Regular regimes in sorption processes : calculation of drying rates and determination of concentration dependent diffusion coefficients

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WILLEM SCHOEBER

REGULAR REGIMES IN SORPTION PROCESSES

Calculation of drying rates and determination of concentration dependent diffusion coefficients

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL EINDHOVEN, OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. IR. G. VOSSERS, VOOR EEN COMMISSIE AANGEWEZEN DOOR HET COLLEGE VAN DEKANEN, IN HET OPENBAAR TE VERDEDIGEN OP VRIJDAG 28 MEI 1976 TE 16.00 UUR

DOOR

WILLEM JAN ANTOON HENRI SCHOEBER

GEBOREN TE HORST

DRUK: WIBRO HELMOND

Dit proefschrift is goedgekeurd door de promotoren:

Prof.Dr.Ir. H.A.C. Thijssen (1^e promotor)

Prof.Dr.Ir. S. Bruin (2^e promotor)

aan Marly

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CURRICULUM VITAE

The author was born on May 31, 1948, in Horst, the Netherlands. Following his secondary education at the "Gymnasium" of the "Lyceum voor jongens I.C." in Venray, he began his studies at the Chemical Engineering Department of the Technische Hogeschool Eindhoven in 1966. Graduate work, leading to the title of "scheikundig ingenieur" in May 1973, was performed under the guidance of Prof.Dr.Ir.H.A.C.Thijssen. From May 1973 to May 1974 the author was research co-worker of Douwe Egberts-Jakobs Research B.V., Utrecht. Since June 1974 he is working as "wetenschappelijk medewerker" in the department of Chemical Engineering at the Technische Hogeschool Eindhoven under the direction of Prof.Ir.M.Tels.
The dissertation has been prepared in the period May 1973 - May 1974 on a full-time basis and from May 1974 on a half-time basis.

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I INTRODUCTION

II EQUATIONS AND SOLUTION

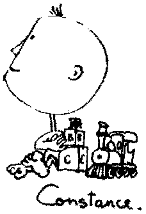
III REGULAR REGIME THEORY

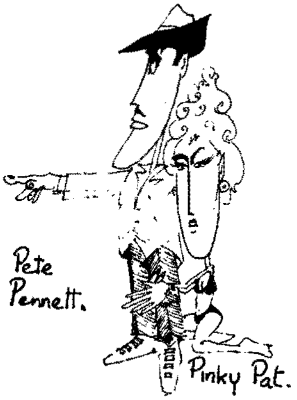
VI DETERMINATION OF CONCENTRATION DEPENDENT DIFFUSION COEFFICIENTS

PRELUDE

This thesis deals with some characteristic properties of sorption processes, in particular of the drying of materials in which the diffusion coefficient of water decreases strongly with decreasing water concentration.

The drying process generally starts with a flat (concentration) profile. During the initial stage of the process, the drying rate is constant (*"Constant rate period"*). The young Constance represents this period.





The initial drying rate depends on the air flow conditions, air temperature and -humidity. However, the drying curves for different initial drying rates coincide after the constant rate period in a single curve: the "parent curve". For every initial moisture content of the drying body there is a parent curve. An important part of this curve reflects the *"Penetration Period"*. The dynamic penetration activities determine the character of the parents: Pete Pennett and Pinky Pat.

The parent curves for every initial concentration all merge after some time into a "grand-parent"-curve, which therefore is independent of the initial concentration. This period is called the *Regular Regime*. The grand-parents Reggie & Regga are the leading characters of this thesis.

Reggie & Regga.

Mr. Steady.

After infinite time the *steady state* is reached, which will last forever.

For the calculation of drying processes, we developed some hereditary rules, with which the different stages of the drying process can be calculated, once we know the grand-parents Reggie and Regga, and Mr.Steady

"The sorptions."

SUMMARY

Dispersed phase mass transfer in sorption processes, such as drying, humidification, leaching and adsorption can generally be described by the diffusion equation. For many kinds of concentration dependence of the diffusion coefficient and many boundary conditions, concentration profiles become after a certain period of time virtually independent of the initial concentration profile: The sorption process enters the so-called *regular regime*. The regular regime sorption curve is determined by the (concentration- and temperature dependent) diffusivity, the geometry and the boundary conditions, and is independent of the initial condition.

This thesis deals with certain properties of regular regimes, in particular regular regimes of sorption with constant surface concentration or constant sorption rate. It appears, that dispersed phase mass transfer in case of concentration dependent diffusion coefficient can conveniently be described by a concentration-averaged diffusivity. The concentration-averaged diffusivity is also used in the definition of a dispersed phase Sherwood number. This Sherwood number has been correlated with a measure of the variation of the diffusivity with concentration. The correlation allows a simple calculation of the regular regime sorption curve from the concentration dependence of the diffusion coefficient. Reversely, the concentration dependence of the diffusion coefficient can be calculated in the whole concentration interval in which the regular regime sorption curve has been determined experimentally. This requires only a single sorption experiment. In addition, rules are given by which the regular regime sorption curve for a certain geometry can be translated into regular regimes for other geometries.

When a sorption process starts with a homogeneous initial

concentration, a so-called *penetration period* precedes the regular regime. For constant surface concentration or constant surface flux this period is characterized by a single parameter (slabs) or at most two parameters (spheres and cylinders). These parameters can be calculated from the regular regime sorption curve by relatively simple methods.

A short-cut method is described for the calculation of drying rates in case of strongly concentration dependent diffusion coefficients. Also non-isothermal drying of slabs, cylinders and spheres can in the absence of temperature gradients inside the drying specimen be calculated according to this method. The drying rate at constant surface concentration appears to be virtually independent of the temperature history. It is determined only by the actual temperature of the specimen and the average and surface concentration.

From experimentally determined isothermal drying curves of a slab of a gelled aqueous glucose solution the concentration and temperature dependence of the diffusion coefficient of water-glucose has been calculated. Values of the diffusion coefficient have been obtained for concentrations down to 10% water by weight. The relation between diffusion coefficient and water concentration, as obtained from these sorption experiments over a large concentration interval, are in good agreement with literature data, obtained from successive measurements over small concentration intervals.

SAMENVATTING

Bij sorptieprocessen als drogen, bevochtigen, adsorptie en vaste-stof extractie, kan het massa-transport in de disperse fase in het algemeen beschreven worden met de diffusievergelijking. Voor een groot aantal concentratie-afhankelijkheden van de diffusiecoefficient en diverse soorten randvoorwaarden blijken de concentratieprofielen na verloop van tijd onafhankelijk te worden van het concentratieprofiel bij het begin van het proces: het sorptie-proces bevindt zich dan in het zgn. *Regulier Regime* ("Regular Regime"). Het sorptie-gedrag in het regulier regime wordt bepaald door de (concentratie- en temperatuurafhankelijke) diffusiecoefficient, de geometrie en de randvoorwaarden en is onafhankelijk van de begintoestand.

In dit proefschrift worden een aantal eigenschappen beschreven van reguliere regimes, in het bijzonder voor sorptie met constante grensvlakconcentratie of constante sorptiesnelheid. Het massa-transport in de disperse fase wordt beschreven met behulp van een concentratie-gemiddelde diffusiecoefficiënt. Deze gemiddelde diffusiecoefficiënt wordt gebruikt voor de definitie van een Sherwood-getal voor de disperse fase. De waarde van het Sherwood getal wordt gecorreleerd met een maat voor de verandering van de diffusiecoefficiënt met de concentratie. Met behulp van deze correlatie kan de sorptie-snelheid gedurende het reguliere regime berekend worden uit de concentratie-afhankelijkheid van de diffusiecoefficiënt. Omgekeerd kan de concentratie-afhankelijkheid van de diffusiecoefficiënt berekend worden in het gehele concentratietrajekt, waarover de sorptie-snelheid gedurende het reguliere regime experimenteel bepaald is. Hiervoor is slechts één experiment noodzakelijk. Verder worden er nog regels gegeven om de reguliere sorptie-curve van een bepaalde geometrie te vertalen naar andere geometrieën.

Een zgn. *penetratie-periode* gaat vooraf aan het reguliere regime wanneer bij het begin van het sorptie-proces de concentratie in de disperse fase homogeen is. Zowel voor het geval van constante grensvlakconcentratie als voor constante sorptie-snelheid wordt deze periode gekarakteriseerd door één parameter (vlakke lagen) of ten hoogste twee parameters (cylinders, bollen). Deze parameters kunnen op een relatief eenvoudige manier berekend worden uit de reguliere sorptie-curve.

De in het proefschrift ontwikkelde theorie wordt toegepast bij de berekening van droogsnelheden van systemen, waarin de diffusiecoefficient sterk varieert met de water-concentratie. De methode kan ook worden toegepast voor de berekening van niet-isotherm drogende lagen, cylinders en bollen wanneer zich daarin geen temperatuurgradienten bevinden. Het is gebleken, dat de droogsnelheid bij constante grensvlakconcentratie praktisch onafhankelijk is van de temperatuurgeschiedenis. Zij wordt alleen bepaald door de actuele temperatuur van het drogend materiaal, de gemiddelde concentratie en de oppervlakte concentratie.

Uit experimenteel bepaalde isotherme droogcurven van een vlakke laag van een waterige, gegeleerde glucose-oplossing is de concentratie- en temperatuurafhankelijkheid van de diffusiecoefficiënt berekend m.b.v. de nieuw ontwikkelde methode. Tot 10 gewichts-procent water in de oplossing zijn waarden voor de diffusiecoefficiënt bepaald. De relatie tussen de diffusiecoefficiënt en de waterconcentratie zoals berekend uit de sorptie-experimenten over een groot concentratietraject, stemmen goed overeen met literatuurgegevens, die verkregen zijn door opeenvolgende metingen over kleine concentratietrajecten.

I. INTRODUCTION

I.1 General

Sorption is an inter-phase mass transfer process in which one or more components are transferred selectively. In general, the process is unsteady from a Lagrangian point of view.
This study deals with sorption in the phase in which

(i) the process is transient
(ii) the transfer rate of a component is proportional to its concentration gradient
(iii) the proportionality factor ("diffusion coefficient") is a function of the migrating component only.

These conditions refer in particular to *dispersed phase mass transport* in processes such as *leaching*, *adsorption*, *absorption*, *desorption*, *ion exchange*, *drying* and *humidification*. Emphasis is laid on the study of dispersed phase mass transfer in drying.

For the design and optimization of a sorption process the calculation of sorption rates is necessary. Many papers and textbooks deal with this subject (e.g. Walker et al. (1937), Treybal (1955), King (1971), Perry et al.(1973), Sherwood et al. (1975)). The subject-matter usually is divided into dispersed- and continuous-phase mass transfer.

Mass transfer in the *continuous phase* generally is described by means of a mass-transfer coefficient, which is defined as the ratio between the mass flux and a concentration difference. Several theories have been developed with respect to these mass transfer coefficients, e.g. film theory (Lewis (1916)), penetration theory (Higbie (1935)) suface renewal theory (Danckwerts (1951)) and boundary layer theory (Schlichting (1955)). In addition, many authors describe experimental correlations between dimensionless groups for the calculation of mass transfer rates (e.g. Ranz & Marshall (1952)). A review of such correlations for mass transfer from and to spheres has been presented by Sideman (1966) and by Sideman & Shabtai (1964). In all relations and correlations a diffusion coefficient is used, which is assumed to be constant. In practice, this assumption appears to be allowable for continuous phase mass transfer in the vast majority of sorption processes.

In *dispersed phase mass transfer* we confine ourselves here to systems in which convection (circulation, oscillation) or temperature gradients do not contribute to mass transfer. Under the restrictions mentioned above, the transport of a component can be described by the "diffusion equation". For various transport mechanisms (e.g. molecular diffusion, capillary transport, evaporation-condensation mechanism) the transfer rate of a migrating component in the absence of pressure gradients and external forces is proportional to the gradient of its chemical potential $\vec{\nabla}\mu_m$:

$$\vec{n}_m = - L_m \rho_m \vec{\nabla}\mu_m \qquad (I.1.1)$$

where $\vec{n}_m$ is the mass flux vector, L_m a phenomenological coefficient and ρ_m the mass concentration of the migrating component. The diffusion equation then follows from a shell mass balance:

$$\frac{\partial \rho_m}{\partial t} = \vec{\nabla}.(D \vec{\nabla}\rho_m) \qquad (I.1.2)$$

in which t is the time and D the diffusion coefficient, which is related to the phenomenological coefficient L_m by

$$D = L_m RT \left(\frac{\partial \ln a_m}{\partial \ln \rho_m}\right)_{P,F_{ext}} \qquad (I.1.3)$$

In this equation a_m is the activity of the migrating component, R the gas constant and T the absolute temperature.

The diffusion coefficient is often dependent on concentration, in particular when water is the migrating component (drying and humidification). This concentration dependence of the water diffusivity has for instance been observed in polyvinylalcohol (Okazaki et.al. (1974), soap, wood, clay (Hougen et.al,(1939)) and many carbohydrate solutions (Gosting & Morris (1949), English & Dole (1950), Gladden & Dole (1953), Fish (1958), Menting (1969), Chandrasekaran & King (1972), v.d. Lijn (1976)). However, also in many other systems the apparent diffusion coefficient varies with concentration (Ghai et.al. (1973)). Diffusion in a porous medium with instantaneous adsorption-equilibrium may serve as another example.

The diffusion equation with constant diffusivity has been solved analytically for numerous initial- and boundary conditions (Newman (1931), Carslaw & Jaeger (1959), Crank (1956), Luikov (1968)). Numerical solutions using strongly concentration dependent diffusion coefficents have been presented by van Arsdel (1947) and, more recently, by several authors, as well for constant surface concentration (Okazaki et.al.(1974), Fels & Huang (1970), Duda & Vrentas (1971)) as for variable surface concentration in a simulation of a drying process (Rulkens & Thijssen (1969), Chandrasekaran & King (1972), Kerkhof et.al. (1972) v.d. Lijn et.al. (1972), Schoeber (1973), Rulkens (1973), Kerkhof & Schoeber (1974), Kerkhof (1975), v.d. Lijn (1976)).

A major problem in the application of numerical methods to the solution of the diffusion equation with variable diffusion coefficient is, that it is often extremely difficult to prove stability and convergence to the unique solution. In some cases it is even hard to obtain a calculation which is not evidently unstable. Even more discouraging is the fact, that data about the concentration dependence of diffusion coefficients are very scarce. This means, that elaborate experiments are required for the determination of this concentration dependence before the mass transfer rates can be calculated.

Therefore, the aim of this investigation has been the development of a relatively simple and fast method for the determination of concentration dependent diffusion coefficients. In addition, we investigated the possibilities of circumventing the numerical calculations and developed correlation methods for the calculation of sorption rates, with particular reference to drying.

The present approach is to a large extent phenomenological: numerical solutions of the diffusion equation have been analyzed for many kinds of concentration dependence of the diffusion coefficient. Some striking regularities were observed of which use can be made in the calculation of sorption processes.

I.2 Regular Regimes

A diffusion process may be divided into three stages (cfr. Luikov (1968)).

In the first stage, the diffusion is strongly influenced by the initial concentration distribution. After a certain period of time the influence of this initial distribution is no longer detectable in the concentration profiles. This second stage is called the *Regular Regime.* In an actual diffusion process the concentration profiles and mass transfer rates belonging to the regular regime are approached asymptotically. Therefore, the characteristic properties of this regime are of great interest for engineering purposes. The third stage corresponds to the *Steady State,* during which the concentration at any point of the body is constant.

In the present work the regular regime is defined as *the period in time during an unstationary diffusion process in which the influence of the initial condition on the process can be neglected, but during which the concentrations still* *change in time.*

The general solution of the diffusion equation can be represented by a function of time and place:

$$m = m(\phi,\tau)$$

where m is a measure of the concentration, τ is a time-coordinate and ϕ is a distance coordinate. During the regular regime the solution is independent of initial condition and therefore independent of the absolute value of τ. If we exclude periodically changing boundary conditions, the average concentration inside the body ($\bar{m}$) can then be used as a measure of the time and the regular regime can be described by a function of ϕ and $\bar{m}$ only:

$$m_{RR} = m_{RR}\ (\phi,\bar{m}) \qquad \text{(I.2.2)}$$

It follows, that *a regular regime does not occur if the boundary condition can not be expressed independently of the absolute value of* τ. If the boundary condition is given as a function of $\bar{m}$ (e.g. according to a mass balance), as a time-derivative (e.g. linearly decreasing surface concentration with time) or as a periodic function of time, this regular regime condition is fulfilled.

The regular regime phenomenon has in literature only been described for constant diffusivity. Kondratiev (1964) and Luikov (1968) introduced the regular regime concept. They used definitions, which were based upon regularities in diffusion processes with constant diffusivity. For the case of a concentration dependent diffusion coefficient these definitions are too restricted, since the regular regime is then less "regular": Overall mass transfer coefficients, which are constant during the regular regime in case of a constant diffusion coefficient, vary with time in case of variable diffusivity. Nevertheless, it is still advantageous to use the regular regime concept: in the regular regime similarity exists between processes with equal boundary conditions but different initial conditions.

In his work on heat diffusion with constant thermal properties Kondratiev (1964) distinguishes different kinds of regular regimes. Analogously we distinguish the following kinds of regular regimes:

1. The concentration profile in the body remains geometrically identical. Kondratiev calls this a *regular regime of the second kind.* The change of the concentration with time does not vary with the space-coordinate, so that this regular regime can be characterized by

   $$\frac{\partial m}{\partial \bar{m}} = 1 \tag{I.2.3}$$

   For constant diffusivity this type of regular regime occurs for a constant surface flux or a linear relation between surface concentration and time.
2. The concentration profile in the body remains geometrically similar: *regular regime of the first kind.* This can be characterized by

   $$\frac{\partial m}{\partial \bar{m}} = \frac{m + f(\bar{m})}{\bar{m} + f(\bar{m})} \tag{I.2.4}$$

   where $f(\bar{m})$ is a function of the average concentration $\bar{m}$ only. An example of this type of regular regime is sorption with constant diffusivity, constant mass transfer Biot-number and constant extraction factor (Thijssen et al. (1973), Vorstman & Thijssen (1971)).
3. For all other regular regimes it holds, that

   $$\frac{\partial m}{\partial \bar{m}} = g(\bar{m},\phi) \tag{I.2.5}$$

   where g is a function of $\bar{m}$ and ϕ only and therefore is independent of the absolute value of the time.

For constant diffusion coefficient the dispersed phase mass transfer coefficient reaches a limit value upon entering a regular regime of the first or the second kind. Vorstman & Thijssen (1971) and Thijssen et al. (1973) made use of this phenomenon in extraction calculations.

For reasons of similarity a Sherwood number for the dispersed phase (Sh_d) is introduced, which is defined by

$$Sh_d = \frac{2\ k_d\ R}{D} \qquad (I.2.6)$$

where k_d is the mass transfer coefficient in the dispersed phase and R a characteristic dimension (radius) of the specimen. This Sherwood number is indicative for the shape of the concentration profile and remains constant when the shape of the concentration profile remains constant (regular regimes of the first and second kind). The authors presented asymptotic values of Sh_d for many values of the mass transfer Biot-number and of the extraction factor.

A first indication of the occurence of regular regimes in case of concentration dependent diffusion coefficients was given by Schoeber (1973). He found, that the drying time of a droplet of an aqueous solution of maltose during the final stage of the process was virtually independent of the initial concentration. Recently, Schoeber & Thijssen (1975) have published an analysis of the (numerical) solutions of the diffusion equation for a slab in which the regular regime approach is introduced for the case of a variable diffusion coefficient. It appears from their analysis, that the regular regime sorption curve is characteristic for a given material and a given set of boundary conditions and temperature. This regular regime sorption curve can serve as a basis for the calculation of the sorption curve for every (homogeneous) initial concentration and for the calculation of the concentration dependence of the diffusion coefficient.

I.3 Drying of aqueous solutions in which the diffusion coefficient of water depends strongly on water concentration

In general, drying histories are divided into two periods: a constant rate period, during which the water activity at the phase boundary is approximately constant, and a falling rate period. If the diffusion coefficient decreases strongly with water concentration, mass transfer during the falling rate period generally is controlled by dispersed phase mass transfer. Therefore, the water concentration at the phase boundary in the dispersed phase is approximately equal to the equilibrium concentration.

The boundary conditions belonging to these two periods both fulfill the requirements for a regular regime to occur after a period of time. In view of the application to the calculation of drying processes particular attention is paid to the boundary conditions which apply for the constant and falling rate period of drying: constant surface activity (e.g. constant surface flux) and constant surface concentration.

I.4 Scope of this thesis

This thesis can be divided into three main parts: an introductory part (chapter II), a fundamental part (chapters III and IV) and an applied part (chapters V and VI).

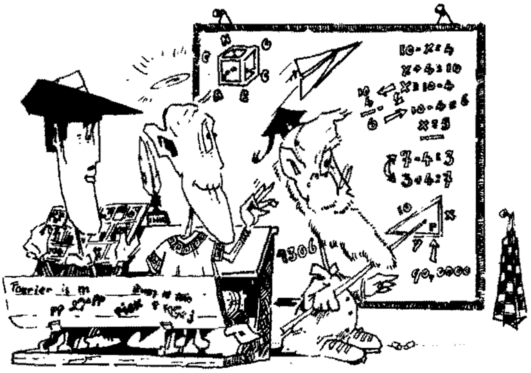
After the introduction, the diffusion equation is given in chapter II for various coordinate systems (slabs, cylinders, spheres, spherical and cylindrical shells, shrinking and non-shrinking systems). This chapter also treats the numerical solution of the diffusion equation.

Chapter III deals with the characteristics of the regular regime of sorption. The influence of the kind of concentration dependence of the diffusion coefficient on the sorption rate is investigated. Furthermore, general relations for the influence of geometry and of shrinkage on the sorption rate are presented.

If the concentration profile at the beginning of the sorption process is flat, it takes some time before the regular regime is reached. In this first period the influence of the change, brought about at the phase boundary, gradually penetrates into the body ("Penetration Period"). The relations describing the sorption rate in the penetration period are presented in chapter IV.

Chapter V describes a short-cut method for the calculation of drying rates in case of strongly concentration dependent diffusion coefficient (e.g. food liquids). It is based on the developments described in the chapters III and IV.

Chapter VI illustrates the significance of the regular regime approach to the calculation of the concentration dependence of the diffusion coefficient from a single sorption experiment. The isothermal drying of a slab of an aqueous solution of glucose is described. From this sorption curve the concentration dependence of the diffusion coefficient is calculated and compared with literature values.



II EQUATIONS AND SOLUTION

II.1 Introduction

This study deals with systems, in which mass transport can be described by the diffusion equation. It depends on the kind of physical system which coordinates are to be prefered for the description of the transport process. If the dispersed phase consists of a porous solid material, its dimensions remain constant during the process. The same can be assumed if the volume fraction of the migrating component in the dispersed phase is negligible. For such non-shrinking systems the description in stationary coordinates (with respect to the rigid dispersed particle) is to be preferred. However, if there is no rigid matrix present, the dimensions of the dispersed body change upon (de)sorption of a considerable volume-fraction. The change of volume is often equal to the volumetric uptake or loss of sorbent (e.g. aqueous carbohydrate solutions, many polymer systems). Dissolved solids- or stationary compound centered-coordinates were shown to be suitable for the description of mass transfer in such shrinking or swelling systems (Crank (1956), V.d.Lijn (1976)).

In this chapter the diffusion equations are presented for non-shrinking systems and for shrinking systems in which the volumetric uptake or loss of sorbent is equal to the volume change of the dispersed body. The equations will be given for *one-dimensional diffusion* in the slab-geometry (infinite flat plate of limited thickness), in an infinite cylinder and in a sphere. The diffusion equations for all systems will then be condensed in a single equation. Such a generalized representation facilitates general derivations and the programming of the numerical solution of the equations in a computer program. Finally the numerical solution of the diffusion equation will be discussed concisely.

