be transferred determines the duration of

the process. In this range the volume change number is the only parameter.

The second range can be seen in Fig. 7. There the curves for the mean Sherwood number deviate from the course of the equimolar transport case ($\Delta V_x^* = 0$) for larger volume change numbers ($\Delta V_x^* = 1$ and 10), where the Henry number has an influence, too. The larger the volume change number, the larger the Sherwood number for small Henry numbers. The change in volume of the particle reduces the resistance to mass transfer; an actual increase in the mass flux densities, however, requires an adequate solubility for the substance. If $H^* > 100$, absorption capability of the phases is essentially diminished so that mass transfer will be inhibited. Then the curves of the Sherwood number are independent of ΔV_x^* .

3.3. Influence of the diffusivity number

3.3.1. General description. The diffusivity number is defined as the ratio of diffusivities; it may be interpreted as the ratio of concentration equalization times. Large diffusivities imply fast equalization of concentration differences, small diffusivities imply slow equalization. Therefore, for large diffusivity numbers, $D^* > 1$, the equalization is faster in phase 1. Conversely, it is faster in phase 2 for small diffusivity numbers, $D^* < 1$.

This is linked to the resistance to mass transfer. For large diffusivity numbers the equalization inside the particle is so fast that resistance to mass transfer actually occurs only in the surrounding phase. On the other hand, the equalization is much faster in the surrounding phase for small diffusivity numbers, so that resistance to mass transfer occurs inside the particle. For values close to $D^* \approx 1$, the rate of concentration equalization is of the same order in both phases, and resistance to mass transfer also occurs in both phases.

The influence of the diffusivity number on mass transfer between the phases will be discussed below by means of concentration patterns as well as by the mean concentration and Sherwood number. The time is expressed in a dimensionless way in the form of the Fourier number $Fo_{m,2}$; using the Fourier number $Fo_{m,1}$ would have led to formally different curves with the same physical content.

3.3.2. Concentration patterns. Figure 8 shows profiles of the local concentrations ξ_1 inside, and ξ_2 around the particle. The series shows absorption ($\Delta V_x^* = 1$) into a particle with high solubility ($H^* = 1$); the diffusivity number is varied in such a way that resistance to mass transfer first predominates inside the particle, then occurs in both phases, and finally predominates in the surrounding phase.

3.3.3. Sherwood number. The mean Sherwood number Sh_2 is shown in Fig. 9 for different diffusivity numbers. For small times the curves follow the analytically based limiting law with a slope of $Fo_{m,2}^{-1/2}$. In the range of large times the curves merge for a limiting