II.2 Non-shrinking systems

Let the (apparent) diffusion coefficient D be defined by

$$n_m = -D \frac{\partial \rho_m}{\partial r} \qquad \text{(II.2.1)}$$

where n_m is the mass flux of the migrating component m with respect to stationary coordinates (kg/m^{2}s), ρ_m the mass concentration of m (kg/m^3) and r the stationary distance coordinate (m). This diffusivity D is equal to the molecular diffusion coefficient $\mathbb{D}$ for equivolumetric diffusion without volume contraction (i.e. zero mean volume velocity) as defined by Bird et.al. (1960) (Van der Lijn (1976)):

$$n_m = \omega_m(n_m + n_s) - \mathbb{D}\,\rho \nabla \omega_m \qquad \text{(II.2.2)}$$

where ω_m is the mass fraction of component m (kg/kg), ρ the total density and the indices m and s refer to the two components m (migrating) and s (e.g. dissolved solid) present in the binary system.

From a shell mass balance then follows the diffusion equation:

$$\left(\frac{\partial \rho_m}{\partial t}\right)_r = \frac{1}{r^\nu} \left\{\frac{\partial}{\partial r}\left(D\ r^\nu \frac{\partial \rho_m}{\partial r}\right)\right\}_t \qquad \text{(II.2.3)}$$

where t is the time and ν is a geometric factor, which is 0 for slabs, 1 for cylinders and 2 for spheres. The use of such a geometric factor was proposed by Kerkhof (1975). For reasons of similarity the following dimensionless variables are defined:

$$\tau^* = D_0\ t/R^2 \qquad \text{(II.2.4)}$$

in which τ^* is the dimensionless time variable and R the dimension of the body (the radius for spheres and cylinders, the half-thickness of a slab in case of mass transfer at both sides of the slab and the thickness of the slab in case of single-side mass transfer). D_0 is an arbitrary value of the diffusion coefficient which is introduced to show the similarity between two sorption processes in which the variable diffusion coefficients differ from each other by a constant factor over the concentration interval of interest. In certain cases, where this similarity is not relevant, D_0 can be considered as a dimensional constant with a numerical value of 1.
A dimensionless space-coordinate z is defined by

$$z = \left(\frac{r}{R}\right)^{\nu+1} \qquad \text{(II.2.5)}$$

Equal increments in z correspond with equal increments in the (relative) volume between $0 < z < z'$.
Finally, a dimensionless diffusion coefficient D_r (reduced) is introduced:

$$D_r = D/D_0 \qquad \text{(II.2.6)}$$

Substitution of the new variables and the reduced diffusivity gives the diffusion equation in reduced variables:

$$\left(\frac{\partial \rho_m}{\partial \tau^*}\right)_z = \left\{\frac{\partial}{\partial z}\left(D_r \quad (\nu+1)^2 \ z^{\frac{2\nu}{\nu+1}} \cdot \frac{\partial \rho_m}{\partial z}\right)\right\}_{\tau^*} \qquad \text{(II.2.7)}$$

Introduction of a dimensionless concentration would not be meaningful, since the diffusivity is a function of the absolute concentration itself and can in general not be expressed as a function of a reduced concentration only.

Generally, the concentration profile is flat at the beginning of the sorption process. The initial condition therefore reads:

$$\tau^* = 0; \quad 0 \leqq z \leqq 1; \quad \rho_m = \rho_{m,0} \qquad \text{(II.2.8)}$$

The boundary condition for the centre of the body reads:

$$z = 0; \quad z^{\frac{\nu}{\nu+1}} \frac{\partial \rho_m}{\partial z} = 0 \qquad \text{(II.2.9)}$$

while at the phase boundary the mass fluxes in the dispersed and continuous phase are equal:

$$n_{m,i} = -D\left(\frac{\partial \rho_m}{\partial r}\right)_{r=R} \qquad \text{(II.2.10)}$$

where $n_{m,i}$ represents the mass flux through the interface. In reduced variables this condition can be formulated as:

$$-D_r \quad (\nu+1) \ \frac{\partial \rho_m}{\partial z} = \frac{n_{m,i} \ R}{D_0} \qquad \text{(II.2.11)}$$

The diffusion process in *a shell* (hollow sphere, hollow cylinder) can be described by the equation

$$\left(\frac{\partial \rho_m}{\partial \tau^*}\right)_z = \left\{\frac{\partial}{\partial z}\left[D_r \quad (\nu+1)^2 \left\{\left(\frac{R_c}{R_s}\right)^{\nu+1} + z\right\}^{\frac{2\nu}{\nu+1}} \frac{\partial \rho_m}{\partial z}\right]\right\}_{\tau^*} \qquad \text{(II.2.12)}$$

In this equation R_c is the radius of the hollow part ("core") and R_s the radius of the massive body (sphere, cylinder) which has a volume equal to the volume of the shell. The parameter $\left(\frac{R_c}{R_s}\right)^{\nu+1}$ represents the ratio of the inert volume to the "active" volume where the diffusion takes place. The initial condition is given by equation (II.2.8) and the boundary condition at z=0 by equation (II.2.9). The boundary condition at z=1 reads:

$$\frac{n_{m,i} \cdot R}{D_0} = -D_r \ (\nu+1) \left\{\left(\frac{R_c}{R_s}\right)^{\nu+1} + 1\right\}^{\frac{\nu}{\nu+1}} \left.\frac{\partial \rho_m}{\partial z}\right|_{z=1} \qquad \text{(II.2.13)}$$

II.3 Shrinking or swelling systems

The diffusion flux relative to reference component-mass centered coordinates (which move with the dissolved solids) is equal to (de Groot & Mazur (1962)):

$$j_m^s = -\mathbb{D}\, \rho_s \ \nabla u \qquad \text{(II.3.1)}$$

where j_m^s represents the mass flux with respect to the reference component-mass centered coordinate and the index s refers to the reference component (e.g. dissolved solid when the solvent is extracted). u is the mass concentration on reference component basis: ρ_m/ρ_s. The equation of continuity then reads:

$$\left(\frac{\partial u}{\partial t}\right)_y = \left[\frac{\partial}{\partial y}\left(\mathbb{D} \cdot \rho_s^2 \cdot r^{2\nu} \ \frac{\partial u}{\partial y}\right)\right]_t \qquad \text{(II.3.2)}$$

In which y is the reference component-mass centered coordinate, defined by

$$y = \int_0^r \rho_s \ r^\nu \ dr \qquad \text{(II.3.3)}$$

The following reduced variables are introduced:

$$\tau^{**} = \frac{\mathbb{D}_0 \ \rho_{s,0}^2 \ t}{d_{s,p}^2 \ R_s^2} \qquad \text{(II.3.4)}$$

where τ^{**} is the dimensionless time variable , $d_{s,p}$ is the density of the pure reference component (at $\rho_m = 0$) and R_s the radius (or thickness) of the body in the absence of the migrating component ($\rho_m = 0$). In terms of the reduced coordinates R_s can be formulated as

$$R_s = \frac{(\nu+1)}{d_{s,p}} \quad Y^{\frac{1}{\nu+1}} \tag{II.3.5}$$

In this relation Y represents the value of y at r=R:

$$Y = \int_0^R \rho_s \, r^\nu \, dr \tag{II.3.6}$$

The combination $\mathbb{D}_0 \, \rho_{s,0}^2$ plays the same role as D_0 in the previous paragraph. A reduced diffusivity is defined by

$$D_r = \frac{\mathbb{D} \, \rho_s^2}{\mathbb{D}_0 \, \rho_{s,0}^2} \tag{II.3.7}$$

and the reduced distance coordinate reads:

$$\xi = y/Y \tag{II.3.8}$$

Increments in ξ correspond to fractional increments in the reference component mass.

Substitution of these new variables in equation (II.3.2) yields:

$$\left(\frac{\partial u}{\partial \tau^{**}}\right)_{\xi} = \left\{ \frac{\partial}{\partial \xi} \left[D_r (\nu+1)^2 \left\{ d_{s,p} \int_0^{\xi} \left(\frac{1}{d_s} + \frac{u}{d_m} \right) d\xi \right\}^{\frac{2\nu}{\nu+1}} \cdot \frac{\partial u}{\partial \xi} \right] \right\}_{\tau^{**}} \tag{II.3.9}$$

with the initial condition

$$\tau^{**} = 0; \quad 0 < \xi < 1 : u = u_0 \tag{II.3.10}$$

and the boundary conditions

$$\tau^{**} > 0; \ \xi = 0 : \left\{ \int_0^{\xi} \left(\frac{1}{d_s} + \frac{u}{d_m} \right) d\xi \right\}^{\frac{\nu}{\nu+1}} \cdot \frac{\partial u}{\partial \xi} = 0 \tag{II.3.11}$$

$\tau^{**} > 0; \quad \xi = 1 :$

$$\frac{j^{s}_{m,i}\, d_{s,p}\, R_{s}}{\mathbb{D}_{0}\, \rho^{2}_{s,0}} = -D_{r}\,(\nu+1)\left\{d_{s,p}\int_{0}^{\xi}\left(\frac{1}{d_{s}}+\frac{u}{d_{m}}\right)d\xi\right\}^{\frac{\nu}{\nu+1}}\cdot\frac{\partial u}{\partial \xi}\Bigg|_{\xi=1} \tag{II.3.12}$$

In these equations d_s and d_m are the partial densities of the reference and migrating component respectively.

If there is no volume change upon mixing ($d_s = d_{s,p}$) the equations can also be written in reference component volume centered coordinates (Kerkhof (1975)). The coordinate system remains the same, because fractional increments in the reference component mass are for constant specific density equal to fractional increments in its volume. Only the concentration (v) is expressed as a volume-fraction

$$v = \frac{d_s}{d_m}\cdot\frac{\rho_m}{\rho_s} \tag{II.3.13}$$

Multiplication of both sides of equation (II.3.9) by d_s/d_m then results in the reduced diffusion equation in volume-centered coordinates:

$$\left(\frac{\partial v}{\partial \tau^{**}}\right)_{\xi} = \left\{\frac{\partial}{\partial \xi}\left[D_{r}\,(\nu+1)^{2}\left\{\int_{0}^{\xi}(1+v)\,d\xi\right\}^{\frac{2\nu}{\nu+1}}\frac{\partial v}{\partial \xi}\right]\right\}_{\tau^{**}} \tag{II.3.14}$$

This notation appears to be somewhat less complex than the notation in mass centered coordinates. The specific densities of the components have been eliminated. Therefore, this notation is to be preferred for the general analysis of diffusion in shrinking systems. The initial condition and the boundary condition at $\xi = 0$ are equal to the conditions for the mass centered coordinate system if v is substituted for u. The boundary condition at $\xi = 1$ reads:

$$\frac{j_{m,i}^{s} \; R_s \; d_s^2}{\mathrm{D}_0 \; \rho_{s,0}^2 \; d_m} = -D_r \; (\nu+1) \left\{ \int_0^{\xi} (1+v) \; d\xi \right\}^{\frac{\nu}{\nu+1}} \left. \frac{\partial v}{\partial \xi} \right|_{\xi=1} \tag{II.3.15}$$

Note that for slabs ($\nu=0$) the diffusion equations (II.3.9) and (II.3.14) take the simple "Fickian" form:

$$\left(\frac{\partial u}{\partial \tau^{**}} \right)_{\xi} = \frac{\partial}{\partial \xi} \left(D_r \frac{\partial u}{\partial \xi} \right)_{\tau^{**}} \tag{II.3.16}$$

and

$$\left(\frac{\partial v}{\partial \tau^{**}} \right)_{\xi} = \frac{\partial}{\partial \xi} \left(D_r \frac{\partial v}{\partial \xi} \right)_{\tau^{**}} \tag{II.3.17}$$

The equations for shrinking hollow particles with constant inner or outer radius will not be derived here. They are included in the generalized description in the next paragraph.

II.4 Generalized formulation

The diffusion equations with boundary conditions for shrinking and non-shrinking systems, slabs, cylinders and spheres can be condensed in a single formulation of the diffusion equation:

$$\frac{\partial m}{\partial \tau} = \frac{\partial}{\partial \phi} \left(D_r \; X^2 \; \frac{\partial m}{\partial \phi} \right) \tag{II.4.1}$$

with initial and boundary conditions:

$$\tau = 0; \quad 0 < \phi < 1 \; : \; m = m_0 \tag{II.4.2}$$

$$\tau > 0; \quad \phi = 0 \; : \; X \frac{\partial m}{\partial \phi} = 0 \tag{II.4.3}$$

$$\phi = 1 \; : \; F = -D_r \; X_i \left. \frac{\partial m}{\partial \phi} \right|_{\phi=1} \tag{II.4.4}$$

In this set of equations m is the concentration, τ the dimensionless time coordinate, ϕ the dimensionless space-coordinate and F the flux parameter (which has the same

Table II.4.1: Meaning of the variables in the reduced equation II.4.1

variable	stationary coordinates	reference component mass centered coordinates	reference component volume centered coordinates
concentration: m	ρ_m	$\frac{\rho_m}{\rho_s}$	$\frac{d_s}{d_m}\,\frac{\rho_m}{\rho_s}$
time: τ	$\frac{D_0 t}{R_s^2}$	$\frac{\mathbb{D}_0\,\rho_{s,0}^2\,t}{d_{s,p}^2\,R_s^2}$	$\frac{\mathbb{D}_0\,\rho_{s,0}^2\,t}{d_s^2\,R_s^2}$
distance: (systems without hollow core) ϕ	$\left\{\frac{r}{R_s}\right\}^{\nu+1}$	$\frac{\int_0^r \rho_s\,r^\nu\,dr}{\int_0^R \rho_s\,r^\nu\,dr}$	$\frac{\int_0^r \frac{\rho_s}{d_s}\,r^\nu\,dr}{\int_0^R \frac{\rho_s}{d_s}\,r^\nu\,dr}$
distance: (hollow systems) ϕ	$\left\{\frac{r}{R_s}\right\}^{\nu+1}-\left\{\frac{R_c}{R_s}\right\}^{\nu+1}$	$\frac{\int_{R_c}^r \rho_s\,r^\nu\,dr}{\int_{R_c}^R \rho_s\,r^\nu\,dr}$	$\frac{\int_{R_c}^r \frac{\rho_s}{d_s}\,r^\nu\,dr}{\int_{R_c}^R \frac{\rho_s}{d_s}\,r^\nu\,dr}$
diffusivity: D_r	$\frac{D}{D_0}$	$\frac{\mathbb{D}\,\rho_s^2}{\mathbb{D}_0\,\rho_{s,0}^2}$	$\frac{\mathbb{D}\,\rho_s^2}{\mathbb{D}_0\,\rho_{s,0}^2}$
surface flux parameter: F	$\frac{n_{m,i}\,R_s}{D_0}$	$\frac{j^s_{m,i}\,d_{s,p}\,R_s}{\mathbb{D}_0\,\rho_{s,0}^2}$	$\frac{j^s_{m,i}\,d_s^2\,R_s}{\mathbb{D}_0\,\rho_{s,0}^2\,d_m}$

X	stationary coordinates	reference component mass centered coordinates	reference component volume centered coordinates
systems without hollow core	$(\nu+1)\ \phi^{\frac{\nu}{\nu+1}}$	$(\nu+1)\left\{d_{s,p}\int_0^{\phi}\left(\frac{1}{d_s}+\frac{m}{d_m}\right)d\phi\right\}^{\frac{\nu}{\nu+1}}$	$(\nu+1)\left\{\int_0^{\phi}(1+m)\,d\phi\right\}^{\frac{\nu}{\nu+1}}$
hollow, constant inner radius R_c	$(\nu+1)\left\{\left(\frac{R_c}{R_s}\right)^{\nu+1}+\phi\right\}^{\frac{\nu}{\nu+1}}$	$(\nu+1)\left\{\left(\frac{R_c}{R_s}\right)^{\nu+1}+d_{s,p}\int_0^{\phi}\left(\frac{1}{d_s}+\frac{m}{d_m}\right)d\phi\right\}^{\frac{\nu}{\nu+1}}$	$(\nu+1)\left\{\left(\frac{R_c}{R_s}\right)^{\nu+1}+\int_0^{\phi}(1+m)\,d\phi\right\}^{\frac{\nu}{\nu+1}}$
hollow, constant outer radius R	$(\nu+1)\left\{\left(\frac{R}{R_s}\right)^{\nu+1}-(1-\phi)\right\}^{\frac{\nu}{\nu+1}}$	$(\nu+1)\left\{\left(\frac{R}{R_s}\right)^{\nu+1}-d_{s,p}\int_{\phi}^{1}\left(\frac{1}{d_s}+\frac{m}{d_m}\right)d\phi\right\}^{\frac{\nu}{\nu+1}}$	$(\nu+1)\left\{\left(\frac{R}{R_s}\right)^{\nu+1}-\int_{\phi}^{1}(1+m)\,d\phi\right\}^{\frac{\nu}{\nu+1}}$
Slab: $\nu = 0$; cylinder: $\nu = 1$; sphere $\nu = 2$;			

Table II.4.2: Meaning of the variable X in equation II.4.1.

dimension as m!). The dimensionless quantity X is $(\nu+1)$ times the surface area of the body at a given ϕ relative to the surface area of the body at the same ϕ, if it would contain no migrating component. X_i is the value of X at $\phi=1$ (interface).

Integration of equation (II.4.1) between $\phi=0$ and $\phi=1$ gives the mass balance:

$$-\frac{d\bar{m}}{d\tau} = F.X_i \qquad \text{(II.4.5)}$$

where $\bar{m}$ is the average concentration in the body:

$$\bar{m} = \int_0^1 m \, d\phi \qquad \text{(II.4.6)}$$

The Tables II.4.1 and II.4.2 give the meaning of the parameters introduced in this paragraph for the various systems under consideration. For hollow systems (cylindrical or spherical shells) the variables have the same meaning as for systems without hollow core with the exception of the space coordinate ϕ and the quantity X. In the description in stationary coordinates the body dimension R_s is equal to R for systems without hollow core.

II.5 Numerical solution of the diffusion equation

Several methods have been presented in literature for the solution of the non-linear parabolic differential equation (II.4.1). Duda & Vrentas (1971) used a *collocation technique*. However, such a technique may involve serious difficulties. Acton (1970) states in the interlude "What not to compute" about this method: "Having chosen the series and fitted the parameters and evaluated the approximate solution, one is still left with more hope than knowledge." Many other authors, who have been mentioned in the introduction, used *finite difference techniques*. Also for these techniques it is difficult to prove stability and to prove convergence to the unique solution.(Ladyzenskaja et al. (1968) proved, that there exists a unique solution to the quasilinear equation (II.4.1) with initial- and boundary conditions (II.4.2-4)). In spite of these uncertainties, we used this technique without proof of convergence and stability, in the first instance incidentally also "left with more hope than knowledge". Where possible, the results of the calculations have been checked either analytically, either by "safe" numerical methods, or experimentally. The results presented in the following chapters reveal that good agreement exists between the numerical solutions on the one hand and on the other hand analytical and numerical relations derived for the regular regimes with geometrically similar or identical concentration profiles and the analytical solutions for constant diffusion coefficient. Furthermore, the calculations for the isothermal drying of a slab of an aqueous solution of glucose could be verified experimentally. Together with the fact, that variation of the grid-size or length of time-intervals did not have a substantial effect on the results of the calculations, there is sufficient reason to believe that the numerical solutions are reliable.

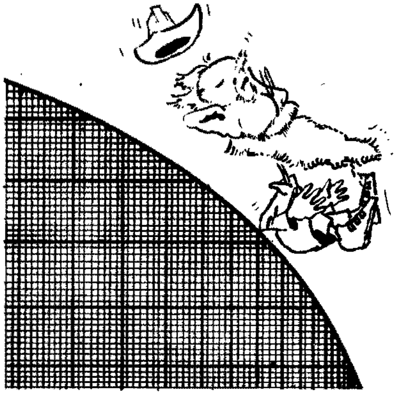
The diffusion equation was solved by application of a modification of the Crank-Nicolson (1947) finite difference technique. The weighting factor used in the calculation of the weighted-mean time derivative $\Delta m/\Delta\tau$, which is .5 in the Crank-Nicolson method, was taken between .5 and .8 for the "new" time level and consequently between .5 and .2 for the "old" time level. It appeared experimentally, that for diffusion coefficients which vary strongly with concentration, a high weighting factor for the new time level (.8) improves stability. The last difference equation near the phase boundary $\phi=1$ and the boundary condition at $\phi=1$ were both taken at the new time level only (weighting factors 1 and 0 respectively).

In order to obtain a linear set of equations, the coefficient D_r was evaluated at the new time level using extrapolated values of the concentration. Also the quantity X was for shrinking systems extrapolated to the new time level.

The distance coordinate ϕ was divided into 20 intervals. In order to attain that the changes of the concentration per distance interval were of the same order of magnitude, the length of these intervals decreased with increasing ϕ. The time intervals were chosen in such a way, that the amount of sorbent transferred per time interval as calculated from the difference between the concentration profiles, did not differ more than one per thousand from the amount calculated from the flux, integrated over the time interval. Moreover, the relative change in any concentration per time interval should not exceed 1 per cent. These conditions resulted in 2000 - 8000 time intervals until a final average concentration of .001 x m_0 had been reached (desorption). The calculations were performed on a Burroughs B 6700 digital computer and required about .04 seconds processing time per time interval.

III REGULAR REGIME THEORY

III.1 General



A regular regime is the period in time during an unstationary diffusion process in which the influence of the initial condition on the process can be neglected, but during which the concentrations still change in time. The regular regime phenomenon can mathematically be formulated in in the following way.

Let $m(\phi,\bar{m},m_0)$ be the solution of the non-linear diffusion equation (II.4.1) with initial and boundary conditions (II.4.2,3,4). The concentration m is a function of the space-coordinate ϕ, of the initial concentration distribution $m_0(\phi)$, and of the average concentration $\bar{m}$, which is taken here as a measure of the time τ.

$$\bar{m} = \int_0^1 m_0 d\phi + \int_0^\tau \int_0^1 \frac{\partial m}{\partial \tau} d\phi\, d\tau \qquad \text{(III.1.1)}$$

The occurrence of a regular regime implies, that there is a function $m_{RR}(\phi,\bar{m})$ for which holds, that for every $\varepsilon>0$ and every $\bar{m}$ there is a M_0, such that

$$\left| \frac{m(\phi,\bar{m},m_0) - m_{RR}(\phi,\bar{m})}{m_{RR}(\phi,\bar{m})} \right| < \varepsilon \qquad \text{(III.1.2)}$$

for every $\phi \in [0,1]$, if $\int_0^1 m_0\, d\phi > M_0$.

In case of periodically varying boundary conditions the functions m and m_{RR} depend also on the value of the argument θ of this periodical function. In that case one should read $m(\phi, \bar{m}, m_0, \theta)$ instead of $m(\phi, \bar{m}, m_0)$ and $m_{RR}(\phi, \bar{m}, \theta)$ instead of $m_{RR}(\phi, \bar{m})$.

For constant diffusion coefficient the above statement is true for sorption with constant surface concentration, constant mass transfer Biot-number, constant surface flux, periodically varying and some other boundary conditions (cfr. Luikov (1968)). More generally speaking, it can be proved analytically if the homogeneous diffusion equation can be transformed to a linear eigen-value problem by separation of variables. The solution $m(\phi, m, m_0)$ can then be written as the sum of a particular solution to the inhomogeneous problem and a number of eigen-functions m_n. The partial derivative to the time variable τ for a certain value of ϕ is then for every eigen-function determined by its eigen-value. The eigen-function with the smallest partial time-derivative (e.g. smallest eigen-value) will dominate the sum of eigen-functions for large values of τ. Hence, this eigen-function reflects the solution of the diffusion equation during the regular regime ("regular solution") in case of homogeneous boundary conditions (e.g. constant surface concentration). An analogous line of reasoning holds in case of inhomogeneous boundary conditions (e.g. constant surface flux), where the solutions of the homogeneous problem may become negligible for high values of the time variable.

However, in the general case of a variable diffusivity the diffusion equation can not be transformed to a linear eigen-value problem. Until now, we have not been able to obtain strict mathematical evidence for the occurrence of the regular regime phenomenon in this case. The phenomenon can however be made plausible by the following line of reasoning.

The diffusion equation (II.4.1) indicates that the concentration distribution inside the specimen under consideration tends to a smooth profile: strong curvatures disappear relatively fast since they cause a relatively high absolute value of the time derivative, $|\partial m/\partial \tau|$. Let us consider two smooth concentration profiles A and B of different shape in a non-shrinking system, both with the same average concentration. A schematic representation of the situation is given in figure III.1.1.

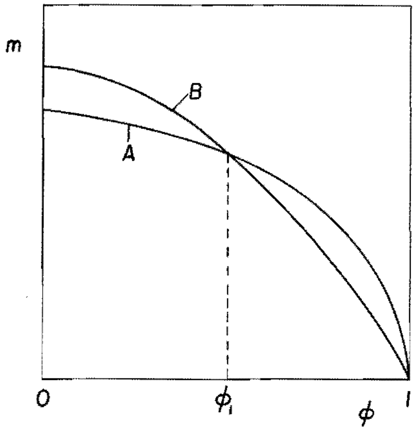


Fig.III.1.1.

Schematic representation of the concentration profiles for two sorption processes with different initial conditions

In this example the boundary condition at $\phi=1$ is taken to be $m_1=0$. We assume, that the concentration is a continuous function of the space variable ϕ, so that the profiles have at least one point in common (at $\phi=\phi_1$). In this common point the concentration dependent diffusion coefficients are equal for the two profiles. Therefore, the ratio between the sorbent fluxes for the two profiles at this point is equal to the ratio of their concentration gradients. From a mass balance over $0<\phi<\phi_1$ then follows, that the average concentration of profile B in this interval must decrease faster with time than the average concentration of profile A in the same interval. The reverse holds analogously for the interval $\phi_1<\phi<1$ (or between the next two intersection points). It can therefore be concluded that both concentration profiles will approach each other: they tend to the same shape. A similar line of reasoning can be set up for shrinking systems. Only then the derivation has to be given in stationary coordinates to make the two mass balances comparable.

Sorption rates and values of mass transfer coefficients during the regular regime form the subject of this chapter. After the description of steady-state mass transfer (in fact the "most regular" regime of all), the special types of regular regimes will be described, during which the concentration profile remains geometrically similar or identical. Next, the regular regimes with constant surface concentration and constant surface flux are analyzed. These two types of boundary conditions are emphasized because of their relevance in drying calculations. Some other boundary conditions will be treated concisely.

III.2 Steady-state transport

Since the concentration m remains constant at any place, the concentration profile during the steady-state is described by the ordinary differential equation

$$\frac{d}{d\phi}\left(D_r X^2 \frac{dm}{d\phi}\right) = 0 \qquad \text{(III.2.1)}$$

with the boundary conditions

$$m = m_c \quad \text{at } \phi = 0 \qquad \text{(III.2.2)}$$

$$m = m_i \quad \text{at } \phi = 1 \qquad \text{(III.2.3)}$$

This yields upon integration (cfr. equation II.4.4):

$$D_r X^2 \frac{dm}{d\phi} = - F X_i \qquad \text{(III.2.4)}$$

For non-shrinking systems in general and for shrinking slabs the factor X^2 is independent of m. Integration of equation (III.2.4) then yields:

$$\int_{m_c}^{m_i} D_r \, dm = - F X_i \int_0^1 \frac{d\phi}{X^2} \qquad \text{(III.2.5)}$$

A concentration-averaged diffusion coefficient $\overline{D}_r$ is introduced by

$$\overline{D}_r = \frac{1}{m_i - m_c} \int_{m_c}^{m_i} D_r \, dm \qquad \text{(III.2.6)}$$

Substitution in equation (III.2.5) gives then

$$\overline{D}_r \, (m_i - m_c) = - F X_i \int_0^1 \frac{d\phi}{X^2} \qquad \text{(III.2.7)}$$

For the systems under consideration it follows, that the mass transfer rate can be calculated analogous to the constant-diffusivity case. The averaged diffusion coefficient $\overline{D}_r$ has then to be substituted as the effective value of the constant diffusion coefficient.

A mass transfer coefficient k'_d can be defined by

$$k'_d = \frac{n_{m,i}}{(m_c - m_i)} \qquad \text{(III.2.8a)}$$

and for non-shrinking systems by

$$k''_d = \frac{j^s_{m,i}}{(m_c - m_i)} \qquad \text{(III.2.8b)}$$

for shrinking systems. The values of mass transfer coefficients as a function of $\overline{D}_r$ are given in table III.2.1. for various geometries.

Geometry	mass transfer coefficient (k'_d or k''_d)
non-shrinking slab	$\overline{D}_r/R$
shrinking slab	$\overline{D}_r/R_s$
hollow cylinder (non shrinking)	$\overline{D}_r/\{R_i \ln (R_i/R_c)\}$
hollow sphere (non-shrinking)	$\overline{D}_r/\{R_i (R_i/R_c - 1)\}$

Table III.2.1. Mass transfer coefficients in stationary mass transfer with concentration dependent diffusion coefficient

III.3 Special kinds of regular regimes

III.3.1 General

For certain combinations of concentration dependence of the diffusion coefficient and boundary conditions separation of variables can be applied for the calculation of sorption rates and concentration profiles during the regular regime. This is the case when the shape of the concentration profile remains geometrically identical or similar during the sorption process and the system does not shrink or swell upon (de)sorption.

III.3.2 Geometrically identical profiles

If the concentration profile remains *geometrically identical* during the regular regime (see Fig.III.3.1), the concentration $m(\phi,\tau)$ can be written as

$$m(\phi,\tau) = g(\phi) + f(\tau) \qquad \text{(III.3.1)}$$

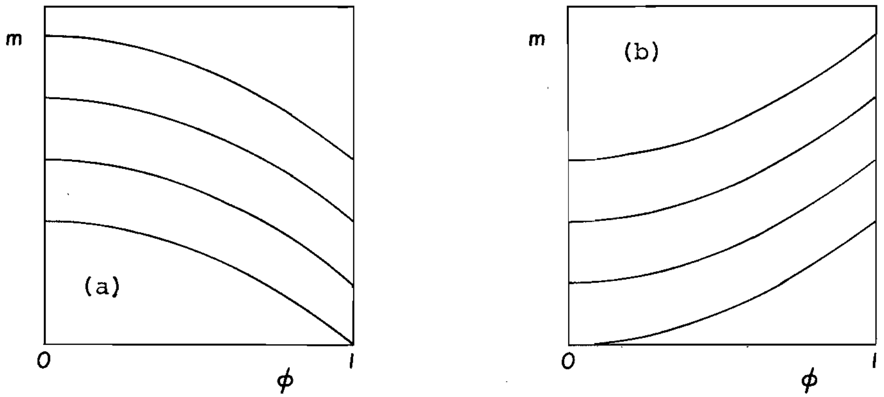


Fig.III.3.1. Geometrically identical profiles
(a) desorption (b) absorption

We assume that the function m is a solution to the diffusion equation with boundary conditions. Substitution of III.3.1 in the diffusion equation (II.4.1) yields:

$$\frac{\partial f}{\partial \tau} = \frac{\partial}{\partial \phi} (D_r X^2 \frac{\partial g}{\partial \phi}) \qquad \text{(III.3.2)}$$

For constant diffusion coefficient the right-hand side of the equation is independent of τ and, of course, the left hand side of the equation is independent of ϕ. Therefore, both sides have to be equal to a constant λ which is positive for sorption and negative for desorption.

$$\frac{df}{d\tau} = \frac{d}{d\phi} (D_r X^2 \frac{dg}{d\phi}) = \lambda \qquad \text{(III.3.3)}$$

It follows, that the concentration at any place in the system changes linearly with time and the value of the flux parameter is constant:

$$\frac{d\bar{m}}{d\tau} = \int_0^1 \frac{\partial f}{\partial \tau} d\phi = \lambda = - FX_i \qquad \text{(III.3.4)}$$

Therefore, equation III.3.1 can for constant diffusivity hold only when the surface flux is constant. The boundary conditions for the part of the equation which depends on ϕ read:

$$\phi = 0; \; X\frac{dg}{d\phi} = 0 \qquad \text{(III.3.5)}$$

$$\phi = 1; \; - D_r X_i \frac{dg}{d\phi} = F \qquad \text{(III.3.6)}$$

According to the line of reasoning of the previous paragraph, the regular solution is the solution of the inhomogeneous problem.

Substitution of $X = (\nu+1)\phi^{\frac{\nu}{\nu+1}}$ and $X_i = (\nu+1)$ and subsequent integration yields for the "basic" concentration profile g:

$$g - g_i = \frac{F}{2 D_r} \left\{ 1 - \phi^{\frac{2}{\nu+1}} \right\} \qquad \text{(III.3.7)}$$

For $\phi = 0$ it therefore holds, independently of the geometry, that

$$g_c - g_i = m_c - m_i = \frac{F}{2\ D_r} \qquad \text{(III.3.8)}$$

while for the average concentration it follows, that

$$\bar{m} - m_i = \bar{g} - g_i = \frac{F}{(3+\nu)D_r} \qquad \text{(III.3.9)}$$

so that the Sherwood number for the dispersed phase equals

$$Sh_d = \frac{2F}{(\bar{m} - m_i)D_r} = 6 + 2\nu \qquad \text{(III.3.10)}$$

The Sherwood numbers for slabs ($Sh_d = 6$), non-shrinking cylinders ($Sh_d = 8$) and non-shrinking spheres ($Sh_d = 10$) obtained in this way are, of course, equal to the limit values, calculated from the analytical solution of the diffusion equation with constant surface flux (Crank (1956)).

In case of a variable diffusion coefficient the above described separation of variables can not be used, unless the diffusion coefficient can be written as

$$D_r = g_1(\phi) \times f_1(\tau) \qquad \text{(III.3.11)}$$

In combination with equation (III.3.1) this implies, that the concentration dependence of the diffusion coefficient must be exponential:

$$D_r = \exp(am) = \exp\ (ag(\phi)) \times \exp\ (af(\tau)) \qquad \text{(III.3.12)}$$

where a is an arbitrary constant. Substitution in equation (III.3.2) yields:

$$\exp\ (-af)\ \frac{df}{d\tau} = \frac{d}{d\phi}\ (\exp\ (ag)\ X^2\ \frac{dg}{d\phi} = \lambda \qquad \text{(III.3.13)}$$

Also here there is only one type of boundary condition at $\phi = 1$ for which this separation of variables leads to a solution:

$$- D_r \, X^2 \, \frac{\partial m}{\partial \phi} = FX_i = - \frac{df}{d\tau} = -\lambda \, \exp(af) \qquad \text{(III.3.14)}$$

This condition does not seem of practical importance since the surface flux changes with surface concentration according to an exponential law with the same exponential coefficient as occurs in the concentration dependence of the diffusion coefficient. This follows also directly from the fact, that concentration gradients remain unchanged during the process, so that fluxes vary proportionally to the variation of the diffusion coefficient.

The boundary condition at $\phi = 0$ reads

$$X \, \frac{\partial m}{\partial \phi} = X \, \frac{dg}{d\phi} = 0 \qquad \text{(III.3.15)}$$

With the substitution of $X = (\nu+1)\phi^{\frac{\nu}{(\nu+1)}}$ the space dependent part of equation (III.3.12) becomes after integration:

$$\exp(ag) \, \frac{dg}{d\phi} = \frac{\lambda}{(\nu+1)^2} \cdot \phi^{\frac{1-\nu}{1+\nu}} \qquad \text{(III.3.16)}$$

Subsequent integration yields the "basic" concentration profile $g(\phi)$:

$$g(\phi) = \frac{1}{a} \, \ln \left\{ 1 - \frac{a\lambda}{2(\nu+1)} \left(1 - \phi^{\frac{2}{1+\nu}}\right) \right\} \qquad \text{(III.3.17)}$$

The value of g_i is here taken to be zero. The absolute level of $g(\phi)$ can be chosen arbitrarily because of the extra integration constant in the integration of the time-dependent part of equation (III.3.13). The average value of g is obtained by integration over ϕ between 0 and 1:

$$\bar{g} = \frac{2}{a(\nu+1)} \int_0^1 \frac{\phi^{\frac{2}{\nu+1}}}{1 - \frac{2(\nu+1)}{a\lambda} - \phi^{\frac{2}{\nu+1}}} \, d\phi \qquad \text{(III.3.18)}$$

Now we introduce an auxiliary parameter p for ease of notation

$$p = 1 - \frac{2(\nu+1)}{a\lambda} \qquad \text{(III.3.19)}$$

From equation (III.3.17) it follows that $p > 1$ or $p < 0$.

For *slabs* ($\nu=0$) the average concentration $\bar{g}$ reads:

$$p > 1: \; a\bar{g} = -2 + \sqrt{p}\,\ln\left\{\frac{\sqrt{p}+1}{\sqrt{p}-1}\right\} \qquad \text{(III.3.20a)}$$

$$p < 0: \; a\bar{g} = -2 + 2\sqrt{(-p)}\,\arctan\frac{1}{\sqrt{(-p)}} \qquad \text{(III.3.20b)}$$

for *cylinders* ($\nu=1$):

$$a\bar{g} = -1 + p\,\ln\left(\frac{p}{p-1}\right) \qquad \text{(III.3.21)}$$

and for *spheres* ($\nu=2$)

$$p > 1: \; a\bar{g} = -2p - \frac{2}{3} + p^{3/2}\,\ln\left\{\frac{\sqrt{p}+1}{\sqrt{p}-1}\right\} \qquad \text{(III.3.22a)}$$

$$p < 0: \; a\bar{g} = -\,2p - \frac{2}{3} - (-p)^{3/2}\,\arctan\frac{1}{\sqrt{(-p)}} \qquad \text{(III.3.22b)}$$

The driving force for mass transport inside the dispersed phase is equal to the average value $\bar{g}$ of $g(\phi)$ and is determined by the auxiliary parameter p only.

In analogy to steady-state mass transfer we introduce a concentration averaged reduced diffusion coefficient $\bar{D}_r$ by

$$\bar{D}_r = \frac{1}{(\bar{m} - m_i)} \int_{m_i}^{\bar{m}} D_r \, dm \qquad \text{(III.3.23)}$$

and use this value for the definition of a Sherwood number for the dispersed phase in case of a variable diffusion coefficient:

$$\overline{Sh}_d = \frac{2F}{(\bar{m} - m_i)\bar{D}_r} \qquad \text{(III.3.24)}$$

For constant diffusivity D the concentration averaged diffusivity is equal to this constant value and the Sherwood number is defined equal to equation (I.2.6). Substitution of (III.3.23), (III.3.12) and (III.3.14) in the relation for $\overline{Sh}_d$ yields, that

$$\overline{Sh}_d = \frac{4}{(p-1)\ \{\exp(a\bar{g})-1\}} \qquad \text{(III.3.25)}$$

It is concluded, that *the Sherwood number $\overline{Sh}_d$ remains constant during the sorption process if the shape of the concentration profile remains constant.*

p	SLAB		CYLINDER		SPHERE	
	$a\bar{g}$	$\overline{Sh}_d$	$a\bar{g}$	$\overline{Sh}_d$	$a\bar{g}$	$\overline{Sh}_d$
↓1	∞	7.389	∞	10.873	∞	14.392
1.002	5.610	7.349	5.229	10.775	4.954	14.210
1.02	3.361	7.190	3.011	10.364	2.762	13.490
1.0667	2.262	6.975	1.957	9.867	1.746	12.675
1.2	1.384	6.688	1.150	9.266	.994	11.753
1.667	.664	6.368	.527	8.645	.440	10.861
3	.281	6.163	.216	8.278	.176	10.364
21	.033	6.016	.025	8.033	.020	10.042
∞	0	6	0	8	0	10
- ∞	0	6	0	8	0	10
-10	- .063	5.962	- .047	7.937	- .037	9.919
- 3	- .186	5.886	- .137	7.813	- .108	9.763
- 1	- .429	5.731	- .307	7.569	- .237	9.462
- .5	- .649	5.586	- .451	7.350	- .342	9.202
- .2	- .971	5.365	- .642	7.039	- .472	8.853
- .1	-1.200	5.203	- .760	6.803	- .547	8.631
- .01	-1.706	4.893	- .954	6.442	- .650	8.290
↑0	-2	4.626	-1	6.328	- .6667	8.221

Table III.3.1: The Sherwood number $\overline{Sh}_d$ and the driving force $a\bar{g}$ in relation to the parameter p in the regular regime during which the shape of the concentraton profile remains identical ($D_r = \exp(am)$).

Table III.3.1 gives $\overline{Sh}_d$ and the driving force $\bar{g}$ in relation to the value of the auxiliary parameter p. For high values of $a(\bar{m} - m_i)$, which means that p approaches 1, the following limit values of $\overline{Sh}_d$ can be calculated by substitution of the equations (III.3.20 - 22) in (III.3.25) and taking the limit for $p \to 1$:

Slab: $$\lim_{a\bar{g}\to\infty} \overline{Sh}_d = \exp(2) \qquad \text{(III.3.26)}$$

Cylinder: $$\lim_{a\bar{g}\to\infty} \overline{Sh}_d = 4e \qquad \text{(III.3.27)}$$

Sphere: $$\lim_{a\bar{g}\to\infty} \overline{Sh}_d = \exp(8/3) \qquad \text{(III.3.28)}$$

III.3.3 Geometrically similar profiles

If the concentraton profile during the regular regime remains *geometrically similar* (see figure III.3.2), the concentration $m(\phi,\tau)$ can be written as

$$m(\phi,\tau) = f(\tau) \times g(\phi) \qquad \text{(III.3.29)}$$

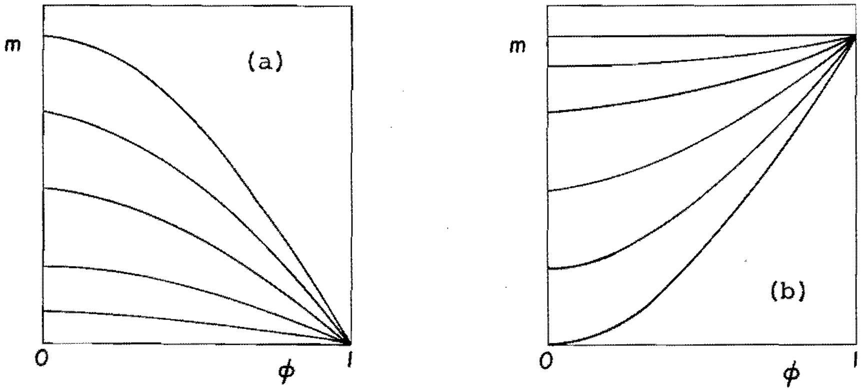


Fig.III.3.2. Geometrically similar profiles
(a) desorption (b) absorption

This formulation is less general than equation I.2.4, which does not lead to a separation of variables in case of variable diffusion coefficient. Again we assume, that $m(\phi,\tau)$ is a solution of the diffusion equation with boundary conditions. Substitution in this equation (II.4.1) yields:

$$\frac{1}{f}\frac{\partial f}{\partial \tau} = \frac{1}{g}\frac{\partial}{\partial \phi}\left(D_r X^2 \frac{\partial g}{\partial \phi}\right) \tag{III.3.30}$$

Separation of variables is possible only if D_r can also be written as the product of a function of τ and a function of ϕ:

$$D_r = f_1(\tau) \times g_1(\phi) \tag{III.3.31}$$

In combination with equation (III.3.29) this means, that the concentration dependence of the diffusion coefficient must be of the form

$$D_r = m^a = f^a \times g^a \tag{III.3.32}$$

After substitution in equation (III.3.30) we can write the diffusion equation as an eigen-value problem:

$$\frac{1}{f^{a+1}}\frac{df}{d\tau} = \frac{1}{g}\frac{d}{d\phi}\left(g^a X^2 \frac{dg}{d\phi}\right) = \lambda \tag{III.3.33}$$

This separation of variables only leads to a solution of the diffusion equation if the boundary conditions are homogeneous. The homogeneous condition (III.3.34a) applies at $\phi=0$.

$$\phi = 0; \quad X\frac{\partial m}{\partial \phi} = 0 \tag{III.3.34a}$$

At $\phi=1$ two types of boundary conditions can be used:

$$\phi = 1; \quad -D_r X \frac{\partial m}{\partial \phi} = F = \alpha m^{a+1} \tag{III.3.34b}$$

or

$$\phi = 1; \quad m_i = 0 \tag{III.3.34c}$$

where α is a constant

When the diffusion coefficient is constant, the above eigen-value problem is linear and has an infinite number of eigen-values. For the regular regime solution we are interested only in the smallest eigen-value: the regular regime is described by a single eigen-function. We assume, that only one eigen-value is involved in the regular regime solution, also in case of a variable diffusion coefficient. Since this assumption will be shown to lead to the same results as the numerical solution of the diffusion equation in the regular regime, this assumption appears to be justifiable.

If only one eigen-value is involved in the regular regime solution, the value of the flux parameter F can be expressed as

$$F = -\frac{1}{X_i}\ \frac{d\bar{m}}{d\tau} = -\frac{1}{X_i}\frac{df}{d\tau} \cdot \bar{g} = -\lambda\ f^{a+1}\ \bar{g} \qquad \text{(III.3.35)}$$

For the Sherwood number $\overline{Sh}_d$ it can be derived that

$$\overline{Sh}_d = \frac{2F}{(\bar{m} - m_i)\bar{D}_r} = -\frac{2\lambda\ \ f^{a+1}\ \bar{g}\ (a+1)}{X_i\,(\bar{m}^{a+1} - m_i^{\ a+1})} \qquad \text{(III.3.36)}$$

$$\overline{Sh}_d = -\frac{2(a+1)\ \lambda\ \bar{g}}{(\bar{g}^{a+1} - g_i^{\ a+1})} \qquad \text{(III.3.37)}$$

This $\overline{Sh}_d$ is determined by the constant a and the function $g(\phi)$ only: *$\overline{Sh}_d$ is also constant if the shape of the concentration profile remains geometrically similar during the regular regime.*

In order to fulfill boundary condition (III.3. 34b) the sorption isotherm has to show the form

$$m^* = m^{a+1} \qquad \text{(III.3.38)}$$

when the mass transfer coefficient and the bulk concentration in the continuous phase are constant. This corresponds with a Freundlich sorption isotherm. The solution for this type of boundary condition has not been worked out in this thesis.