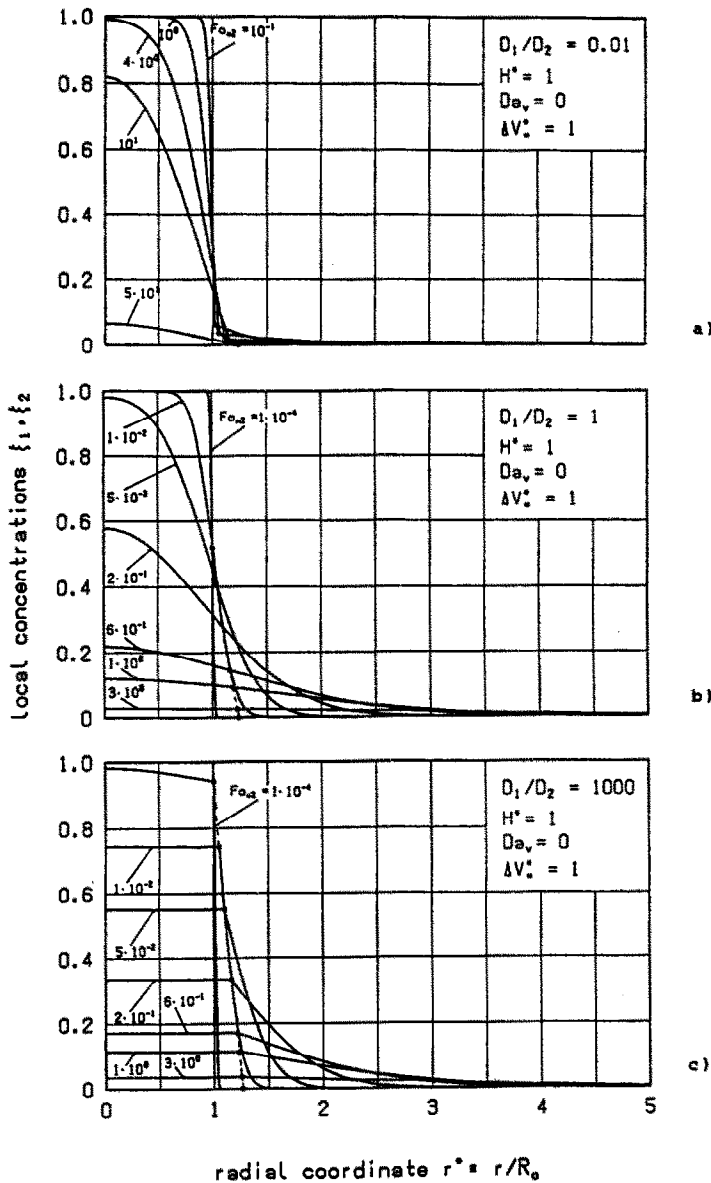


FIG. 8. Local concentrations ξ_1 and ξ_2 inside and around the particle plotted vs the radial coordinate r^* for several Fourier numbers Fo_{m2} : (a) resistance inside the particle: diffusivity number $D^* = 0.01$; (b) resistance in both phases: diffusivity number $D^* = 1$; (c) resistance in the surrounding phase: diffusivity number $D^* = 1000$.

curve the location of which depends only on the volume change number.

3.3.4. *Interaction between the influences of the diffusivity number and the volume change number.* If resistance to mass transfer occurs in both phases, mass transfer is ruled by the diffusivity number as well as the volume change number. As was explained in the previous sections, the influence of the diffusivity number is found in the range of small times, while the influence of the volume change number is restricted to the range of large times. Therefore, three distinct ranges of time are distinguished concerning the interaction of the parameters.

(1) For small times the influence of the diffusivity number predominates due to only slight volume changes.

(2) In the range of intermediate times, both the diffusivity number and the volume change number determine mass transfer.

(3) For large times the influence of the volume change number predominates; the amount of mass transferred determines that instant when equilibrium will be reached.

3.3.5. *Interaction between the influences of the diffusivity number and the Henry number.* The diffusivity number and the Henry number jointly control mass

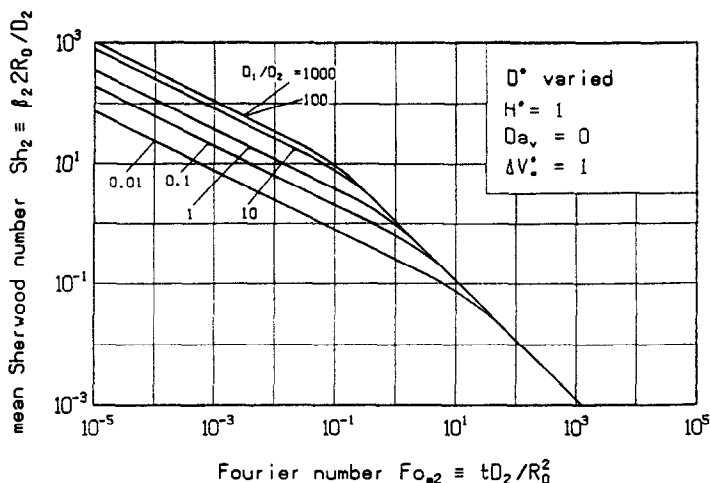


Fig. 9. Mean Sherwood number Sh_2 plotted vs the Fourier number Fo_{m2} for several diffusivity numbers D^* .

transfer if resistance to mass transfer occurs in both phases. Then both parameters have the largest influence in the range of small Fourier numbers.

Real systems generally have a large Henry number combined with a large diffusivity number, or both have small values. This results in compensation of the influences of these two parameters.