In case of zero surface concentration ($m_i = g_i = 0$) the Sherwood number $\overline{Sh}_d$ and the concentration profile can be calculated in relation to the exponent a by solving the space-variable dependent part of equation (III.3.33):

$$\frac{d}{d\phi}\left(g^a \, \phi^{\overline{\nu+1}^{\,\nu}} \frac{dg}{d\phi} \right) = \frac{\lambda}{(\nu+1)} g \qquad \text{(III.3.39)}$$

We normalize this equation by introducing a "normalized" g

$$g' = g/g_c \qquad \text{(III.3.40)}$$

where g_c is the value of $g(\phi)$ at $\phi=0$.
Equation (III.3.39) goes over into

$$\frac{d}{d\phi}\left((g')^a \, \phi^{\overline{\nu+1}^{\,\nu}} \frac{dg'}{d\phi} \right) = -P.g' \qquad \text{(III.3.41)}$$

in which the auxiliary parameter P represents

$$P = \frac{-\lambda}{(\nu+1)\ g_c^a} \qquad \text{(III.3.42)}$$

The boundary conditions to equation (III.3.41) read

$$X \frac{dg'}{d\phi} = 0 \quad \text{at } \phi = 0 \qquad \text{(III.3.43)}$$

$$g' = 0 \quad \text{at } \phi = 1 \qquad \text{(III.3.44)}$$

In addition, there is an inhomogeneous boundary condition, given by the "norm"

$$g' = 1 \qquad \text{at } \phi = 0 \qquad \text{(III.3.45)}$$

This extra condition enables the calculation of the parameter P in the equation, the "normalized" concentration profile $g'(\phi)$ and the normalized average concentration $\bar{g}' = \bar{g}/g_c$. $\overline{Sh}_d$ can then be calculated from P and $\bar{g}'$ by application of

$$\overline{Sh}_d = \frac{2(a+1)(\nu+1)}{(\bar{g}')^a} \cdot P \qquad \text{(III.3.46)}$$

This relation follows from elimination of the eigen-value λ from equations (III.3.42) and (III.3.37)

The solution of equation (III.3.41) with boundary conditions is described in appendix A. The results of the calculations are presented in table III.3.2. It gives $\overline{Sh}_d$ and $\bar{g}'$ in relation to the exponent a in the concentration dependence of the diffusion coefficient ($D_r = m^a$).

a	SLAB		CYLINDER		SPHERE	
	$\overline{Sh}_d$	$\bar{g}/g_c$	$\overline{Sh}_d$	$\bar{g}/g_c$	$\overline{Sh}_d$	$\bar{g}/g_c$
-1	2	0				
-.99	2.1087	.0195				
-.9	2.6886	.1622				
-.8	3.1453	.2745	2.08	.036		
-.5	4.0671	.4754	3.975	.217	3.750	.088
0	4.9348	.6366	5.783	.432	6.580	.304
.5	5.4400	.7209	6.836	.557	8.207	.448
1	5.7720	.7731	7.528	.637	9.272	.545
1.5	6.0070	.8087	8.020	.693	10.027	.613
2	6.1823	.8346	8.390	.733	10.59	.663
2.5	6.3181	.8543	8.680	.764	11.03	.702
3	6.4264	.8698	8.91	.789	11.39	.733
3.5	6.5148	.8823	9.11	.809	11.68	.757
4	6.5883	.8927	9.29	.825	11.93	.778
4.5	6.6504	.9013	9.43	.839	12.15	.795
5	6.7035	.9087	9.55	.851	12.3	.811
6	6.7898	.9205	9.8	.869	12.6	.834
7	6.8567	.9296	9.9	.884	12.9	.853
8	6.9102	.9369	10.1	.895	13.0	.868
9	6.9540	.9428	10.2	.905	13.2	.880
10	6.9904	.9476	10.3	.912	13.3	.890
20	7.1720	.9718	10.7	.915	14.	.940
∞	7.3891	1	10.873	1	14.392	1

Table III.3.2. The Sherwood number $\overline{Sh}_d$ and the average "normalized" concentration $\bar{g}/g_c$ in relation to the exponent a. $D_r=m^a$; surface concentration $m_i=0$.

$\overline{Sh}_d$ is plotted in relation to the exponent a in figure III.3.3. It appears, that the intersection points of the three curves for slabs, cylinders and spheres fall so close together that they may be approximated by a single intersection point. At this point $\bar{g}'$ for slabs is approximately .5. $\overline{Sh}_d$ is approximately 4.2.

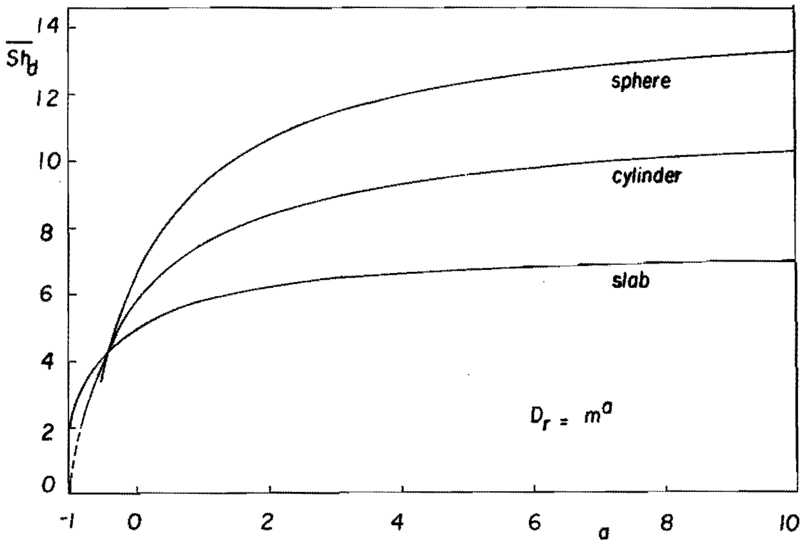


Fig.III.3.3. $\overline{Sh}_d$ in relation to the exponent a for the regular regime with $D_r=m^a$ and zero surface concentration (geometrically similar profiles)

It is interesting to note, that the limit value of $\overline{Sh}_d$ for high values of a (see appendix A) is equal to the limit values of $\overline{Sh}_d$ in case of geometrically identical profiles for high values of $a(\bar{m} - m_i)$ (section III.3.2).
These limit values are:

slab: $\overline{Sh}_d = \exp(2)$ (III.3.47)

cylinder: $\overline{Sh}_d = 4e$ (III.3.48)

sphere: $\overline{Sh}_d = \exp(8/3)$ (III.3.49)

Also the concentration profiles have then the same shape: the average concentration is equal to the concentration at the centre of the body and the profile very nearly approximates a rectangular shape.

III.4 Boundary condition of the first kind: constant surface concentration

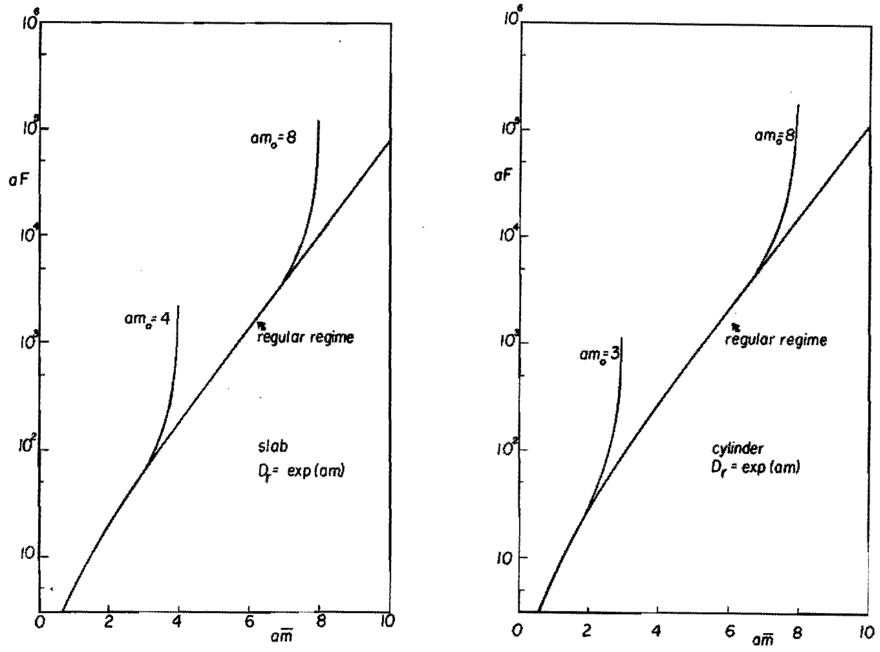
III.4.1 Non-shrinking systems and slabs: examples

The effect of the kind of concentration dependence of the diffusion coefficient on the sorption rate during the regular regime has been determined by solving the diffusion equation numerically for a number of diffusivity-concentration relations. First, the systems will be considered for which the variable X is independent of concentration: non-shrinking slabs, cylinders and spheres and shrinking slabs.

For *constant diffusion coefficient* and a *power-law concentration dependence* ($D_r = m^a$) the concentration profiles remain geometrically similar and a constant value of $\overline{Sh}_d$ is obtained upon entering the regular regime. These dependences are described in paragraph III.3.

The relation between the surface flux and the average concentration for an *exponential concentration dependence* ($D_r = \exp(am)$) is given in the figures III.4.1a-c. Parameter is the (homogeneous) initial concentration am_0. The common part of the curves with different initial concentration apparently is independent of this initial condition. and represents the regular regime. At moderate values of $a\bar{m}$ these regular regimes can be approximated by

slab: $$(a\bar{m} < 3) \quad F \simeq \frac{\pi^2}{4}(\bar{m} - m_i) \exp(.72\, a(\bar{m} - m_i)) \qquad \text{(III.4.1)}$$



(a) (b)

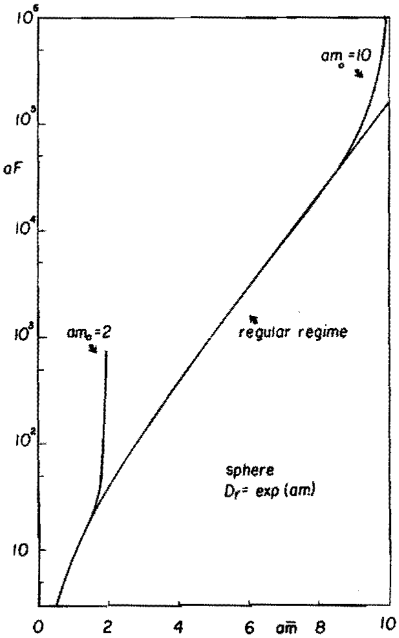


Fig. III.4.1 a-c

Relation between the flux parameter and the average concentration for an exponentially dependent diffusion coefficient. Desorption with zero surface concentration. Paramenter: am_0.

(a) Slab, (b) Cylinder, (c) Sphere

(c)

cylinder: $(a\bar{m} < 1) \quad F \simeq 2.89(\bar{m} - m_i)\exp(.77\, a(\bar{m} - m_i))$ (III.4.2)

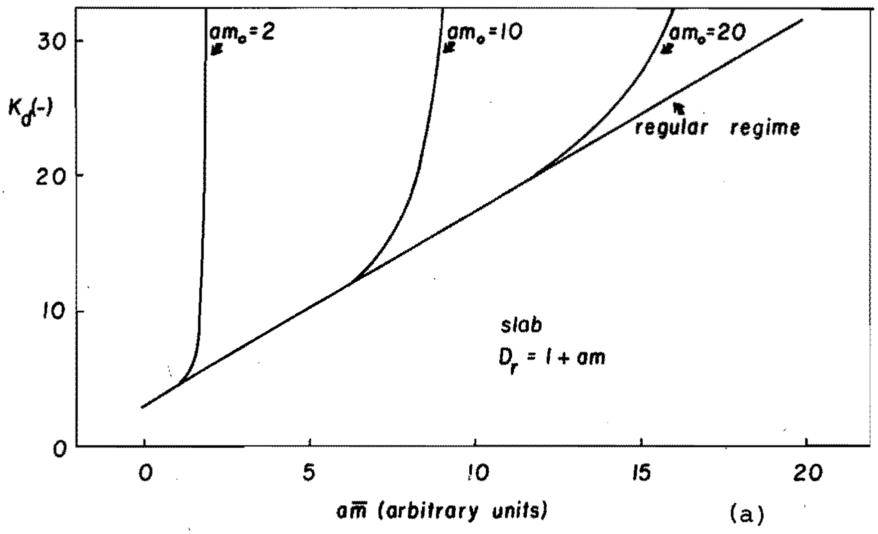
sphere: $(a\bar{m} < 1) \quad F \simeq \frac{2}{3}(\bar{m} - m_i)\exp(.95\, a(\bar{m} - m_i))$ (III.4.3)

$a(\bar{m}-m_i)$	$\overline{Sh}_d$ SLAB	$\overline{Sh}_d$ CYLINDER	$\overline{Sh}_d$ SPHERE
0	4.935	5.783	6.580
.5	5.48	6.94	8.54
1	5.88	7.87	9.92
1.5	6.23	8.60	11.02
2	6.52	9.18	11.89
2.5	6.75	9.64	12.56
3	6.9	10.00	13.07
4	7.1	10.44	13.74
5	7.3	10.67	14.09
6	7.35	10.81	14.26
∞	7.39	10.87	14.39

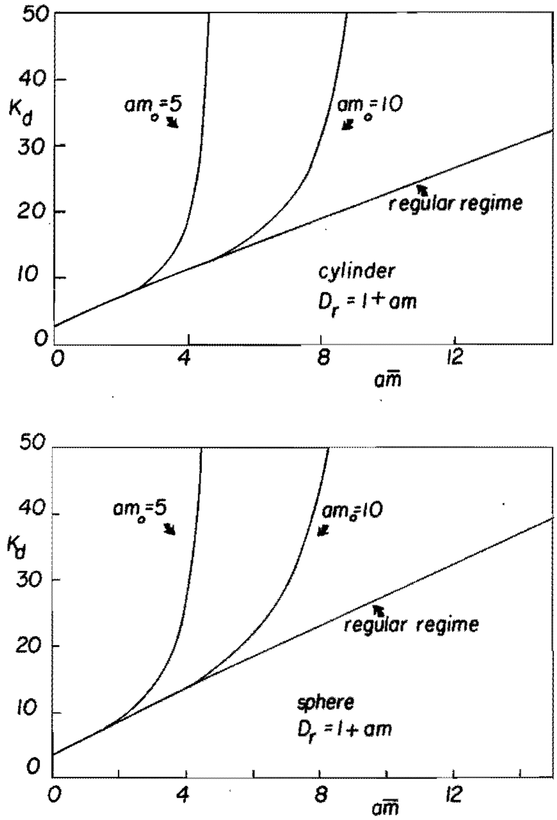
Table III.4.1. $\overline{Sh}_d$ in relation to $a(\bar{m} - m_i)$ for exponential concentration dependence of the diffusion coefficient ($D_r = \exp(am)$). Constant surface concentration.

Table III.4.1 shows the Sherwood number $\overline{Sh}_d$ during the regular regime as a function of the measure of the average concentration $a(\bar{m} - m_i)$. It appears, that for high values of $a(\bar{m} - m_i)$ a constant limit value of $\overline{Sh}_d$ is obtained. The occurrence of this constant Sherwood number can be shown analytically. This is derived in appendix B for slabs, cylinders and spheres. The limit value of $\overline{Sh}_d$ for these high values of $a(\bar{m} - m_i)$ appears to be equal to the limit for high values of $a(\bar{m} - m_i)$ in case of a regular regime with geometrically identical profiles or geometrically similar profiles (paragraph III.3). This is also shown in appendix B.

For *linearly dependent diffusion coefficients* ($D_r = 1 + am$) the sorption behaviour is given in terms of a dimensionless



(a)



(b)

Fig. III.4.2 a-c

The dimensionless mass transfer coefficient K_d in relation to the average concentration. Linear concentration dependence of the diffusion coefficient. Desorption with zero surface concentration. Parameter: am_0.

(a) Slab
(b) Cylinder
(c) Sphere

(c)

dispersed phase mass transfer coefficient K_d:

$$K_d = F/(\bar{m} - m_i) \tag{III.4.4}$$

The value of this coefficient in relation to $a\bar{m}$ is given in the figures III.4.2a-c for a number of initial concentrations. The common part of the curves represents again the regular regime. Only zero surface concentration is considered here, since any linear concentration dependence (also for different m_i) can be transformed into the form $D_r = 1 + am$, by adjusting the arbitrary constant D_0 or $D_0\ \rho^2_{s,0}$. For low values of $a\bar{m}$, ($a\bar{m} < 1$) the following relations hold by good approximation during the regular regime:

slab: $$F \simeq \frac{\pi^2}{4}\ \bar{m}\ (1 + .72\ a\bar{m}) \tag{III.4.5}$$

cylinder: $$F \simeq 2.89\ \bar{m}\ (1 + .77\ a\bar{m}) \tag{III.4.6}$$

sphere: $$F \simeq \frac{\pi^2}{3}\ \bar{m}\ (1 + .95\ a\bar{m}) \tag{III.4.7}$$

$a\bar{m}$	$\overline{Sh}_d$ SLAB	$\overline{Sh}_d$ CYLINDER	$\overline{Sh}_d$ SPHERE
0	4.935	5.783	6.580
.1	5.04	5.97	6.90
.2	5.12	6.17	7.21
.3	5.19	6.32	7.44
.4	5.24	6.44	7.62
.5	5.29	6.53	7.78
1	5.46	6.87	8.28
2	5.61	7.16	8.75
4	5.71	7.35	9.00
∞	5.772	7.51	9.20

Table III.4.2. $\overline{Sh}_d$ in relation to $a\bar{m}$ for linear concentration dependence of the diffusion coefficient ($D_r = 1 + am$). Zero surface concentration.

The change of $\overline{Sh}_d$ with the average concentration is given in table III.4.2. If $a\bar{m}$ is large (>5) the regular regime starts to approach the regular regime of $D_r = a\bar{m}$. The corresponding Sherwood numbers are 5.772 for slabs, 7.528 for cylinders and 9.272 for spheres. Hence, K_d is a linear function of the driving force for mass transfer $(\bar{m} - m_i)$.

A similar line of reasoning holds when D_r is a *polynomial function* of concentration: the term with the highest power of m dominates when the concentration is sufficiently high. The Sherwood number is approximately equal to $\overline{Sh}_d$ for a regular regime with $D_r = m^a$ (geometrically similar profiles). This line of reasoning can not strictly be extended to infinite polynomial series (e.g. Taylor series). It is encouraging however, that for strong exponential concentration dependences (an example of an infinite Taylor series) the limit of $\overline{Sh}_d$ is equal to the limit for the power function $D_r = m^a$ for high values of a.

The concentration dependent diffusion coefficient of *glucose in a shrinking coordinate system* $D.\rho_s^2$ at 30°C is given in figure III.4.3. The molecular diffusion coefficient is here assumed to depend exponentially on the mole fraction of glucose in the solution. Coefficients have been determined by Van der Lijn (1971) after measurements by Gladden and Dole (1953). The relation for D reads:

$$D = \exp\{-19.353 - 36.61(x_s+.147)\,\frac{(397-T)}{T}\} \quad [m^2/s] \tag{III.4.8}$$

where x_s is the mole fraction of glucose (total basis) and T the absolute temperature. The density of water is taken 1000 kg/m^3 and the partial density d_s of glucose is taken to be

$$d_s = 1613 - \frac{53}{1+\frac{\rho_w}{\rho_s}} \; [kg/m^3] \tag{III.4.9}$$

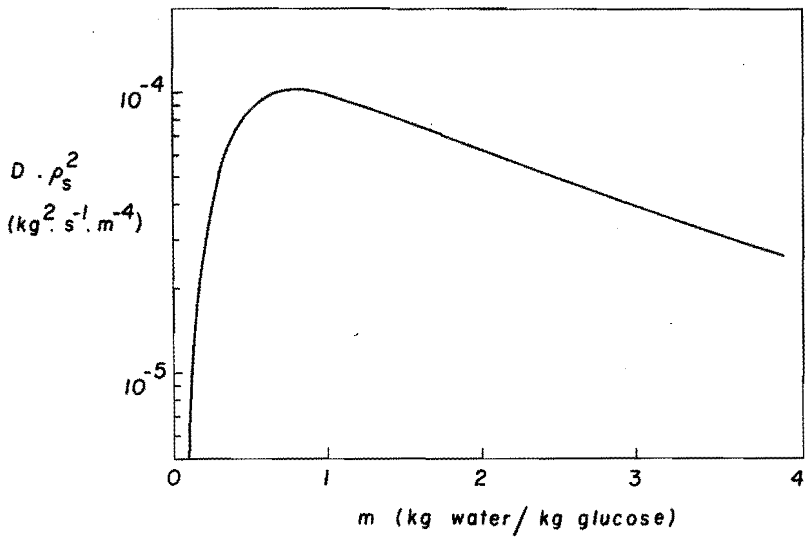


Fig.III.4.3. The diffusion coefficient of water in an aqueous glucose solution at 30°C: D x ρ_s^2 in relation to the water concentration ρ_m/ρ_s. Values of D after Gladden & Dole(1953).

This relation is an approximation to the results of density measurements by Pulvermacher (1920).
For a number of initial concentrations the dimensionless dispersed phase mass transfer coefficient during isothermal drying of slabs is given in figure III.4.4. The regular regime curve shows a maximum which is caused by the occurrence of a maximum in the relation between the diffusion coefficient D_r and the concentration.

III.4.2 Non-shrinking systems: generalization

In an attempt to describe the sorption rate of slabs, cylinders and spheres in case of a variable diffusion coefficient by a general relation, we introduced a concentration averaged diffusion coefficient $\bar{D}_r$ and a Sherwood number $\overline{Sh}_d$. However, this Sherwood number is determined by the concentration dependence of the diffusion coefficient and

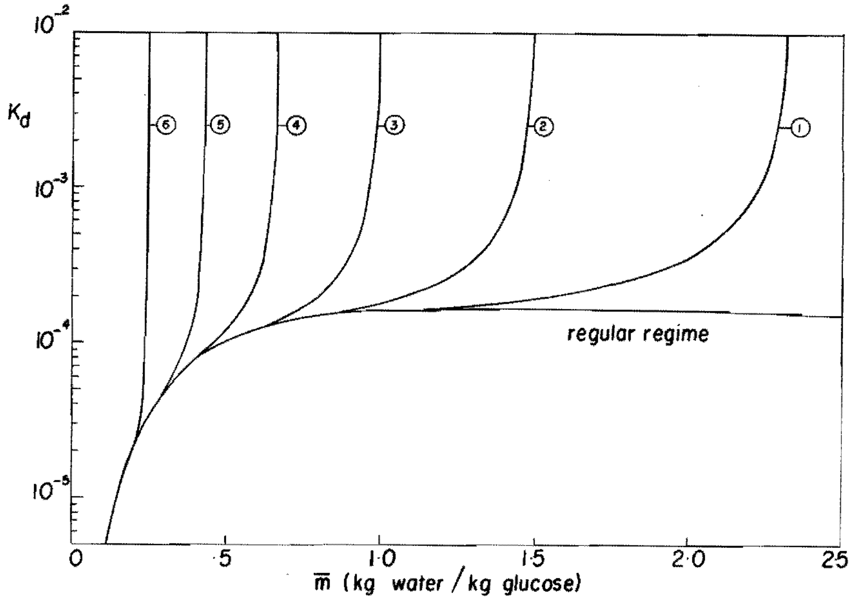


Fig.III.4.4. The dimensionless mass transfer coefficient in the dispersed phase $K_d = F/(\overline{m} - m_i)$ in relation to the average concentration $\overline{m} = \overline{\rho_m/\rho_s}$ during isothermal drying of slabs of an aqueous glucose solution at 30°C. Parameter is the initial water concentration m_0. Zero surface concentration ($m_i = 0$).

changes with time during the sorption process unless the shape of the concentration profile remains similar ($D_r = m^a$). Although a constant value of $\overline{Sh}_d$ might be taken for order of magnitude calculations, a further refinement of the general description is desired for more accurate calculations.