3.4. Influence of the Damköhler number

3.4.1. *General description.* The volumetric Damköhler number Da_v describes the intensity of homogeneous chemical reactions. According to its definition, equation (14), it can be interpreted as the ratio of the rate of reaction $k_v R_0$ and the rate of diffusion D_2/R_0 . A large Damköhler number implies a vigorous reaction, while a small value stands for a weak reaction. Two limiting cases occur: the limiting case of $Da_v \rightarrow 0$ is called reaction inhibition. Here the rate of reaction is negligibly small compared to the rate of diffusion; actually no reaction takes place. This case of pure physical mass transfer has been discussed in the previous sections. The second limiting case of $Da_v \rightarrow \infty$ is called diffusion inhibition or transport inhibition. The reaction is so vigorous that the rate of mass transfer to the place of reaction limits the mass transfer. For a homogeneous reaction, i.e. a reaction taking place all over the volume of a phase, this second limiting case leads to a mass transfer within infinitely short times and therefore may be seen as an 'inhibition' only at the end of the process.

An investigation of combined mass transfer and first-order homogeneous chemical reaction makes sense for the considered system of a single particle and continuous surroundings, only if the reaction takes place in the surrounding phase, and if mass transfer is directed from the particle into the surrounding phase. In this paper the influence of the Damköhler number will, therefore, be discussed only for the case of resistance to mass transfer in the surrounding phase

($D^* \geq 1$) and a shrinking particle due to evaporation ($\Delta V_\infty^* \leq 0$).

The substance transferred is about to be changed into the reaction product by chemical reaction with its reaction partner that is assumed to exist in surplus. Thus, the homogeneous reaction diminishes the concentration of substance A in the surrounding phase, causing larger concentration gradients at the interface, and enhancing molecular transport across the interface. The homogeneous reaction promotes the mass transfer. The larger the Damköhler number, the better the mass transfer is. For very large Damköhler numbers, i.e. $Da_v \rightarrow \infty$, every molecule of substance A will be changed immediately after passing across the interface; then concentration ξ_p is zero, and the concentration gradient $(\partial \xi_2 / \partial r^*)_p$ is infinite. Mass transfer will be completed within an infinitely short time.

The influence of the volumetric Damköhler number on mass transfer will be discussed in the following section by means of selected concentration patterns and quantities derived therefrom.

3.4.2. *Concentration patterns.* Figure 10 shows the influence of homogeneous chemical reaction in the surrounding phase on the concentrations ξ_1 inside and ξ_2 outside the particle. In this series of figures only the Damköhler number is varied between its two limiting values $Da_v = 0$ and $Da_v \rightarrow \infty$; all other parameters remain constant. Partial evaporation of the particle ($\Delta V_\infty^* = -0.8$) at moderate solubility ($H^* = 100$) is considered. Resistance to mass transfer is restricted to the surrounding phase ($D^* \rightarrow \infty$). The path of the interface is marked by a dashed line; the final radius of $R^* = 0.585$ is marked by a double circle.

3.4.3. *Sherwood number and enhancement factor.* In Fig. 11 the mean Sherwood number Sh_2 is plotted vs the Fourier number Fo_{m2} for different Damköhler numbers. The curve for pure physical transport, i.e. $Da_v = 0$, has already been discussed in previous sec-