For an arbitrary concentration dependence of the diffusivity D_r we develop a criterion with which $\overline{Sh}_d$ can be correlated. Since $\overline{Sh}_d$ is constant for $D_r = m^a$, the criterion must have a one-one correspondence with the exponent a in this case. With this starting point two parameters have been

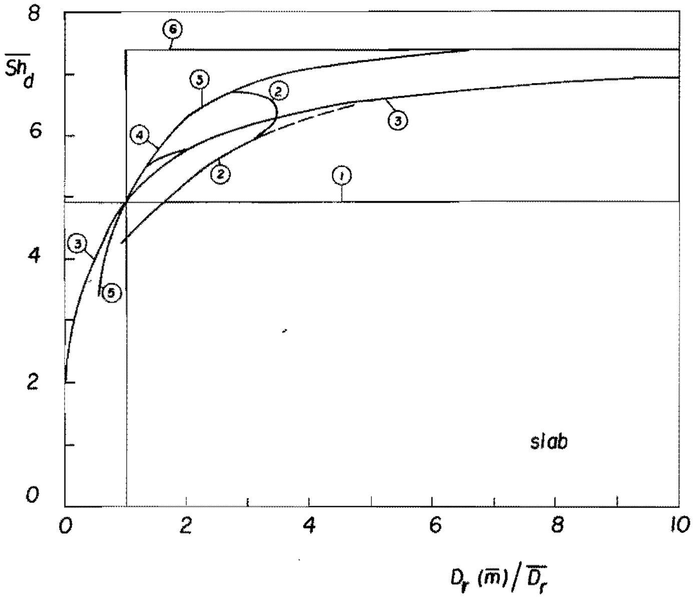


Fig.III.4.5a

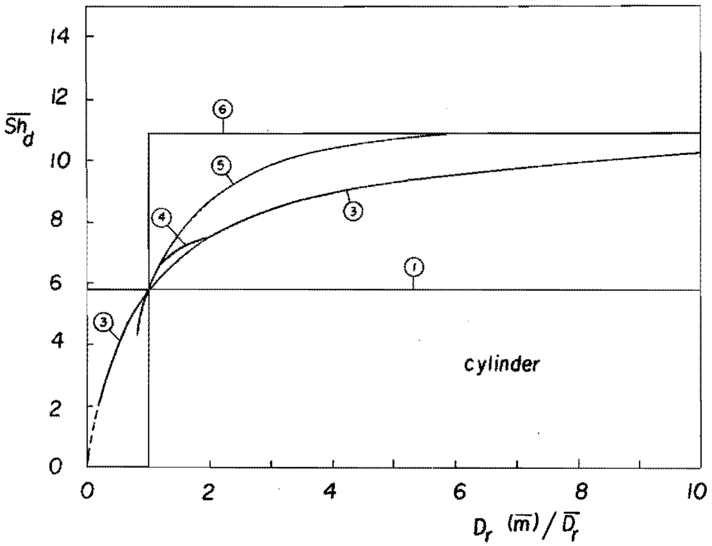


Fig.III.4.5b

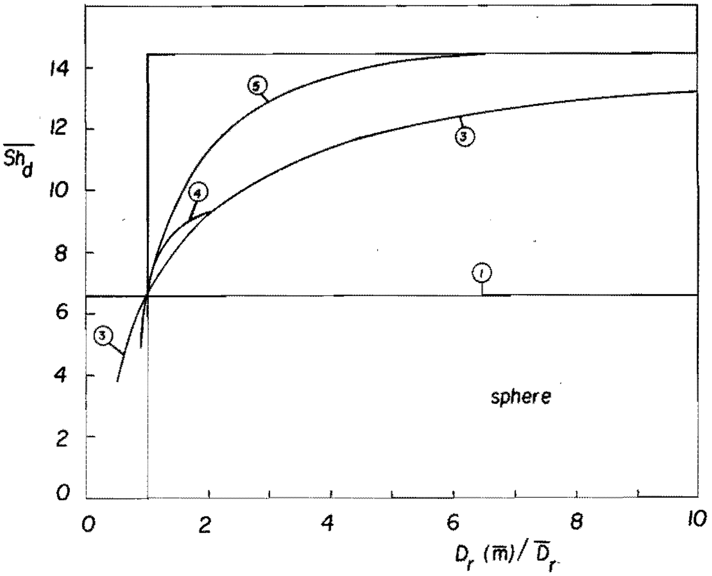


Fig.III.4.5c

Fig.III.4.5 a-c Relation between the Sherwood number $\overline{Sh}_d$ and the criterion $D_r(\bar{m})/\bar{D}_r$ for the regular regime with constant surface concentration

Concentration dependences:

(1) $D_r = 0$ for $m<m_d$; $D_r =$ constant for $m>m_d$

(2) water-glucose 30°C; shrinking coordinate system

(3) $D_r = (m - m_i)^a$

(4) $D_r = 1 + a(m - m_i)$

(5) $D_r = \exp\{a(m - m_i)\}$

(6) $D_r =$ constant for $m<\bar{m}$; $D_r \to \infty$ for $m>\bar{m}$

(a) slab

(b) non-shrinking cylinder

(c) non-shrinking sphere

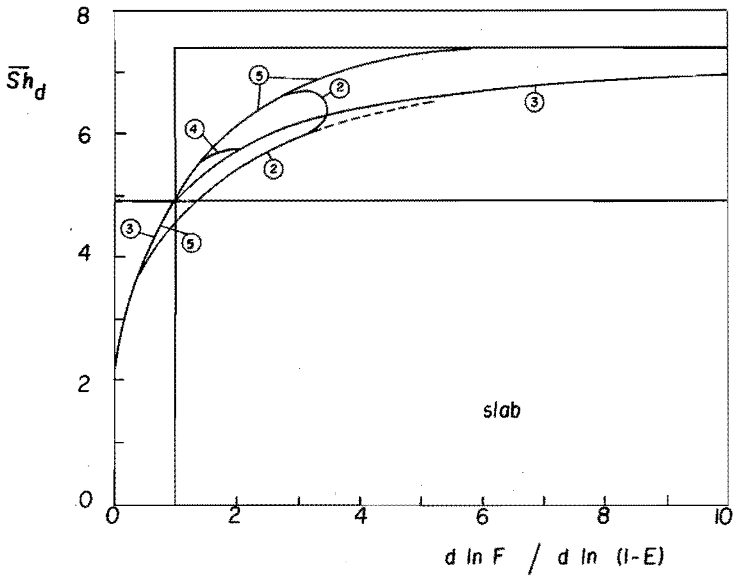


Fig.III.4.6a

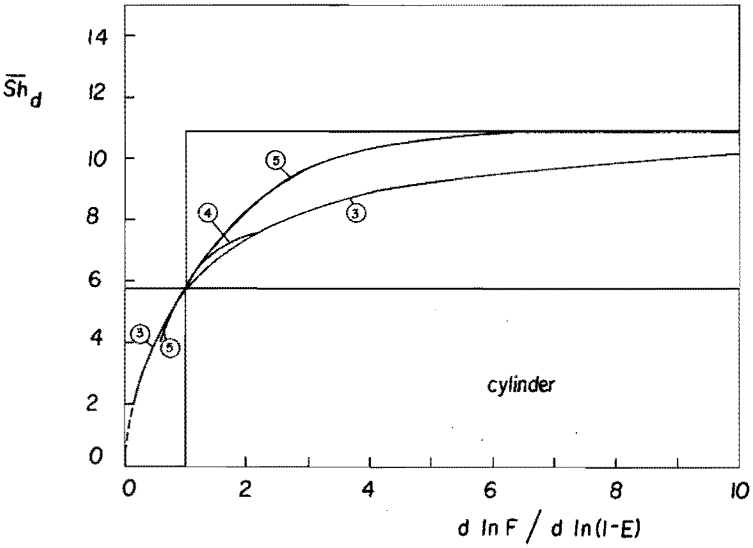


Fig.III.4.6b

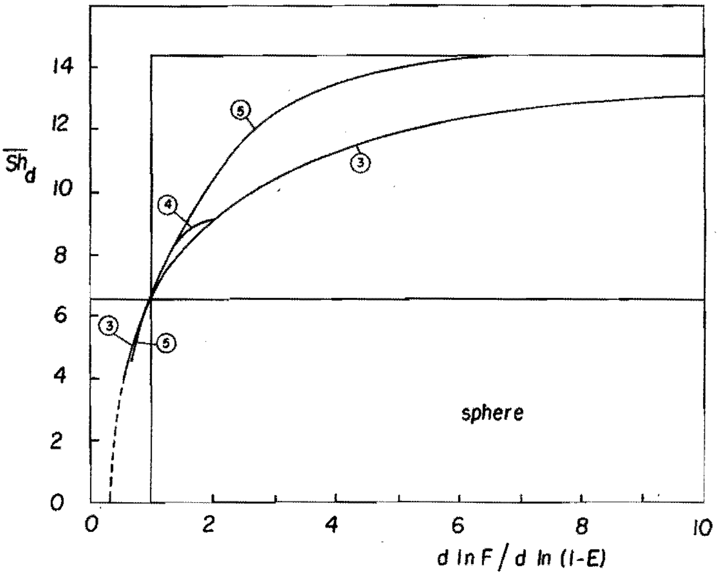


Fig.III.4.6c

Fig.III.4.6 a-c Relation between the Sherwood number $\overline{Sh}_d$ and the criterion d ln F/d ln(1-E) for the regular regime with constant surface concentration. Concentration dependences:

(1) $D_r = 0$ for $m<m_d$; $D_r =$ constant for $m>m_d$
(2) water-glucose 30°C; shrinking coordinate system
(3) $D_r = (m - m_i)^a$
(4) $D_r = 1 + a(m - m_i)$
(5) $D_r = \exp\{a(m - m_i)\}$
(6) $D_r =$ constant for $m<\bar{m}$; $D_r \to \infty$ for $m>\bar{m}$

(a) slab
(b) non-shrinking cylinder
(c) non-shrinking sphere

derived:

$D_r(\bar{m})/\bar{D}_r$: The value of the diffusion coefficient at the average concentration divided by the concentration averaged diffusion coefficient.

$d \ln F / d \ln (\bar{m}-m_i)$: The relative variation of the flux parameter F with the relative variation of the driving force $\bar{m} - m_i$.

For constant Sherwood number ($D_r = m^a$) the two criteria are equal and are related to the exponent a by

$$\frac{d \ln F}{d \ln (\bar{m} - m_i)} = \frac{D_r(\bar{m})}{\bar{D}_r} = a+1 \qquad \text{(III.4.10)}$$

Correlation of $\overline{Sh}_d$ with both of these parameters is of practical interest. The criterion $D_r(m)/\bar{D}_r$ may be used for sorption calculations when the diffusion coefficient is known as a function of concentration. The concentration dependence of the diffusion coefficient can be calculated from kinetic sorption measurements when the relation between $d \ln F / d \ln(\bar{m} - m_i)$ and $\overline{Sh}_d$ is known. In the figures III.4.5a-c and III.4.6a-c $\overline{Sh}_d$ is given as a function of both criteria for slabs, cylinders and spheres. The types of concentration dependence used in the desorption calculations are illustrated in figure III.4.7. In this figure, concentration dependences are compared at the same value of $D_r(\bar{m})/\bar{D}_r = 1.5$. Of all monotonous relations possible, two extremes are given by the functions 1 and 6. In case 1 the diffusion effectively takes place with constant diffusion coefficient and a surface concentration equal to the concentration where the diffusivity falls to zero (Crank (1956)). It can be derived that $\overline{Sh}_d = Sh_d$ for constant diffusion coefficient. The other extreme is the dependence nr. 6. When at $m>\bar{m}$ the relative variation of D_r with the concentration is large, this curve can be assumed to represent the end of a period where $\overline{Sh}_d$ has maximally been equal to the limits of $\overline{Sh}_d$ for strongly exponential

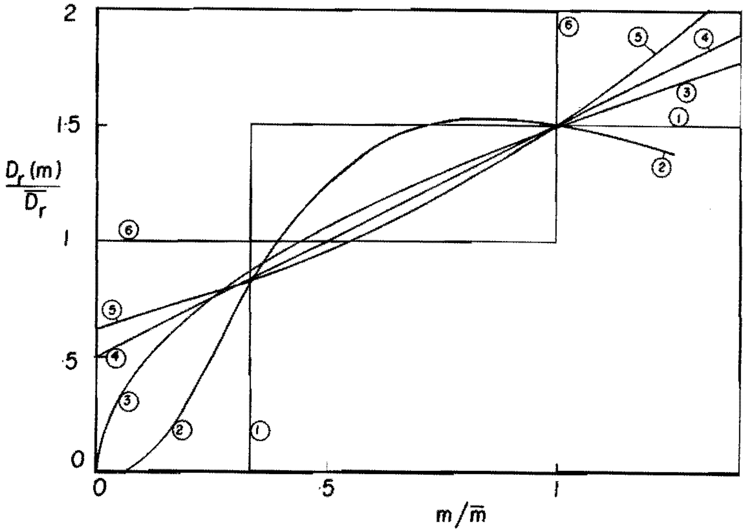


Fig.III.4.7. Concentration dependences used in the sorption calculations. Examples for $D_r(\bar{m})/\bar{D}_r = 1.5$

(1) $D_r = 0$ for $m<1/3$; $D_r = 1.5$ for $m>1/3$;

(2) water-glucose 30°C; shrinking coordinate system $\bar{m} = .955$ kg water/kg glucose

(3) $D_r = m^a$; $a = 0.5$

(4) $D_r = 1+am$; $a = 2$; $m_i = 0$; $\bar{m} = 1$

(5) $D_r = \exp(am)$; $a\bar{m} = .874$;

(6) $D_r = 1$ for $m<\bar{m}$; $D_r \rightarrow \infty$ for $m>\bar{m}$.

and power-dependences.
Between these extremes $\overline{Sh}_d$ increases with increasing number in figure III.4.7. In the part of the figures III.4.5a-c where $D_r(\bar{m})/\bar{D}_r$ is less than unity, the upper limit of $\overline{Sh}_d$ is equal to the Sherwood number in case of constant diffusivity.

Thus, we have stated the limits between which the relation between $\overline{Sh}_d$ and $D_r(\bar{m})/\bar{D}_r$ can be found for monotonous concentration dependences: the two rectangles in the figures III.4.5a-c. If the diffusion coefficient is a smooth function of concentration (linear, exponential, power) the relation between $\overline{Sh}_d$ and the two criteria introduced in this paragraph is not very dependent on the type of concentration dependence. Its position in the figures III.4.5 and III.4.6 can be specified further. When $D_r(\bar{m})/\bar{D}_r$ increases with progress of the sorption process, the relation lies below the relation for $D_r = m^a$. The opposite is found when $D_r(\bar{m})/\bar{D}_r$ decreases with progress of the sorption process. The same holds for changes of the parameter d ln F/d ln(1-E) with time. Good illustrations of this phenomenon are the curves for water-glucose in the figures III.4.5a and III.4.6a. At high water concentrations, $D_r(\bar{m})/\bar{D}_r$ and d ln F/d ln(1-E) increase with progress of drying. At low water concentrations the concentration dependence becomes approximately exponential and these parameters start to decrease with time: the relations between $\overline{Sh}_d$ and $D_r(\bar{m})/\bar{D}_r$ or d ln F/d ln(1-E) show a loop.

If the relation between diffusion coefficient and concentration is not monotonous (e.g. aqueous glucose solution) the Sherwood number as a function of $D(\bar{m})/\bar{D}_r$ may come beyond the limits for monotonous dependences. For smooth concentration dependences the deviations can however be expected to be small.

Also when the relation between the diffusion coefficient and concentration shows a considerable discontinuity, the relation between $\overline{Sh}_d$ and d ln F/d ln (1-E) or $D_r(\bar{m})/\bar{D}_r$ may deviate considerably from the general trend of the curves of figures III.4.5-6. Curve 6 in figure III.4.7 is an example of a concentration dependence where this will happen (in a desorption process). As long as the average concentration is higher than the concentration corresponding with the discontinuity (m_d), the desorption with zero surface concentration is identical to desorption with surface concentration m_d. Hence, when the average concentration $\bar{m}$ approaches m_d, the concentration profile becomes flat. At the moment when $\bar{m}$ passes m_d, the desorption starts in fact with a new, homogeneous "initial"-concentration, and can initially be described by the relations for the penetration period. Later, the process follows a second regular regime.

III.4.3 Shrinking or swelling systems

From the equations, derived in chapter II, it is clear, that the diffusion process in shrinking slabs can be described by simply transforming the diffusion equation to dissolved solids-coordinates. The diffusion coefficient then reads $D = D\,\rho_s^2$ and the concentrations are expressed in m^3 migrating component per m^3 dissolved solids (or kg/kg). The solution of the equation is then completely analogous to the solution of non-shrinking slabs.

For shrinking spheres and cylinders this transformation alone is not sufficient. The diffusion equation then reads *in reference component volume centered coordinates:*

$$\frac{\partial m}{\partial \tau} = \frac{\partial}{\partial \phi}\left[D_r\ (1+\nu)^2 \left\{\int_0^{\phi} (1+m)\,d\phi\right\}^{\frac{2\nu}{\nu+1}} \frac{\partial m}{\partial \phi}\right] \qquad \text{(III.4.11)}$$

This can also be written as

$$\frac{\partial m}{\partial \tau} = \frac{\partial}{\partial \phi}\left[D_r\ (1+\nu)^2\ \phi^{\frac{2\nu}{\nu+1}}\ (1+\bar{m}_\phi)^{\frac{2\nu}{\nu+1}} \cdot \frac{\partial m}{\partial \phi}\right] \qquad \text{(III.4.12)}$$

where $\bar{m}_\phi$ is the average concentration in the volume $0 < \phi < \phi'$:

$$\bar{m}_\phi = \frac{1}{\phi'} \int_0^{\phi'} m\,d\phi \qquad \text{(III.4.13)}$$

This representation of the diffusion equation shows, that the sorption process is faster than would be predicted from the diffusion equation for a "non-shrinking system" with the "shrinking variables" (D_r and m). The presence of the sorbent (migrating component) causes an increase in surface area through which the diffusion flux flows. This effect appears quadratic in the equation. The surface area is also involved (linearly) in the mass balance:

$$\frac{d\bar{m}}{d\tau} = -F\ (\nu+1)\ (1+\bar{m})^{\frac{\nu}{\nu+1}} \qquad \text{(III.4.14)}$$

From the results of many calculations it is concluded, that the Sherwood number for such a shrinking system can conveniently be expressed as:

$$\overline{Sh}_d = \overline{Sh}_{d,\text{non-shrinking}} + \Delta\overline{Sh}_d \qquad \text{(III.4.15)}$$

where $\overline{Sh}_{d,\text{non-shrinking}}$ represents the value of $\overline{Sh}_d$ of the non-shrinking body with diffusion coefficient and concentration expressed in the transformed variables. $\Delta\overline{Sh}_d$ is the effect of the increase in volume caused by the sorbent. Figures (III.4.8a-b) show $\Delta\overline{Sh}_d$ in relation to the average concentration $\bar{m}$ for a few concentration dependences (spheres and cylinders). From the results of many calculations it follows, that this absolute contribution to the Sherwood number is hardly dependent on the kind of concentration dependence of this diffusion coefficient. The average concentration $\bar{m}$ (m^3 migrating component/m^3 solute) appears to be the factor which mainly determines $\Delta\overline{Sh}_d$. For strongly concentration dependent diffusion coefficients ($D_r(\bar{m})/\bar{D}_r >> 1$) the limit value of $\overline{Sh}_d$ for non-shrinking systems is 10.87 and 14.39 for cylinders and spheres respectively. In this limit the concentration profile is rectangular, so that $\Delta\overline{Sh}_d$ can be calculated analytically. Since the surface area effect is linearly accounted for in the mass balance (equation III.4.14), the diffusion coefficient is effectively increased by a factor $(1+\bar{m})^{\nu/(\nu+1)}$ (cfr.equation III. 4.12). The expressions for $\Delta\overline{Sh}_d$ then read:

cylinder $$\Delta\overline{Sh}_d = 10.87\ \{(1+\bar{m})^{1/2} - 1\} \qquad \text{(III.4.16)}$$

sphere $$\Delta\overline{Sh}_d = 14.39\ \{(1+\bar{m})^{2/3} - 1\} \qquad \text{(III.4.17)}$$

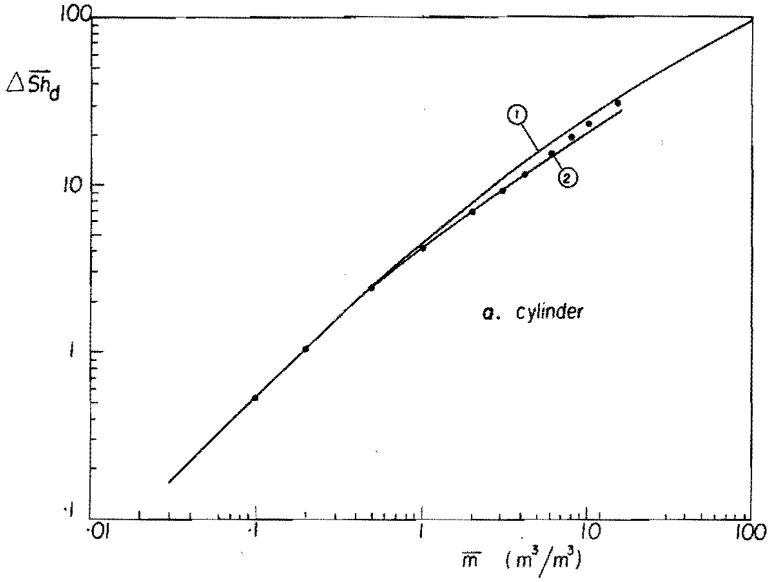
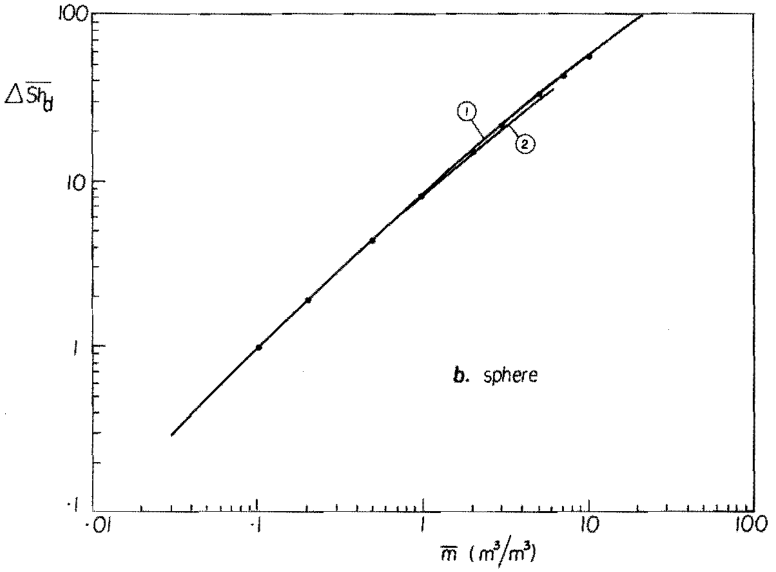


Fig.III.4.8 a-b Absolute effect of shrinkage or swelling on $\overline{Sh}_d$, $\Delta\overline{Sh}_d$, in relation to the volume fraction sorbent (m^3 sorbent/m^3 sorbate)

(1) limit for $D_r(\overline{m}) >> \overline{D}_r$

(2) constant diffusivity D_r

● $D_r = \exp(m)$



From the results of numerical calculations it appears, that $\Delta\overline{Sh}_d$ is equal for constant and strongly variable diffusion coefficient within numerical accuracy if $\bar{m} < .5$ (m^3/m^3). At higher concentrations a certain deviation is observed. However, these deviations are so small, that the logarithmic average between $\Delta\overline{Sh}_d$ for constant diffusivity and for strong concentration dependence appears to be a good approximation for dependences with $D_r(\bar{m})/\bar{D}_r > 1$. The maximum error in $\overline{Sh}_d$, caused by this approximation is given in table III.4.3. This table also gives the relative amount to which $\overline{Sh}_d$, obtained with the equations III.4.16 or 17, is to be lowered to come to the logarithmic averaged relation.

Table III.4.3 Relative error in $\overline{Sh}_d$ for constant D_r and strong concentration dependence if calculated from the logarithmic averaged $\Delta\overline{Sh}_d$.

$\bar{m}$	rel.error CYLINDER	rel.error SPHERE
.5	1 %	-
1	1.5%	1.5%
1.5	3 %	3 %
2	4 %	4 %
3	5 %	4 %
4	7 %	4 %
6	9 %	
8	9 %	
10	9 %	
15	10 %	

Also when the diffusion process is described in reference component mass centered coordinates $\Delta\overline{Sh}_d$ *can be read directly from the figures presented here if only the average concentration* $\bar{m}$ *on the coordinate is expressed as a volume fraction* (m^3 *migrating component*/m^3 *solute*). This is allowed only if the partial densities of the two components are (by good approximation) constant.

III.5 Boundary condition of the second kind: Constant surface flux

The water vapor sorption isotherm of many aqueous systems is generally such that the water activity does not differ much from unity above a certain critical moisture content m_{cr}. As long as the surface concentration is higher than this critical value during the air drying of such a system, the water concentration in the gas phase at the phase boundary is approximately constant and the drying rate is determined by gas phase mass transfer.

When the gas phase mass transfer coefficient and the water vapor concentration in the air are constant, a constant drying rate results: "constant rate period".

The mass transfer coefficient in the continuous phase is related to the body size for spheres and cylinders (Ranz & Marshall (1952), Bird et.al. (1960)). At low air velocities (low values of the Reynolds number) this relation is given by a constant value of the Sherwood number for the continuous phase: Sh_c. It follows, that the gas phase mass transfer coefficient k_c is inversely proportional to the radius of the sphere or cylinder if the air flow conditions are constant:

$$k_c = \frac{Sh_c \, D_c}{R} \tag{III.5.1}$$

where D_c is the binary diffusion coefficient of water in the continuous phase (air). Hence, the surface flux of water in shrinking systems increases with decreasing average concentration when the air humidity is constant:

$$F(1+\bar{m})^{\frac{1}{\nu+1}} = \text{constant} \tag{III.5.2}$$

where $\bar{m}$ is the average volume fraction water (m^3/m^3) The term "constant rate period" is therefore confusing when applied to shrinking systems or drying processes with variable air flow conditions or humidity. "Constant activity period" might be a better alternative.

Because of the relevance for the calculation of drying processes some attention is paid here to the regular regime with constant surface activity and constant Sh_c. Of particular interest is the length of the constant activity period for the calculation of drying times and for the calculation of the retention of volatile trace components (aroma compounds) in drying food liquids. For the latter purpose a rough estimate of $\overline{Sh}_d$ in the regular regime is sufficient, since the volatile components have already evaporated to a large extent when the regular regime is reached. Kerkhof (1975) showed, that even the assumption of a flat water concentration profile in the regular regime ($\overline{Sh}_d = 0$) gives good results in the prediction of aroma retention. With respect to the calculation of drying times it is interesting to determine the relation between $\overline{Sh}_d$ at the end of the constant activity period ("critical point") and the value of $\overline{Sh}_d$ for sorption with constant surface concentration. This, because the constant activity period is followed by a "falling rate period", during which the surface concentration can often be taken constant although it still changes with time in reality (see paragraph III.6.2 and chapter V).

The Sherwood number $\overline{Sh}_{d,CRP}$ during the constant rate period (F = constant) is independent of F and is given in figure III.5.1 relative to $\overline{Sh}_{d,CSC}$, the Sherwood number for constant surface concentration. The ratio of both Sherwood numbers is given in relation to $D_r(\overline{m})/\overline{D}_r$ at the same average and surface concentrations. Obviously, $\overline{Sh}_{d,CRP}$ is higher than $\overline{Sh}_{d,CSC}$. The relation between both Sherwood numbers appears to be hardly dependent on the kind of concentration dependence of the diffusion coefficient.

In shrinking spheres and cylinders the ratio $\overline{Sh}_{d,CRP}$ / $\overline{Sh}_{d,CSC}$ can be expected to be higher than for non-shrinking systems, because the surface flux increases with progress of drying during the constant activity period.

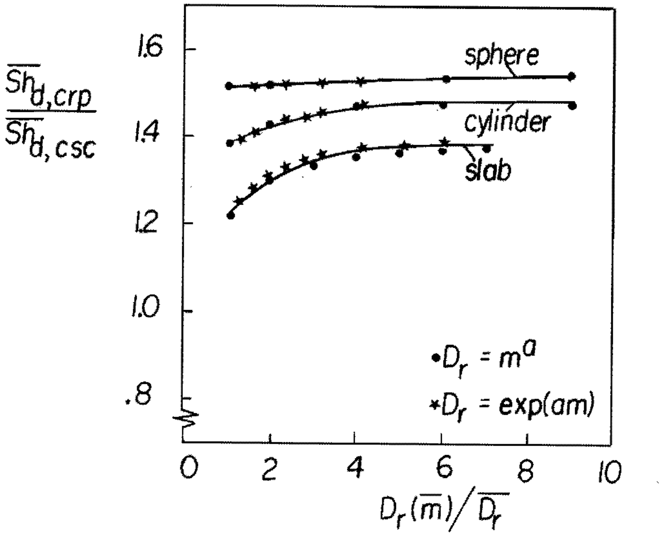


Fig. III.5.1 The ratio between the Sherwood number for the constant rate period $\overline{Sh}_{d,CRP}$ and the Sherwood number for constant surface concentration $\overline{Sh}_{d,CSC}$ at the same average and surface concentration versus $D_r(\overline{m})/\overline{D}_r$. Concentration dependences: $D_r = m^a$; $m_i = 0$ and $D_r = \exp(am)$. Slabs, non-shrinking cylinders and spheres.

The idealized description of the constant activity period by constant Sh_c and in particular by constant air humidity is never encountered in practice, however. The increase in air humidity will cause a decrease of the drying rate. Hence, *the Sherwood number in the dispersed phase during the constant activity period will in practice be close to the Sherwood number for constant surface concentration.* We will use this observation in a short cut method for the calculation of drying rates (chapter V).

III.6 Other boundary conditions

III.6.1 Constant D_r, Bi_m and equilibrium concentration

For the case of constant diffusion coefficient, constant equilibrium concentration and constant external mass transfer coefficient Luikov (1968) describes the sorption rate for slabs, non-shrinking cylinders and non-shrinking spheres. In the regular regime the concentration profile remains geometrically similar and it holds, that

$$\frac{dm}{d\tau} = - \mu_1^2 \, (\bar{m}-m^*) \qquad \text{(III.6.1)}$$

where μ_1 is the first (smallest) root of the characteristic equation

$$\cot \mu = \frac{\mu}{Bi} \qquad \text{(slab)} \qquad \text{(III.6.2a)}$$

or

$$\frac{J_0(\mu)}{J_1(\mu)} = \frac{\mu}{Bi} \qquad \text{(cylinder)} \qquad \text{(III.6.2b)}$$

or

$$\tan \mu = \frac{-\mu}{Bi-1} \qquad \text{(sphere)} \qquad \text{(III.6.2c)}$$

Here $J_0(\mu)$ and $J_1(\mu)$ are the zero-th and first order Besselfunctions of the first kind.
Sh_d can then be calculated by (Thijssen et.al. (1973)):

$$\frac{2}{Sh_d} = \frac{1}{\mu_1^2} - \frac{1}{Bi_m} \qquad \text{(III.6.3)}$$

Table III.6.1 shows the Sherwood numbers for the dispersed phase calculated from Luikov's data using equation (III.6.3). The Sherwood number varies between the values for the regular regime with constant surface concentration and the regular regime with constant surface flux.

Table III.6.1 Sh_d for constant diffusion coefficient, constant mass transfer Biot-number and constant equilibrium concentration

Bi_m	$2\mu_1^2$ SLAB	Sh_d SLAB	$2\mu_1^2$ non-shrinking CYLINDER	Sh_d non-shrinking CYLINDER	$2\mu_1^2$ non-shrinking SPHERE	Sh_d non-shrinking SPHERE
0	0	6	0	8	0	10
.02	.03976		.03980		.03985	
.04	.07896		.07919		.07935	
.1	.1936		.1951		.1961	
.4	.7038	5.9	.7252	7.8	.7389	9.7
.8	1.251	5.74	1.320	7.54	1.367	9.39
1	1.480	5.69	1.577	7.46	1.645	9.27
2	2.319	5.52	2.558	7.10	2.744	8.74
4	3.198	5.33	3.641	6.68	4.020	8.08
10	4.084	5.13			5.363	7.33
∞	4.935	4.935	5.783	5.783	6.580	6.580

III.6.2 Influence of surface concentration on the sorption rate if the diffusion coefficient becomes very small at concentrations close to the equilibrium concentration

For many systems (e.g. aqueous carbohydrate solutions) the diffusion coefficient decreases strongly with decreasing concentration of the migrating component. As an extreme, we take for instance the desorption with a diffusion coefficient, which is zero in the concentration range $0 < m < m_d$ and is a function of m at $m > m_d$ (e.g. concentration dependence nr. 1 in figure III.4.7). Then, the concentration gradient at the phase boundary is infinite if the surface concentration $m_i < m_d$. Effectively, the diffusion process is equal to sorption with surface concentration m_d: *A change of the surface concentration below a certain value* m_d *has no influence on the desorption rate if the diffusion coefficient is effectively zero at concentrations lower than* m_d.

The criteria which have been introduced in paragraph III.3 and have been correlated with $\overline{Sh}_d$, can be modified to account for the above observation. The diffusivity ratio can then for surface concentrations $m_i < m_d$ be defined as

$$\frac{D_r(\bar{m})}{\frac{1}{\bar{m}-m_d} \int_{m_d}^{\bar{m}} D_r \, dm} \quad \text{instead of} \quad \frac{D_r(\bar{m})}{\bar{D}_r}$$

and the relative variation of the flux with concentration

$$\frac{d \ln F}{d \ln (\bar{m}-m_d)} \quad \text{instead of} \quad \frac{d \ln F}{d \ln (\bar{m}-m_i)}$$

These parameters are not dependent on the surface concentration m_i if $m_i < m_d$. It indicates, that $\overline{Sh}_d$ does not change with m_i in this interval.

In practice, the diffusion coefficient may be low, but will not be zero at low concentrations (e.g. diffusion of water in aqueous glucose solutions). In order to quantify the influence of surface concentration on the surface flux the parameter F is written as:

$$F = \frac{1}{2} \overline{Sh}_d \int_{m_i}^{\bar{m}} D_r \, dm \qquad \text{(III.6.4)}$$

This can also be formulated as

$$F = \left\{ 1 - \frac{\int_0^{m_i} D_r \, dm}{\int_0^{\bar{m}} D_r \, dm} \right\} \frac{1}{2} \overline{Sh}_d \int_0^{\bar{m}} D_r \, dm \qquad \text{(III.6.5)}$$

Two effects of m_i on F can now be distinguished:

1. The influence on $\overline{Sh}_d$. The Sherwood number does not change with m_i if D_r is effectively zero. If the diffusivity is relatively low, the variation of Sh_d with m_i will also be small. The Sherwood number does not change

very much with $D_r(\bar{m})/\bar{D}_r$ and the variation of this parameter is maximum proportional to the change in $\bar{m}-m_i$.

2. The influence on $\int_{m_i}^{\bar{m}} D_r\, dm$. If D_r is relatively low at low concentrations the contribution of $\int_0^{m_i} D_r\, dm$ contributes little to the total integral. Figure III.6.1 shows the influence of m_i on the integral $\int_{m_i}^{\bar{m}} D_r\, dm$ for glucose in a shrinking coordinate system (at 30°C) for various surface concentrations m_i and various average concentrations $\bar{m}$. In the same figure the sorption isotherm of glucose is plotted (surface relative humidity versus surface concentration). It appears, that the relative effect of m_i on $\int_{m_i}^{\bar{m}} D_r\, dm$ is less than 5% when at an average concentration of $\bar{m}$ = .5 kg water /kg glucose the surface concentration does not exceed .15 kg/kg. This corresponds to a water activity at the surface of about 50%. Only if the average concentration becomes very close to the surface (equilibrium) concentration the relative influence becomes considerable.

It can be concluded, that up to high surface activities the drying of a glucose solution can by good approximation be described as if the surface concentration were zero, unless the average concentration approaches the surface concentration closely. Since of all carbohydrates the diffusion coefficient of glucose shows one of the weakest concentration dependences, the above observation is also (even more) valid for many other carbohydrate solutions.

If the surface concentration m_i deviates from the equilibrium concentration due to a limited mass transfer coefficient in the gas phase, the above line of reasoning still applies. It is even reinforced by the increase of the Sherwood number due to the decrease in surface concentration (cfr. paragraph III.6.1).

A practical consequence of these observations is, that the drying of for instance liquid foods with high relative air humidity (up to 60%) does not result in significantly lower drying rates than drying with completely dry air. Only at concentrations near the equilibrium, the air humidity becomes of considerable importance. The length of the constant rate period is however markedly increased by a high air humidity. Thus, a high air humidity has a detremental effect on aroma retention in drying aroma containing food liquids. Also this aspect therefore pleads for multiple stage drying processes for such systems (cfr. Kerkhof (1975)).

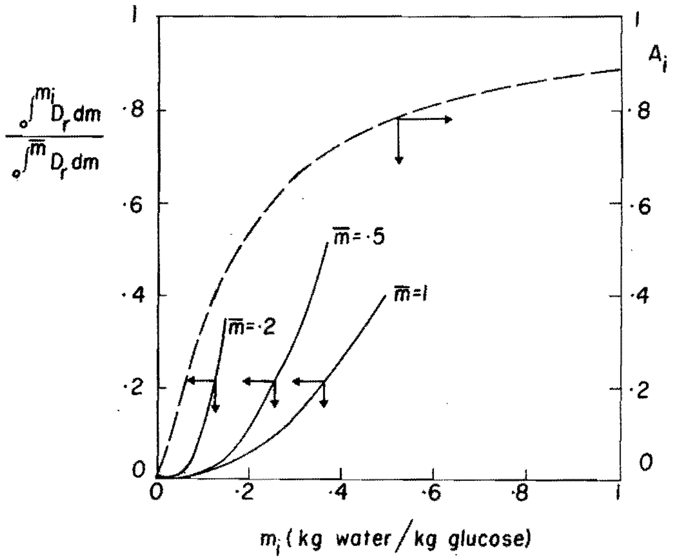


Fig. III.6.1 Relative contribution of $\int_0^{m_i} D_r\, dm$ to $\int_0^{\bar{m}} D_r\, dm$ as a function of the surface water concentration m_i. Parameter: the average water concentration $\bar{m}$. System: water-glucose at 30 °C in shrinking coordinates. The broken line represents the water vapor sorption isotherm of glucose at 30 °C. (Hinskens (1974)).

III.7 Influence of geometry

For some applications it would be convenient to have the possibility to calculate for instance the sorption rate of a sphere or cylinder from the (known) sorption rate of a slab. Such a possibility can be found in the relation between the Sherwood numbers $\overline{Sh}_d$ of the various geometries during the regular regime for equal average and surface concentration. These relations appear for non-shrinking systems to be practically independent of the concentration dependence of the diffusion coefficient and the kind of boundary condition (constant surface concentration, constant surface flux or constant Biot-number with constant diffusivity). Figure III.7.1 shows the relations between the Sherwood numbers for the three geometries.

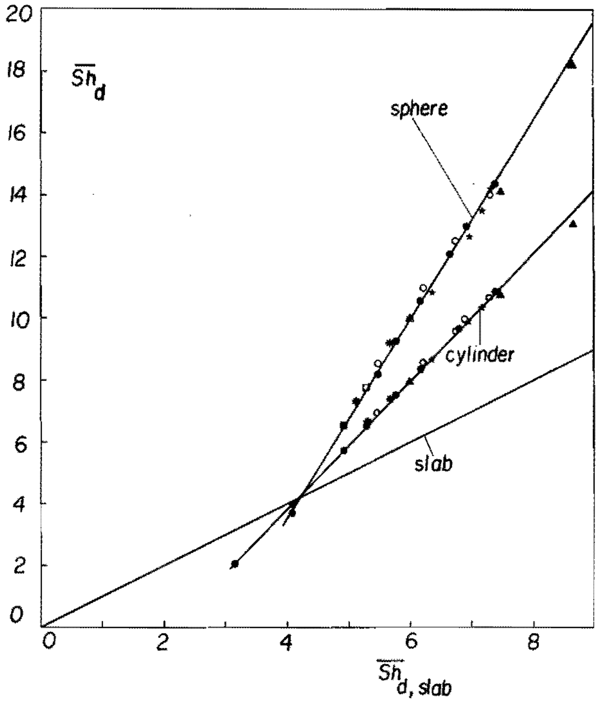


Fig. III.7.1 Relation between the Sherwood number Sh_d of slabs, non-shrinking cylinders and spheres and Sh_d for slabs at the same average and surface concentration.

● $D_r = m^a$; $m_i = 0$

✱ $D_r = 1$; Bi=constant; m^*=constant

✶ $D_r = \exp(am)$; $m_i = 0$

□ $D_r = 1 + am$; $m_i = 0$

○ $D_r = \exp(am)$; geometrically similar profiles; $(p>0)$

▲ $D_r = m^a$; F=constant

A good analytical representation is the equation describing the straight line between two analytically calculated limit values of $\overline{Sh}_d$: for constant diffusivity and $D_r = m^a$, $a \rightarrow \infty$, both with constant surface concentration

$$\overline{Sh}_{d,sphere} = 3.18\ \overline{Sh}_{d,slab} - 9.13 \qquad (III.7.1)$$

$$\overline{Sh}_{d,cylinder} = 2.07\ \overline{Sh}_{d,slab} - 4.45 \qquad (III.7.2)$$

$$\overline{Sh}_{d,sphere} = 1.54\ \overline{Sh}_{d,cylinder} - 2.30 \qquad (III.7.3)$$

For shrinking or swelling systems the same expressions can be applied to the "non-shrinking part" of the Sherwood number (equation III.4.15). $\overline{Sh}_d$ is then obtained by adding the appropriate $\Delta\overline{Sh}_d$, which can be calculated with the equation (III.4.16 or 17).

III.8 Onset and occurrence of regular regimes

"The sorption rate becomes -after a certain induction period- independent of initial condition". Without any specification of the length of this induction period this statement is not very relevant. Therefore, it is necessary to analyze the factors determining the length of this induction period.

In general, it can be stated, that the induction period is shorter, the more closely the initial concentration profile resembles the profile belonging to the regular regime. Starting from a flat concentration profile, the approximately rectangular profile belonging to highly concentration dependent diffusion coefficients (decreasing D_r with de-(in)creasing concentration in de(ab)sorption will be reached after a relatively shorter period than the cosine profile belonging to a constant diffusion coefficient. The induction period with flat initial concentration profile is subject of chapter IV.

Although the majority of sorption processes start with a flat initial profile, a sudden change in boundary conditions may cause a transition from one type of regular regime to another. An important example is the transition from the "constant rate period" to the "falling rate period" in a drying process. If D_r is constant this implies a change of a parabolic profile to a cosine-profile. These profiles are so close to each other, that the transition takes place in a very short period (cfr. Newman (1931)). For diffusivities which decrease strongly with decreasing concentration the profiles are even closer and the transition therefore is faster.

There are also concentration dependences for which a regular regime is never reached. If D_r increases strongly with decreasing concentration in a desorption process, a small decrease of the concentration results in a considerable increase of the diffusion coefficient so that the amount of sorbent at a place of lower concentration disappears relatively fast. This results in a front which moves into the dispersed phase and from which mass transfer can approximately be described as quasi-stationary. In absorption with a diffusion coefficient which decreases strongly with increasing concentration the same phenomenon will happen. This phenomenon will be found if $D_r(\bar{m})/\bar{D}_r = 0$ or, in practice, considerably less than unity. The quasi-stationary description of mass transfer during the induction period will be discussed in more detail in chapter IV.

III.9 Conclusions

The observations of this chapter can be summarized in the following conclusions.

1. For a number of widely differing concentration dependences of the diffusion coefficient it is observed, that the influence of the initial concentration on the sorption rate becomes negligible after a certain induction

period. This second stage is called the regular regime.

2. The occurrence of the regular regime phenomenon can be proved analytically for constant diffusion coefficient (Luikov (1968)). For the general case of a variable diffusion coefficient the phenomenon is made plausible.
3. We introduced a concentration-averaged diffusivity $\bar{D}_r$ and Sherwood number for the dispersed phase $\overline{Sh}_d$, with which sorption processes with variable diffusion coefficient conveniently can be described.
4. Two criteria have been developed to characterize the concentration dependence of the diffusion coefficient. The relation between these criteria and $\overline{Sh}_d$ is not very dependent on the kind of concentration dependence.
5. The effect of shrinkage or swelling due to uptake or loss of sorbent can be accounted for in a simple way: it can be expressed as an absolute contribution to the Sherwood number: $\Delta\overline{Sh}_d$, which is by good approximation determined by the volume fraction of sorbent only.
6. The Sherwood number in the dispersed phase at the end of the constant activity period in a drying process is in practice close to the Sherwood number for drying with constant surface concentration.
7. When the diffusion coefficient decreases strongly with decreasing concentration (e.g. drying of food liquids) the value of the surface concentration - within certain limits - has only minor influence on the drying rate in the falling rate period.
8. There is a linear relation between the Sherwood number $\overline{Sh}_d$ of two different geometries at the same average and surface concentration. This relation is hardly dependent on the kind of concentration dependence or boundary condition.
9. If $D_r(\bar{m})/\bar{D}_r << 1$ a regular regime of sorption is never reached.

IV PENETRATION THEORY

IV.1 Introduction

In the initial stage of a (de)sorption process, the influence of the change brought about at the phase boundary gradually penetrates into the body. For short times the concentration change at the centre of the body is still negligible. This means that concentration profiles inside the dispersed phase are not yet influenced by its limited thickness: the process is identical with sorption in a semi-infinite medium. In the calculation of mass transfer rates for short contact times use can be made of this phenomenon (Higbie (1935)).

For cylinders and spheres the dimensions of the body play a role due to the curvature of the surface. This influence is only negligible in a small shell near the surface which therefore behaves like an infinite slab for very short times.

This chapter deals with the early stage of a sorption process in a specimen of uniform initial concentration. Two types of boundary conditions are considered: constant surface concentration and constant surface flux.

IV.2 Constant surface concentration

IV.2.1 Slabs

Diffusion in a slab of homogeneous initial concentration and constant surface concentration can for short times be described as diffusion in a semi-infinite medium. Boltzmann (1894) showed, that the diffusion equation then can be reduced to an ordinary differential equation by the introduction of a new variable, η, which is defined as

$$\eta = \frac{1-\phi}{2\sqrt{\tau}} \qquad \text{(IV.2.1)}$$

Since the diffusion process can be described as a function of η only, it follows, that

$$D_r \left(\frac{dm}{d\eta}\right)_{\eta=0} = \beta(m_0-m_i) \qquad \text{(IV.2.2)}$$

where β is a constant. Partial differentiation of (IV.2.1) gives

$$-\frac{\partial\eta}{\partial\phi} = \frac{1}{2\sqrt{\tau}} \qquad \text{(IV.2.3)}$$

which yields after combination with (IV.2.2):

$$F = -D_r \left(\frac{\partial m}{\partial\phi}\right)_\tau \Bigg|_{\phi=1} = \frac{\beta(m_0-m_i)}{2\sqrt{\tau}} \qquad \text{(IV.2.4)}$$

For the slab of finite thickness therefore holds:

$$-\frac{d\bar{m}}{d\sqrt{\tau}} = \beta(m_0-m_i) \qquad \text{(IV.2.5)}$$

Integration of this differential equation gives the efficiency E of the sorption process in relation to time:

$$E = \beta \sqrt{\tau} \qquad \text{(IV.2.6)}$$

where

$$E = \frac{m_0 - \bar{m}}{m_0 - m_i} \qquad \text{(IV.2.7)}$$

Irrespectively of the concentration dependence of the diffusion coefficient there is a period during which the amount of mass (de)sorbed is proportional to the square root of time.