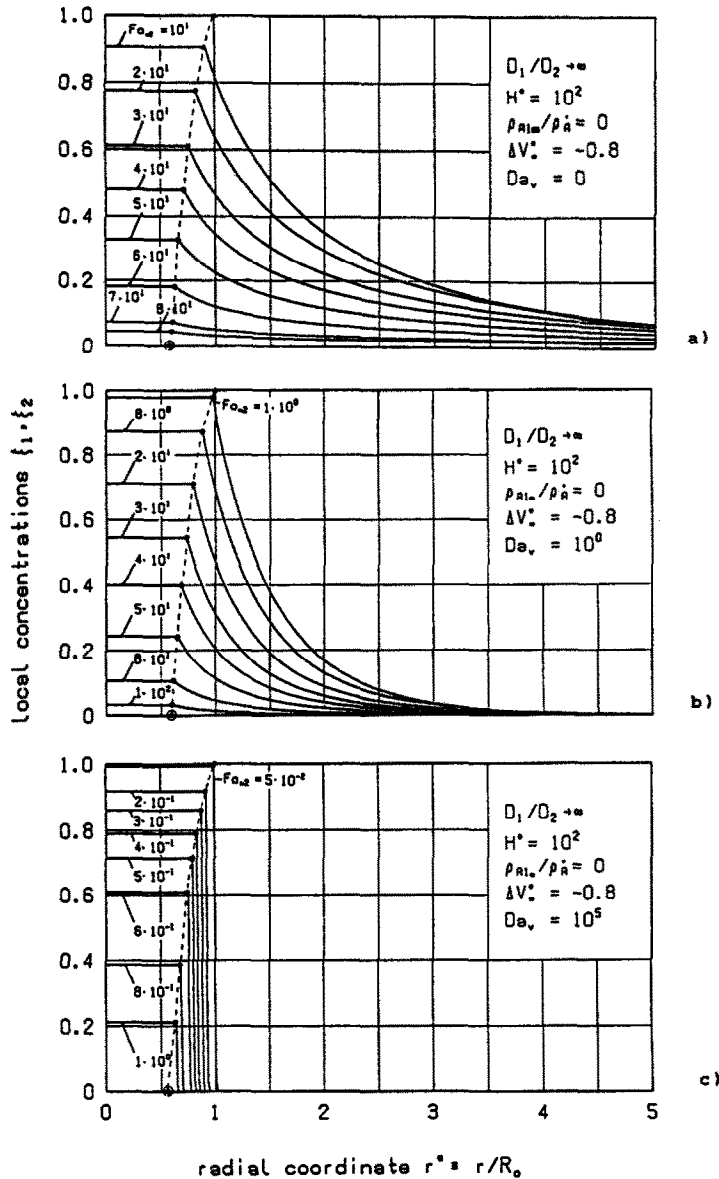


FIG. 10. Local concentrations ξ_1 and ξ_2 inside and around the particle plotted vs the radial coordinate r^* for several Fourier numbers Fo_{m2} : (a) pure physical transfer: Damköhler number $Da_v = 0$; (b) slight chemical reaction: Damköhler number $Da_v = 1$; (c) intense chemical reaction: Damköhler number $Da_v = 10^5$.

tions and will be used as reference again. In the range of small and intermediate times, the curves of the mean Sherwood number leave the limiting curve of $Da_v = 0$ and then pass to a range of constant Sherwood numbers. Approaching the state of equilibrium, all the curves run into a common limiting curve. This limiting curve has a slope of Fo_{m2}^{-1} and depends on the volume change number only.

The enhancement factor Φ will be used as a measure for the enhancement of mass transfer by chemical reaction. It is defined by

$$\Phi \equiv \beta_2 / \beta_{2,ph} \tag{23}$$

Here, $\beta_{2,ph}$ is the mass transfer coefficient for pure physical transport. Figure 12 shows the enhancement factor Φ plotted vs the Fourier number Fo_{m2} for different Damköhler numbers. The curve for slight chemical reaction, $Da_v = 1$, will be discussed first.

The enhancement factor is $\Phi = 1$ up to a Fourier number of about $Fo_{m2} = 10^{-2}$; chemical reaction does not have any influence on mass transfer yet. In the following range of intermediate Fourier numbers, the enhancement factor increases to a maximum value of about $\Phi = 1.5$ and then goes back to $\Phi = 1$. Thus, chemical reaction influences mass transfer only in a distinct, limited range of time.