From equations (IV.2.6) and (IV.2.4) the time variable can be eliminated and we find a relation between the flux parameter F and the efficiency E:

$$FE = \frac{m_0 - m_i}{2} \beta^2 = \text{constant} \qquad \text{(IV.2.8)}$$

Once a single combination of F and E is known, the value of F in the penetration period can be calculated very simply by application of this relation. Another general relation - independent of the concentration dependence of the diffusion coefficient - is found by differentiation of F to E:

$$\frac{d \ln F}{d \ln (1-E)} = \frac{1-E}{E} \qquad \text{(IV.2.9)}$$

It can be concluded, that *the penetration period of slabs can be characterized by a single parameter*, e.g. the product EF or the derivative $dE/d\sqrt{\tau}$. These two parameters are related by

$$EF = \frac{m_0 - m_i}{2} \left(\frac{dE}{d\sqrt{\tau}}\right)^2 \qquad \text{(IV.2.10)}$$

In addition to these parameters it is important to know the length of the penetration period and the way in which this period goes over into the regular regime of sorption.

It is obvious, that there must be a relation between the sorption rate during the penetration period and the regular regime. From the onset of the process the concentration profile gradually tends to the shape belonging to the regular regime. As soon as the concentration at the centre of the slab ($\phi=0$) starts to deviate appreciably from its initial value, the penetration period ends. The regular regime, however, can evidently not start before this has happened, because the regular regime is characterized by the fact, that the initial concentration no longer influences the concentration profile. With regard to the surface flux, however, the penetration period extends effectively longer than is indicated by the change of concentration at the slab centre. This is illustrated for a constant diffusivity in figure IV.2.1, which shows the efficiency E versus the square root of the time variable, $\sqrt{\tau}$. For the penetration

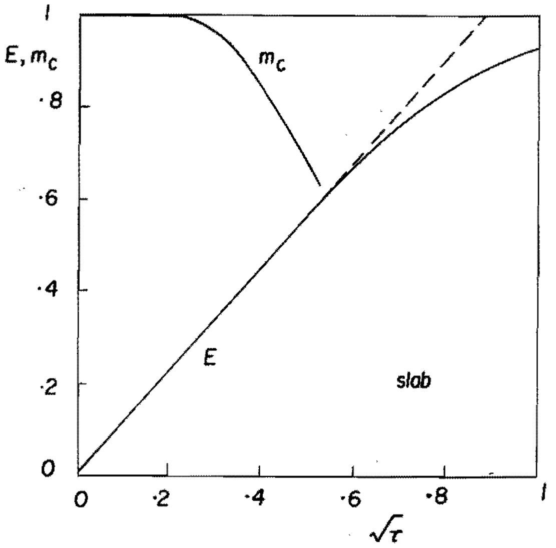


Fig.IV.2.1. The efficiency E and the centre concentration m_c in relation to the square root of the time coördinate $\sqrt{\tau}$. Desorption from a slab with constant surface concentration and constant diffusivity. Initial concentration $m_0 = 1$.

period this relation is linear (equation IV.2.6). In the same figure, also the dimensionless concentration at the centre of the slab, $(m_c-m_i)/(m_0-m_i)$ is given in relation to $\sqrt{\tau}$. It appears, that at the time when the relation between E and $\sqrt{\tau}$ starts to deviate from linearity ($E \simeq .5$) the concentration at the centre of the slab has changed by 22% of its final change already.

We assume as a working hypothesis, that the penetration period extends to the regular regime and that the transition period can be approximated by a transition point. If we then know the value of E at this transition point, the product EF for the penetration period can be calculated from the value of F in the regular regime at this transition point and E.

We developed two methods for the calculation of this transition point. The first can be applied in case the relation between F and the average concentration during the regular regime is known. In the second method we make use of the (known) relation between the diffusion coefficient and the concentration.

1. We assume that the transition between the penetration period and the regular regime is smooth. Hence, the derivative $dF/d\bar{m}$ and F and consequently $d \ln F/d \ln(\bar{m}-m_i)$ is assumed to be equal for the regular regime and the penetration period. By differentiation of the regular regime curve (F versus $\bar{m}$) the value of $d \ln F/d \ln(\bar{m}-m_i)$ can be found in relation to the efficiency E. For the penetration period a general relation has been derived between these two variables, which is independent of the concentration dependence of the diffusion coefficient (equation IV.2.9). In order to find the transition point, the relation between $d \ln F/d \ln (1-E)$ and E is plotted for the penetration period and for the regular regime in the same figure. The intersection point of these

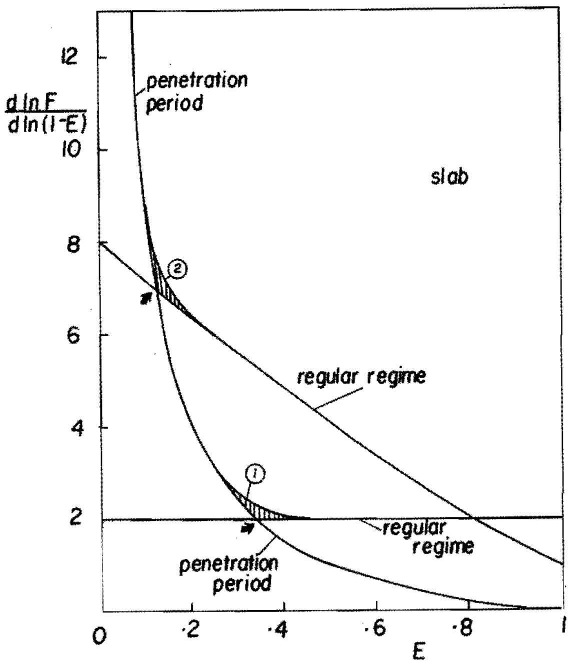


Fig.IV.2.2. Graphical method for the determination of the point of transition (E_t) from the penetration period to the regular regime (slabs). Curve 1: $D_r = m$; curve 2: $D_r = \exp(8m)$; $m_0 = 1$ and $m_1 = 0$. Arrows indicate the transition points.

curves belongs to either period and thus represents the transition point.

In fig.IV.2.2 the procedure is illustrated for two concentration dependences of the diffusion coefficient. It shows the general relation for the penetration period, the two relations for the regular regimes and the two actual curves which follow from the solutions of the diffusion equations. The shaded areas are a measure of the relative error in $dE/d\sqrt{\tau}$ calculated according to the present method. The results obtained by this method

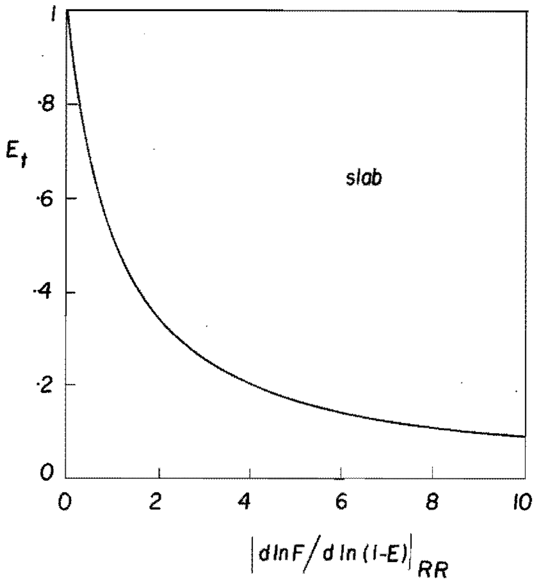


Fig.IV.2.3. The value of E at the transition point (E_t) in relation to the value of d ln F/d ln(1-E) at the transition point (slabs)

are listed in table IV.2.1. for several concentration dependences. They are compared with the values obtained from the (numerical) solutions of the diffusion equation. Good agreement can be observed between the values calculated by the two methods. It is concluded, that the present method enables an accurate calculation of the length of the penetration period.

Figure IV.2.3 shows the relative amount of mass (de)sorbed at the transition between penetration period and regular regime, E_t, in relation to the value of the parameter d ln F/d ln $(\bar{m}-m_i)$ at the transition point. At high values of this parameter in the regular regime (the diffusion coefficient decreases strongly with de(in)-creasing concentration in de(ab)sorption) the penetration period is relatively short. For constant diffusivity the transition takes place at $E_t = 0.5$, for a diffusion coef-

Type of concentration dependence	Value of parameter	$dE/d\sqrt{\tau}$ from the solution of the diff.equn.	$dE/d\sqrt{\tau}$ calculated from regular regime	E_t	Relative difference in $dE/d\sqrt{\tau}$	$EF/(m_o-m_i)$ from the solution of diff. equn.
constant	$D_r = 1$	1.1284	1.1107	.500	.016	.6366
exponential:	$am_o = 12$	56.00	55.43	.083	.010	1568
$D_r=\exp(am)$	8	11.44	11.25	.125	.017	65.44
	2	1.729	1.698	.338	.018	1.495
	-2	.829	.822	.662	.008	.344
linear:	$am_o = 2$	1.488	1.463	.42	.017	1.107
$D_r = 1-am$	4	1.766	1.732	.39	.020	1.559
	$am_o \to \infty$	$.669\times\sqrt{am_o}$	$.654\times\sqrt{am_o}$	.333	.023	$.224\times am_0$
power:	$m_o=1;\ a=1$	.669	.654	.333	.023	.224
$D_r = m^a$	2	.476	.466	.250	.021	.113
	4	.302	.297	.167	.017	.0456
	7	.19	.193	.111	-	.0186
	10	.14	.143	.083	-	.0102

Table IV.2.1. The value of $dE/d\sqrt{\tau}$ in the penetration period for various concentration dependences of the diffusion coefficient. Comparison of the values obtained from the numerical solution of the diffusion equation with the values calculated from the regular regime. The surface concentration m_i is in all cases taken to be zero.

ficient which increases with de(in)creasing concentration in de(ab)sorption the penetration period extends longer. When

$$\frac{d \ln F}{d \ln (\bar{m}-m_i)} \simeq \frac{D_r(\bar{m})}{\bar{D}_r} << 1 \qquad (IV.2.11)$$

the penetration period extends up to $E \simeq 1$: there is no regular regime for such concentration dependences and the complete sorption process is covered by the penetration period. These observations are in agreement with the qualitative considerations described in paragraph III.8.

When $\overline{Sh}_d$ is constant during (part of) the regular regime, it holds that

$$\frac{d \ln F}{d \ln (\bar{m}-m_i)} = \frac{D_r(\bar{m})}{\bar{D}_r} \qquad (IV.2.12)$$

and the transition point can be calculated directly from the parameter $D_r(\bar{m})/\bar{D}_r$. For the concentration dependence $D_r = m^a$ and $m_i = 0$ it follows, that

$$E_t = \frac{1}{a+2} \qquad (IV.2.13)$$

In case of an exponential concentration dependence (D_r= exp(am) with high values of the exponent (am) the following expression for E_t can be derived (m_i= 0):

$$E_t = \frac{1}{am_0} \qquad (IV.2.14)$$

2. A second method for the calculation of the transition point has as a starting point, that the concentration profile at this transition point resembles the profile for the case of steady-state mass transfer through the slab. If the diffusion coefficient decreases strongly with de(in)creasing concentration in de(ab)sorption

$(D_r(\bar{m})/\bar{D}_r \gg 1)$ this assumption seems to be reasonable: also in stationary mass transfer the derivative $\partial m/\partial \phi$ at $\phi=0$ will be approximately zero so that this steady-state profile satisfies the boundary conditions for the non-steady state by good approximation. On the other hand, a rather sharp front will move inside the slab when the diffusion coefficient increases strongly with de(in)creasing concentration in de(ab)sorption $(D_r(\bar{m})/\bar{D}_r \ll 1)$. Since mass transfer can then by good approximation be assumed to be quasi-stationary, the end of the penetration period is given by the time when this quasi-stationary profile reaches the centre of the slab. It can be concluded, that the concentration profile for steady state mass transfer will be a good indication of the shape of the profile at the transition point if $D_r(\bar{m}) \gg \bar{D}_r$ or $D_r(\bar{m}) \ll \bar{D}_r$. If the diffusion coefficient does not depend strongly on concentration $(D_r(\bar{m}) \simeq \bar{D}_r)$, this assumption can not be expected to be valid. Nevertheless, we will calculate the value of E_t following the above assumption.

Consider a slab with constant surface concentration m_i and constant centre concentration $m_c = m_0$. The mass flux in the steady state is then given by (cfr. table III.2.1.)

$$F = \overset{\sqcap}{D}_r \; (m_0 - m_i) \qquad \text{(IV.2.15)}$$

where $\overset{\sqcap}{D}_r$ is defined as

$$\overset{\sqcap}{D}_r = \frac{1}{m_c - m_i} \int_{m_i}^{m_c} D_r \, dm \qquad \text{(IV.2.16)}$$

The concentration profile then satisfies the differential equation

$$- D_r \frac{dm}{d\phi} = \overset{\sqcap}{D}_r \; (m_0 - m_i) = \text{constant} \qquad \text{(IV.2.17)}$$

Hence, it follows for the average concentration

$$\bar{m} = \int_0^1 m \, d\phi = \frac{1}{\bar{D}_r (m_0 - m_i)} \int_{m_i}^{m_c} D_r \, m \, dm \qquad \text{(IV.2.18)}$$

We introduce a reduced concentration m_r by

$$m_r = \frac{m - m_i}{m_0 - m_i}$$

Substitution in equation (IV.2.18) gives:

$$\bar{m}_r = \frac{1}{\bar{D}_r} \int_0^1 D_r \, m_r \, dm_r \qquad \text{(IV.2.19)}$$

If the steady-state profile is close to the concentration profile at the transition point it must hold, that

$$E_t = 1 - \bar{m}_r = 1 - \frac{\int_0^1 D_r \, m_r \, dm_r}{\int_0^1 D_r \, dm_r} \qquad \text{(IV.2.20)}$$

D_r	E_t
constant	.5
m_r^a	$\frac{1}{a+2}$
$\exp(am_r)$	$\frac{e^a - (a+1)}{a(e^a - 1)}$ at high values of a: $1/a$
$1 + am_r$	$\frac{1 + a/3}{2 + a}$
$\frac{1}{1 + am_r}$	$\frac{a - (a+1) \ln (a+1)}{a - \ln (a+1)}$

Table IV.2.2. Analytical expressions for E_t, according to the approxmation by a steady-state profile

Table IV.2.2 gives analytical expressions for E_t for various concentration dependences of the diffusion coefficient. When applied to the entries of table IV.2.1 these expressions appear to give exactly the same results for the intersection point. Surprisingly enough, this agreement is also found for weak concentration dependences and constant diffusivity. It can be concluded, that also this second method appears to be suitable for the calculation of the length of the penetration period. The value of F during the penetration period can again be calculated from E_t and F for the regular regime at the intersection point.

Time-averaged mass transfer coefficients

For the constant diffusivity case the penetration theory has been applied on mass transfer with short contact times by Higbie (1935). The driving force is then expressed as the difference between initial and surface concentration $(m_0 - m_i)$. The mass transfer coefficient in the dispersed phase k_d' (m/s) is then by definition of F for non-shrinking systems equal to

$$k_d' = \frac{F\ D_0}{R(m_0 - m_i)} \qquad \text{(IV.2.21a)}$$

and for shrinking systems (reference component mass centered coordinates)

$$k_d'' = \frac{F\ D_0\ \rho_{s,0}^2}{d_{s,p}\ R_s\ (m_0 - m_i)} \qquad \text{(IV.2.21b)}$$

The value of F at the transition point can be expressed as:

$$F_t = \frac{1}{2}\ \overline{Sh}_{d,t}\ \bar{D}_{r,t}\ (1-E_t)\ (m_0 - m_i) \qquad \text{(IV.2.22)}$$

where the index t refers to the transition point. Upon substitution in equation (IV.2.10) it follows, that

$$\frac{dE}{d\sqrt{\tau}} = \left\{\overline{Sh}_{d.t}\ \bar{D}_{r,t}\ E_t\ (1-E_t)\right\}^2 \qquad \text{(IV.2.23)}$$

which means, that the flux parameter as a function of time reads:

$$F = \frac{m_0-m_i}{2\sqrt{\tau}} \left\{\overline{Sh}_{d,t}\ \bar{D}_{r,t}\ E_t\ (1-E_t)\right\}^{1/2} \qquad \text{(IV.2.24)}$$

The mass transfer coefficient k'_d during the penetration period is then equal to

$$k'_d = \frac{1}{2\sqrt{t}} \left\{\overline{Sh}_{d,t}\ \bar{D}_t \cdot E_t\ (1-E_t)\right\}^{1/2} \qquad \text{(IV.2.25a)}$$

for non-shrinking systems, while for shrinking or swelling systems holds, that

$$k''_d = \frac{1}{2\sqrt{t}} \left\{ \overline{Sh}_{d,t}\ \frac{E_t(1-E_t)}{(\bar{m}_t-m_i)} \int_{m_i}^{\bar{m}} D\ \rho_s^2\ dm \right\}^{1/2} \qquad \text{(IV.2.25b)}$$

The variable t in these equations represents the time (s). The time-averaged mass transfer coefficient $\bar{k}'_d$ during the residence time t_{res} follows from integration:

$$\bar{k}'_d = \frac{1}{t_{res}} \int_0^{t_{res}} k_d\ dt \qquad \text{(IV.2.26)}$$

Application to the equations (IV.2.25a-b) then gives:

non-shrinking systems:

$$\bar{k}'_d = \left\{\overline{Sh}_{d,t}\ E_t\ (1-E_t)\right\}^{1/2} \left\{\frac{\bar{D}_t}{t_{res}}\right\}^{1/2} \qquad \text{(IV.2.27a)}$$

shrinking systems:

$$\bar{k}''_d = \left\{\overline{Sh}_{d,t}\ E_t\ (1-E_t)\right\}^{1/2} \left\{\frac{\frac{1}{\bar{m}_t-m_i} \int_{m_i}^{\bar{m}_t} D\ \rho_s^2\ dm}{t_{res}}\right\}^{1/2}$$

(IV.2.27b)

In these equations the value of E_t can be obtained from equation (IV.2.20). Bij calculating

$$\frac{d \ln F}{d \ln (\bar{m}-m_i)} = \frac{1 - E_t}{E_t} \qquad \text{(IV.2.28)}$$

we can find $\overline{Sh}_d$ from figure (III.4.6a). The value $\bar{m}_t$ is equal to

$$\bar{m}_t = (1 - E_t)(m_0-m_i) + m_i \qquad \text{(IV.2.29)}$$

For constant diffusion coefficient this approximate relation for $\bar{k}'_d$ becomes:

$$\bar{k}'_d = \frac{\pi}{2\sqrt{2}} \left\{\frac{D}{t_{res}}\right\}^{1/2} \simeq 1.11 \left\{\frac{D}{t_{res}}\right\}^{1/2} \qquad \text{(IV.2.30)}$$

whereas Higbie's relation reads:

$$\bar{k}'_d = \frac{2}{\sqrt{\pi}} \left\{\frac{D}{t_{res}}\right\}^{1/2} \simeq 1.13 \left\{\frac{D}{t_{res}}\right\}^{1/2} \qquad \text{(IV.2.31)}$$

Calculations for $D_r(\bar{m}) \ll \bar{D}_r$

Application of the present method to the calculation of the sorption rate during the penetration period leads to erroneous results when the diffusion coefficient increases strongly with de(in)creasing concentration in de(ab)sorption: $D_r(\bar{m}) \ll \bar{D}_r$. In the limit (e.g. $D_r = 1/m_r$) the regular regime "starts" at E = 1. The driving force for mass transfer is then zero and therefore the flux-parameter F is zero. This would result in EF = 0 for the penetration period: In the limit the above method can not be applied. For these systems, however, a simple alternative is at hand. From qualitative considerations we concluded already, that there will be a more or less sharp "front" moving inwards. Mass transfer from this front can then be assumed to be quasi-stationary, since the accumulation term will be negligible in the space between the front and the phase boundary. We can calculate the product EF for the penetration period as follows. The value of E_t is obtained by application of equation (IV.2.20). The value of F_t follows also from the steady state profile:

$$F = (m_0 - m_i)\ \bar{D}_r \tag{IV.2.32}$$

so that the product EF for the penetration period is equal to

$$EF = (m_0 - m_i) \left\{ \int_0^1 D_r\ dm_r - \int_0^1 D_r\ m_r\ dm_r \right\} \tag{IV.2.33}$$

and

$$\frac{dE}{d\sqrt{\tau}} = \sqrt{2} \left\{ \int_0^1 D_r\ dm_r - \int_0^1 D_r\ m_r\ dm_r \right\}^{1/2} \tag{IV.2.34}$$

In table IV.2.3 the results of such calculations are presented for $D_r = \exp(am_r)$, at negative values of a. It appears, that with increasing E_t the agreement between this quasi-stationary approach and the numerically calculated values of EF becomes better. At $E_t > .8$ good agreement can be claimed.

a	EF from numerical calculations	E_t	EF quasi-stationary calculations	relative difference in EF
0	.6366	.5	0.5	27%
- .1	.624	.508	.483	29%
- .2	.601	.517	.469	28%
- .4	.560	.533	.439	28%
-1	.461	.582	.368	25%
-2	.343	.657	.284	21%
-4	.210	.769	.189	11%
-6	.140	.836	.139	1%
-8	.11	.875	.109	-

Table IV.2.3 Values of the product EF calculated following the assumption of quasi-stationary mass transfer. $D_r = \exp(am_r)$

IV.2.2 Cylinders and spheres with constant total volume

We recall the general formulation of the diffusion equation:

$$\frac{\partial m}{\partial \tau} = \frac{\partial}{\partial \phi} (D_r X^2 \frac{\partial m}{\partial \phi}) \qquad \text{(IV.2.35)}$$

For short penetration distances, X^2 can effectively be considered to be independent of ϕ :

$$\frac{\partial m}{\partial \tau} = X_i^2 \frac{\partial}{\partial \phi} (D_r \frac{\partial m}{\partial \phi}) \qquad \text{(IV.2.36)}$$

If we account for the constant X_i^2 in the time variable τ, the equation goes over into the diffusion equation for a slab. For short penetration distances it follows therefore, that

$$\frac{dE}{d\sqrt{\tau}} = (\nu+1) \left\{\frac{dE}{d\sqrt{\tau}}\right\}_{slab} \qquad \text{(IV.2.37)}$$

Unfortunately, this relation holds only for very short times and is certainly not sufficient to describe the complete period that procedes the regular regime.

Figure IV.2.4 shows the flux parameter F for a sphere with constant diffusion coefficient ($D_r = 1$) versus the relative amount which has not been (de)sorbed: 1-E. In this figure also the "penetration period" according to relation IV.2.37 is given. It appears, that the difference between the exact analytical solution and the curve obtained by application of equation IV.2.37 is approximately constant:

$$F = \frac{(\nu+1)(EF)_{slab}}{E} - \Delta F \qquad \text{(IV.2.38)}$$

where ΔF is a constant. This can also be shown from the analytical solution of the diffusion equation, which can be formulated as (Luikov (1968)):

$$E = \frac{6\sqrt{\tau}}{\sqrt{\pi}} - 3\tau - 12\sqrt{\tau} \sum_{n=1}^{\infty} \text{ierfc}\ (n/\sqrt{\tau}) \qquad \text{(IV.2.39)}$$

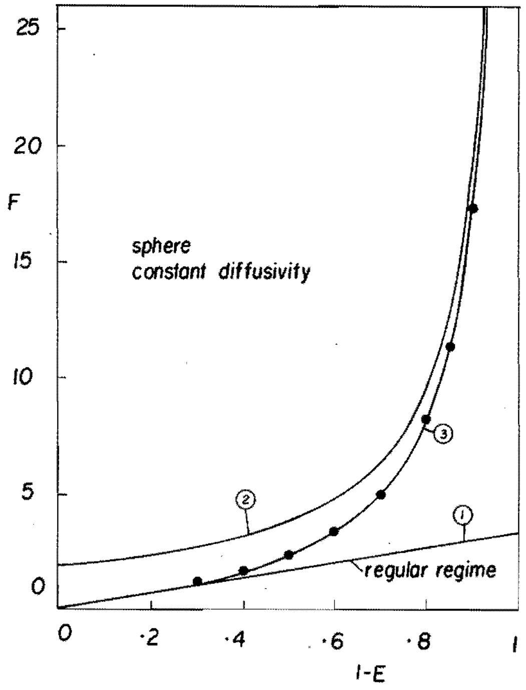


Fig. IV.2.4 Sorption in a sphere with constant diffusion coefficient and constant surface concentration ($m_i=0$). Initial concentration $m_0=1$. 1. Regular Regime; 2. penetration curve from slab (equation IV.2.37); 3. actual sorption curve. Points indicate values for the penetration period according to equation (IV.2.48).