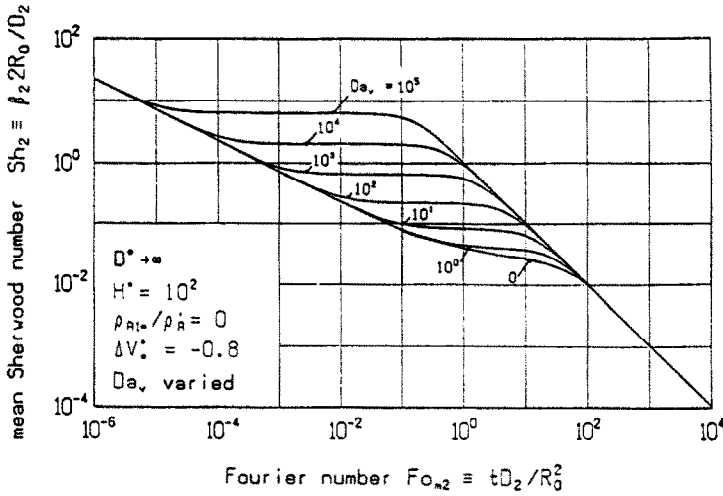


FIG. 11. Mean Sherwood number Sh_2 vs the Fourier number Fo_{m2} for several Damköhler numbers Da_v .

The size of this distinct range, as well as the maximum enhancement factor, increases with increasing Damköhler numbers. With increasing intensity of chemical reaction, the influence becomes evident earlier; the maximum enhancement factor shifts to lower Fourier numbers. All the curves merge into one limiting curve the location of which depends on the volume change number only.

3.4.4. *Interaction between the influences of the Damköhler number and the volume change number.* The Damköhler number and the volume change number jointly control transport processes if large amounts of mass have to be transferred with a simultaneous chemical reaction. The parameters interact concerning their influence on mass transfer. There are three distinct ranges of time.

(1) For small times the concentration gradients at the interface are so large that neither the Damköhler number nor the volume change number can influence mass transfer.

(2) In the range of intermediate times, the where

Damköhler number and the volume change number jointly control mass transfer. Interaction between the parameter occurs here.

(3) For large times, mass transfer as well as chemical reaction come to an end. The volume change number is predominating in this range of time.

3.5. *Correlation for the Sherwood number*

The results for the mean Sherwood number discussed in the previous section are summed up in one equation. The mass transfer coefficient may be calculated for arbitrary values of the parameters Fo_{m2} , ΔV^* , H^* , D^* and Da_v by means of this correlation

$$Sh_2 = \left\{ \left[\left(\frac{4/\sqrt{\pi}}{H^* + (D_1/D_2)^{-1/2}} Fo_{m2}^{-1/2} \right)^E + \left(\frac{2 + 2Da_v^{1/2}}{H^*} \right)^E \right]^{-2, E} + [(0.4 + \Delta V^* \cdot 3/2)^{4/9} Fo_{m2}^{-1}]^{-2} \right\}^{-1/2} \quad (24)$$

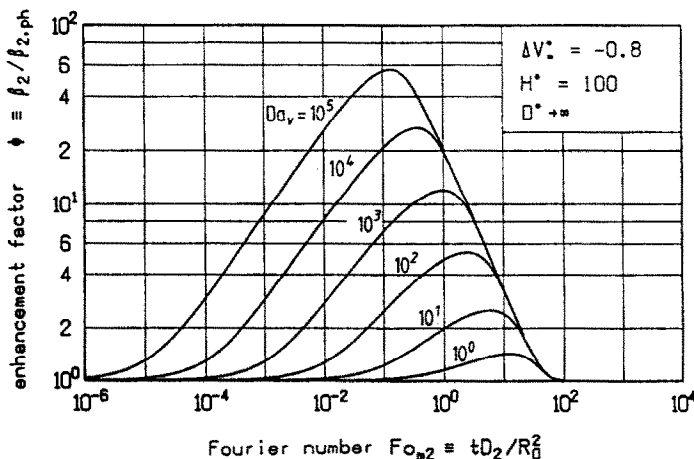


FIG. 12. Enhancement factor Φ plotted vs the Fourier number Fo_{m2} for several Damköhler numbers Da_v .

$$E = 1 + 1.5 \arctan \sqrt{(Da_v)}. \quad (25)$$

The mass transfer coefficient may be obtained by rearranging the defining equation for the Sherwood number

$$\beta_2 = Sh_2 D_2 / (2R_0) \quad (26)$$

the mass flux density is then given by

$$\dot{m}_{A2} = \beta_2 (\rho_{A10} / H^* - \rho_{A2\infty}). \quad (27)$$

The range of application of equation (24) has been tested for the following values of the parameters:

$$\begin{aligned} 0 &\leq Fo_{m2} \leq \infty \\ 0 &\leq \Delta V_{\infty}^* \leq 10^6 \\ 100 &\leq H^* \leq 10^5 \\ 0.01 &\leq D^* \leq 10^3 \\ 0 &\leq Da_v \leq 10^5. \end{aligned} \quad (28)$$

The design of equation (24) has been chosen in such a way that analytically based limiting laws are included, and therefore, the application of the equation is not restricted to the range of results checked.

4. CONCLUSION

Unsteady-state mass transfer across the interface of fluid particles has been investigated by means of theoretical-numerical methods. The influence of a volume change due to mass transfer has been taken into account. For the description of the transport processes the following parameters are used: volume change number ΔV_{∞}^* , Henry number H^* , diffusivity number D^* , and Damköhler number Da_v .

The volume change number ΔV_{∞}^* is defined as the ratio of the maximum volume change of the particle to its initial volume. The motion of the interface in the radial direction enhances mass transfer during absorption and diminishes it during evaporation. The end of the mass transfer process is determined by the amount of transferable mass in the particle. The larger

the volume change number, the later the state of equilibrium is reached.

The Henry number H^* is a measure of the solubility of the transferred substance in the system considered. The smaller the Henry number, the more intense the mass transfer.

The diffusivity number D^* is defined by the ratio of diffusivities and is a measure of the distribution of the resistance to mass transfer in the two phases. For an intense mass transfer, a fast equalization of concentration differences inside the particle is necessary. Therefore, the larger the diffusivity number, the more intense the mass transfer.

The Damköhler number Da_v characterizes the intensity of a homogeneous chemical reaction. The transferred substance will be changed into the reaction product by a chemical reaction in the bulk of the surrounding phase; thus the concentration gradients at the interface become larger. The larger the Damköhler number, the more intense the mass transfer.

The results are summed up by a correlation for the mean Sherwood number. This equation makes it possible to calculate the mass transfer coefficient for arbitrary values of the parameters Fo_{m2} , ΔV_{∞}^* , H^* , D^* , and Da_v .

Acknowledgements—The author wishes to thank L. Biermaier, R. Derafsheh, M. Koz, and C. Walter for carrying out numerous calculations as part of their Diploma theses. Thanks to Judy.

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TRANSFERT VARIABLE DE MASSE PAR DES PARTICULES FLUIDES A VOLUME VARIABLE

Résumé—Les configurations de concentration dépendant du temps sont calculées ainsi que les nombres de Sherwood pour des mécanismes diphasiques à gouttes et bulles. On rapporte des résultats pour des particules qui se résorbent ou qui croissent, et pour des particules à volume constant. On prend en considération les influences de la solubilité, de la résistance au transfert de masse et d'une réaction homogène du premier ordre.

INSTATIONÄRER STOFFTRANSPORT DURCH FLUIDE PARTIKEL VERÄNDERLICHER GRÖSSE

Zusammenfassung—Es werden sowohl zeitabhängige Konzentrationsmodelle als auch Sherwood-Zahlen für Zweiphasenströmungsvorgänge mit Blasen und Tropfen berechnet. Ergebnisse werden für schrumpfende und wachsende Partikel und für Partikel gleichbleibender Größe vorgestellt. Einflüsse der Löslichkeit, des Stofftransportwiderstandes und homogener Reaktionen erster Ordnung werden berücksichtigt.

НЕСТАЦИОНАРНЫЙ МАССОПЕРЕНОС ЧАСТИЦАМИ ЖИДКОСТИ ПЕРЕМЕННОГО ОБЪЕМА

Аннотация—Проведен расчет пространственно-временных структур, а также значений числа Шервуда для двухфазных процессов с образованием пузырьков и капель. Результаты получены как для случаев уменьшающихся и увеличивающихся в объеме частиц, так и для частиц постоянного объема. Учитывается роль растворимости, сопротивления массопереносу и химической реакции первого порядка, протекающей в объеме.