Up to high values of E the last term of this equation can be neglected:

$$E \simeq \frac{6\sqrt{\tau}}{\sqrt{\pi}} - 3\tau \qquad \text{(IV.2.40)}$$

The error, caused by this omission is less than 1% if $E < .90$ and less than 10% if $E < .95$. The value of F in relation to τ follows by differentiation:

$$F = -\frac{(m_0-m_i)}{3}\frac{dE}{d\tau} = (m_0-m_i)\left(\frac{1}{\sqrt{\pi\tau}} - 1\right) \tag{IV.2.41}$$

Elimination of τ from the equations (IV.2.40) and (IV.2.41) yields:

$$\frac{F}{(m_0-m_i)} = \frac{1+\sqrt{1-\pi E/3}}{\pi E/3} - 1 \tag{IV.2.42}$$

For small values of E this can be written as:

$$\frac{F}{m_0-m_i} = \frac{6}{\pi E} - 1.5 \tag{IV.2.43}$$

which corresponds with the formulation (IV.2.38). It is interesting to notice, that ΔF is approximately equal to the value of F at the beginning of the regular regime.

For *cylinders*, the solution for short times reads (Crank (1956)):

$$E = \frac{4\sqrt{\tau}}{\sqrt{\pi}} - \tau \tag{IV.2.44}$$

from which analogously can be derived, that

$$\frac{F}{m_0-m_i} = \frac{1}{2}\left\{\frac{1-\sqrt{1-\pi E/4}}{\pi E/4} - 1\right\} \tag{IV.2.45}$$

For small values of E this can be written as:

$$\frac{F}{m_0-m_i} = \frac{4}{\pi E} - \frac{3}{4} \tag{IV.2.46}$$

Also for cylinders formulation (IV.2.38) appears to be valid for constant diffusivity and not too high values of E.

Also when the *diffusivity increases strongly with de(in)creasing concentration in de(ab)sorption* ($D_r(m_0) << \overline{D}_r$) an analytical treatment of the penetration period is possible. We adopt again the "shrinking core" approach: a front moves into the dispersed phase. From this front, mass transfer can be assumed to be quasi-stationary. From the relations for stationary mass transfer in spherical and cylindrical shells (table III.2.1) the following equations can be derived for the shrinking core-model:

cylinder $$F = \frac{2(EF)_{slab}}{-\ln(1-E)} \qquad \text{(IV.2.47)}$$

sphere $$F = \frac{(EF)_{slab}}{(1-E)^{-1/3} - 1} \qquad \text{(IV.2.48)}$$

Although these relations only hold strictly in the limit $D_r(m_0)/\overline{D}_r = 0$, they appear to give excellent agreement with the actual sorption rates for constant diffusion coefficient in the penetration period. *The above relations can therefore successfully be applied if the diffusion coefficient is constant or increases with de(in)creasing concentration in de(ab)sorption* $(D_r(m_0) \leq \overline{D}_r)$.
In the figures IV.2.4 and IV.2.5 the curves are given, which follow from these equations for constant diffusivity in spheres and cylinders respectively.

For diffusivities which decrease with de(in)creasing concentration in de(ab)sorption the equation derived from the shrinking core model may result in considerable deviations from the actual penetration curves. For these dependences a different approach is adopted here. It is based upon the observation that the difference between the sorption flux F, calculated from the "slab-penetration"-equation (IV.2.37) and the actual sorption flux is constant for small values of E. This has been observed not only for constant diffusion coefficient, as described above, but also for many other concentration dependences. It can even be derived analytically for the equations (IV.2.47) and (IV.2.48). We correlate the sorption flux parameter F with the efficiency E by

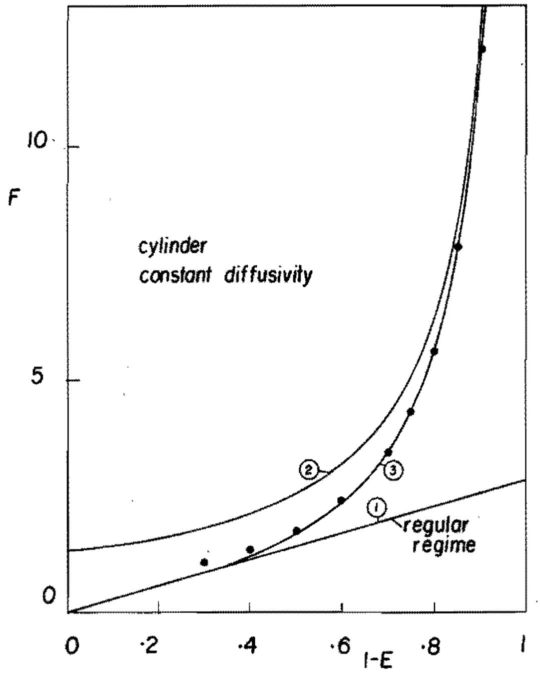


Fig. IV.2.5 Sorption in a cylinder with constant diffusion coefficient and constant surface concentration (m_i=0). Initial concentration m_0=1. 1. Regular Regime; 2. penetration curve from slab (equation IV.2.37); 3. actual sorption curve. Points indicate values for the penetration period according to equation (IV.2.47).

$$F = (\nu+1) \left\{ \frac{(EF)_{slab}}{E} \right\} - q\, \bar{D}_r\, (m_0 - m_i) \qquad \text{(IV.2.49)}$$

where q is a constant, which depends on the variation of the diffusion coefficient and on the geometry. The constant coefficient q is given in figure IV.2.6 for nonshrinking spheres and cylinders in relation to $D_r(m_0)/\bar{D}_r$.
For cylinders, q can generally be taken .75, so that the penetration period can then be described by

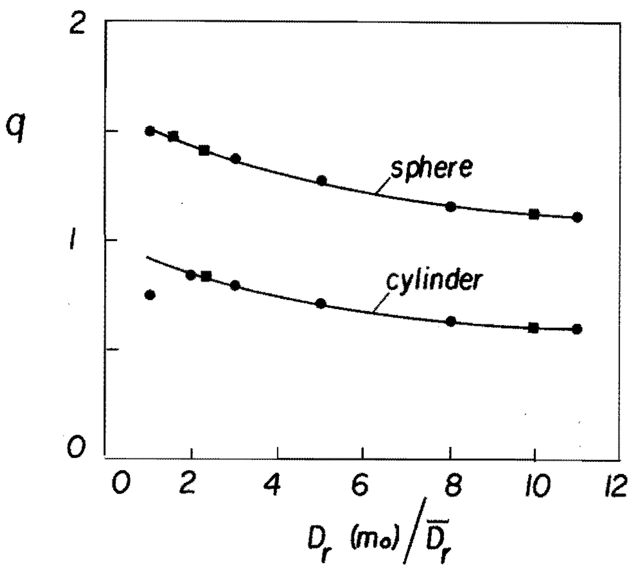


Fig. IV.2.6 $\Delta F/(\overline{D}_r(m_0-m_i))$ for the penetration period of non-shrinking spheres and cylinders in relation to the concentration dependence of the diffusion coefficient $D_r(m_0)/\overline{D}_r$.
$D_r = m^a$; $D_r = \exp(am)$.

cylinder $$F = \frac{2(EF)_{slab}}{E} - .75 \int_{m_i}^{m_0} D_r \, dm \qquad \text{(IV.2.50)}$$

The constant q varies for spheres slightly more with the concentration dependence of the diffusion coefficient. However, for not too strong dependences ($D_r(m_0)/\overline{D}_r < 5$) the value for constant diffusivity may be used:

sphere
$(0 < D_r(m_0)/\overline{D}_r < 5)$ $$F = \frac{3(EF)_{slab}}{E} - 1.5 \int_{m_i}^{m_0} D_r \, dm \qquad \text{(IV.2.51)}$$

whereas for strong dependences a good correlation is found in:

sphere
$(D_r(m_0)/\bar{D}_r > 5)$

$$F = \frac{3(EF)_{slab}}{E} - 1.2 \int_{m_i}^{m_0} D_r \, dm \qquad \text{(IV.2.52)}$$

It should be noted, that the last term, ΔF, plays an important role only near the transition from penetration period to regular regime. At this transition point the value of F is of the same order of magnitude as ΔF. For smaller times a relative error in ΔF will therefore cause a considerably lower relative error in F, so that the above relations will be sufficiently accurate for practical purposes. Figures IV.2.7 and IV.2.8 show examples of the above calculations for $D_r = m_r^3$ for a sphere and a cylinder respectively. *It can be concluded, that the penetration period for spheres and cylinders is characterized by two*

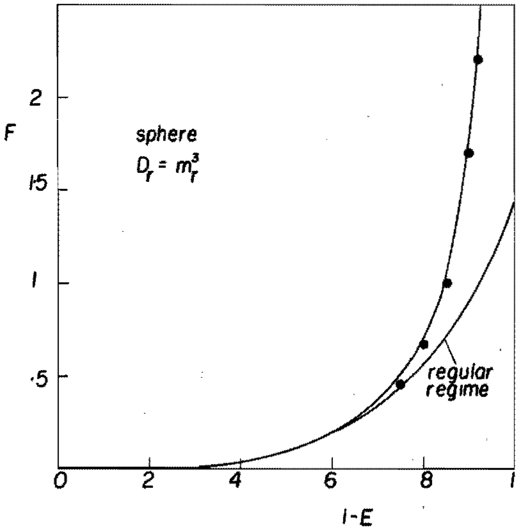


Fig. IV.2.7 Sorption in a sphere with constant surface concentration. Points indicate values for the penetration period according to equation (IV.2.51).

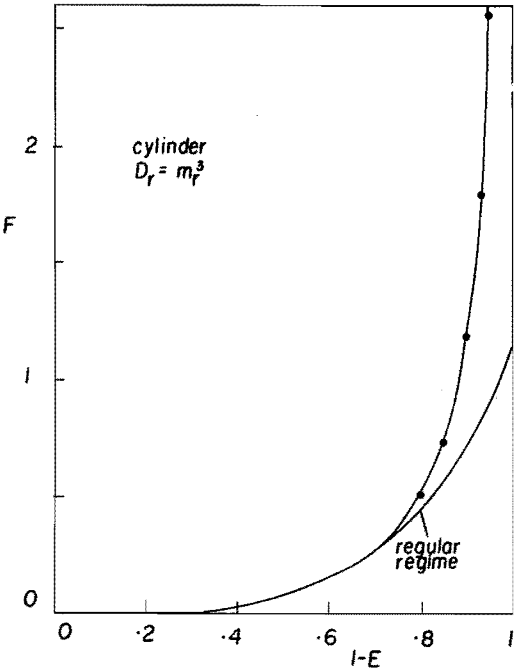


Fig. IV.2.8 Sorption in a cylinder with constant surface concentration. Points indicate values for the penetration period according to equation (IV.2.50).

parameters when the diffusion coefficient decreases with de(in)creasing concentration in de(ab)sorption: $(EF)_{slab}$ *and* ΔF.

Graphical method.

The penetration period can also be calculated from the regular regime sorption curve by a graphical method, which is analogous to the graphical method for slabs. In this method we make use of the observation, that the value of $d \ln F/d \ln (1-E)$ is in the regular regime by good approximation independent of geometry at the same average and surface concentration. This holds exactly in case $\overline{Sh}_d$ is constant. By plotting $d \ln F/d \ln (1-E)$ versus E we can find E_t for a slab: $E_{t,slab}$ is the value of E at the intersection point of this curve with the general relation for the penetration period of slabs:

$$\frac{d \ln F}{d \ln (1-E)} = \frac{1-E}{E} \qquad \text{(IV.2.53)}$$

We can calculate the sorption flux for a slab at this average concentration in the following way. From figure III.4.5a we can read $\overline{Sh}_{d,\ slab}$ at the value of d ln F/d ln (1-E) of the intersection point. The sorption flux parameter for the slab, $F_{t,slab}$ is then related to F for the cylinder or sphere at the same concentration by

$$F_{t,slab} = \frac{\overline{Sh}_{d,slab}}{\overline{Sh}_d} \cdot F \qquad \text{(IV.2.54)}$$

where $\overline{Sh}_d$ is the Sherwood number for the sphere or cylinder, which is given in figure III.7.1 in relation to $\overline{Sh}_{d,slab}$. The product $(EF)_{slab}$ then reads:

$$(EF)_{slab} = E_{t,slab} \times F_{t,slab} \qquad \text{(IV.2.55)}$$

This value of $(EF)_{slab}$ can now be used in the calculations according to equations (IV.2.47) if $D_r(m_0) < \overline{D}_r$ and equation (IV.2.38) if $D_r(m_0) > \overline{D}_r$. In the latter case, only the constant ΔF is then left to be determined.

Determination of ΔF if $D_r(m_0) > \overline{D}_r$

If we know $\overline{D}_r$, ΔF can be calculated with one of the equations (IV.2.50-53). By differentiation of the regular regime curve at the average concentration equal to m_0 we can find d ln F/d ln (1-E), with which $\overline{Sh}_d$ can be estimated (fig. III.4.5b-c) we find now

$$\overline{D} = \frac{2F_{RR}(m_0)}{(m_0-m_i)\ \overline{Sh}_{d,RR}(m_0)} \qquad \text{(IV.2.56)}$$

The constant ΔF can also be found if the value of E at the transition from the penetration period to the regular regime (E_t) is known. At this point it must hold that

$$\Delta F = \frac{(\nu+1)\ (EF)_{slab}}{E_t} - F_{RR} \qquad \text{(IV.2.57)}$$

Since the transition between the two periods is smooth, the determination of this transition point does not have to be exact: the two curves F versus (1-E) -"slab-penetration" and regular regime- are parallel over a certain range.

From equation (IV.2.49), which describes the penetration period, can as such no relation be derived which is independent of the concentration dependence of the diffusion coefficient. We found, however, that at the transition point the value of $F(=F_t)$ is related to F by

$$\Delta F = \frac{\nu}{2} F_t \qquad \text{(IV.2.58)}$$

Equation (IV.2.49) can therefore be written as

$$F = \frac{(\nu+1)\ (EF)_{slab}}{E} - \frac{\nu(\nu+1)}{(\nu+2)} \cdot \frac{(EF)_{slab}}{E_t} \qquad \text{(IV.2.59)}$$

By differentiation then follows:

$$\frac{d\ \ln\ F}{d\ \ln\ (1-E)} = \frac{1-E}{E} \times \frac{(\nu+2)E_t}{(\nu+2)\ E_t - \nu E} \qquad \text{(IV.2.60)}$$

The change of d ln F/d ln (1-E) during the sorption process appears to be dependent on the transition point E_t, unless $\nu=0$ (slabs). Since we are interested only in the transition point itself, we can substitute E_t for E and find the following relation between d ln F/d ln (1-E) at the transition point and E_t:

$$\frac{d\ \ln\ F}{d\ \ln\ (1-E)} = \frac{(\nu+2)}{2} \frac{(1-E_t)}{E_t} \qquad \text{(IV.2.61)}$$

Analogously to the procedure for slabs we can find the transition point as the intersection of this relation with the relation between d ln F/d ln $(\overline{m}-m_i)$ for the regular regime. An example is given in figure IV.2.9 for a sphere with the concentration dependences of the diffusion coefficient $D_r = \exp(10.m_r)$ and $D_r = m_r^2$.

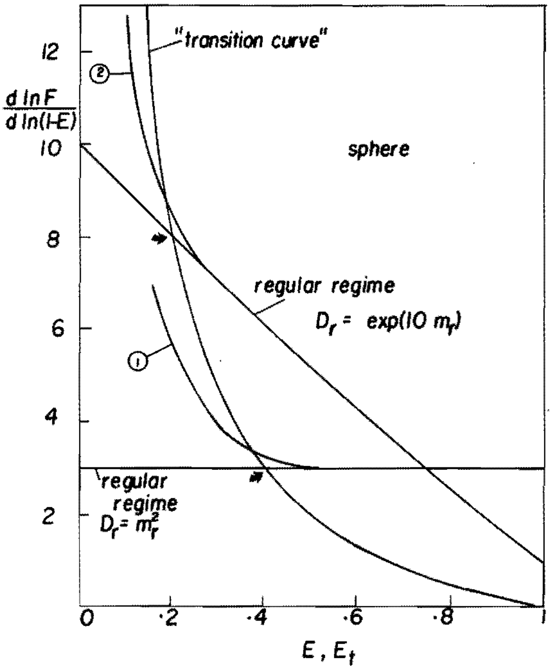


Fig. IV.2.9 Graphical determination of the transition point E_t (spheres). The intersection between the regular regime relation and the "transition curve" reflects the transition point, indicated by an arrow. The curves 1 and 2 give the actual relation between $d \ln F/d \ln(1-E)$ and E for (1) $D_r = m_r^2$ and (2) $D_r = \exp(10.m_r)$.

If the Sherwood number $\overline{Sh}_d$ is constant, E_t can also be calculated analytically according to the above method:

$$D_r = m_r^a \quad : E_t = \frac{\nu + 2}{2a + \nu + 4} \qquad \text{(IV.2.62)}$$

$$D_r = \exp(am_r);\ a > 6 : E_t = \frac{\nu+2}{2a} \qquad \text{(IV.2.63)}$$

Table IV.2.4 shows the results of some calculations for the concentration dependence $D_r = m_r{}^a$ (cylinders and spheres). The value of q appears to be in good agreement with the numerical calculations. Only for constant diffusion coefficient (indicated by an asterisk) a difference of approximately 20% between the results of this calculation and the analytical values is observed. These analytical values only hold for small values of E. At the transition point, where the relative influence of ΔF on F is maximum, a better approximation is given by ΔF = 1.61 and .86 for spheres and cylinders respectively. It can be concluded, that the present method is suitable for the prediction of the transition point. Tests on linear and exponential concentration dependences confirm this conclusion.

For strong concentration dependences $D_r = m^a$ or $D_r = \exp(am_r)$, $a \to \infty$, a limit value of q can be calculated analytically. The limit is equal for both kinds of concentration dependences:

$$\textit{cylinder} : q = \frac{2e}{3} - 2\sqrt{e} = .5991 \qquad \text{(IV.2.64)}$$

$$\textit{sphere} : q = \frac{3e}{4} - \frac{1}{2}\exp(2/3) = 1.065 \qquad \text{(IV.2.65)}$$

We are inclined to believe, that these limits are also valid for other kinds of concentration dependence of the diffusion coefficient provided that $D_r(m_0) >> \bar{D}_r$.

Another method for the estimation of the point of transition from the penetration period to the regular regime is also valid for shrinking or swelling systems and is described in the next section, which deals with such systems.

	a	E_t	$F_{RR,t}$	$\frac{(\nu+1)(EF)_{slab}}{E_t}$	ΔF	q graphical method	q numerical solution
sphere: $\nu=2$	0	.667	1.097	2.865	1.77	1.77	1.5*
	1	.500	.580	1.344	.764	1.53	1.44
	2	.400	.381	.848	.467	1.43	1.38
	4	.286	.221	.478	.257	1.29	1.28
	7	.200	.135	.279	.144	1.15	1.2
	10	.154	.0961	.199	.103	1.13	1.1
	100	.0194	.00985	.0205	.0106	1.07	
	∞					1.065	
cylinder: $\nu=1$	0	.600	1.157	2.122	.965	.965	.75*
	1	.429	.614	1.044	.430	.861	.8
	2	.33	.414	.678	.264	.792	.8
	4	.231	.250	.395	.145	.726	.7
	7	.158	.156	.235	.0787	.629	.6
	10	.120	.115	.170	.055	.605	
	100	.0146	.0122	.0182	.0061	.603	
	∞					.5991	

Table IV.2.4. Results of some calculations for the penetration period of spheres and cylinders. $D_r = m^a$; $q = \Delta F/(\overline{D}_r(m_0 - m_i))$; $m_i = 0$; Comparison of the values of q obtained by the graphical method and by numerical calculations.

IV.2.3 Shrinking or swelling cylinders and spheres

In the early stage of a sorption process, the sorption process is identical with diffusion in a shrinking slab, so that it must hold:

$$\frac{dE}{d\sqrt{\tau}} = X_i \left\{\frac{dE}{d\sqrt{\tau}}\right\}_{slab} \tag{IV.2.66}$$

where $X_i = (\nu+1)\left[1 + (1-E)(m_0-m_i) + m_i\right]^{\frac{\nu}{\nu+1}}$. For ease of notation we describe shrinking or swelling systems *in reference component volume centered coordinates*. The value of F is derived from

$$F = -\frac{1}{X_i}\;\frac{d\bar{m}}{d\tau} = \frac{m_0-m_i}{2\sqrt{\tau}}\;\frac{dE}{d\sqrt{\tau}}_{slab} \tag{IV.2.67}$$

$\sqrt{\tau}$ can be expressed as a function of E by integration of equation (IV.2.66) with the initial condition E=0 at τ=0:

$$\sqrt{\tau} = \frac{(1+m_0)^{\frac{1}{\nu+1}} - \left[1 + m_0 - E(m_0-m_i)\right]^{\frac{1}{\nu+1}}}{(m_0-m_i)\;\left\{\frac{dE}{d\sqrt{\tau}}\right\}_{slab}} \tag{IV.2.68}$$

and F as a function of $\bar{m}$ is given by:

$$F = \frac{1}{2}\left\{\frac{(m_0-m_i)^2}{(1+m_0)^{1/(\nu+1)} - (1+\bar{m})^{1/(\nu+1)}}\right\}\cdot\left\{\frac{dE}{d\sqrt{\tau}}\right\}^2_{slab} \tag{IV.2.69}$$

With equation (IV.2.10) this goes over into

$$F = \left\{\frac{(m_0-m_i)}{(1+m_0)^{1/(\nu+1)} - (1+\bar{m})^{1/(\nu+1)}}\right\}(EF)_{slab} \tag{IV.2.70}$$

For small values of m_0 and $\bar{m}$ this equation approaches the relation for systems with constant volume. This equation is valid only for very short penetration distances and we will need refinements in order to be able to describe the complete period that precedes the regular regime.

In analogy with the non-shrinking systems we distinguish 2 cases: (i) a more or less sharp front moves inside the dispersed phase or (ii) the sorption takes place more homogeneously over the dispersed phase.

(i) When a sharp front moves through the dispersed phase during the penetration period we can use the "shrinking core model", analogously to systems with constant total volume. The equations for this model are derived in Appendix C and read:

cylinder :

$$F = \frac{2(1+m_i)\,(EF)_{slab}}{\{(1+m_i)+(1-E)(m_0-m_i)\}^{\frac{1}{2}}\ \ln\left\{\dfrac{(1+m_i)+(1-E)(m_0-m_i)}{(1-E)(1+m_0)}\right\}} \qquad \text{(IV.2.71)}$$

sphere :

$$F = \frac{(1+m_i)\ (EF)_{slab}}{\left\{\dfrac{(1+m_i)\ +\ (1-E)(m_0-m_i)}{(1-E)(1+m_0)}\right\}^{1/3} - 1} \qquad \text{(IV.2.72)}$$

It should be noted that m represents here the volume fraction of the sorbent (m^3 sorbent/m^3 solute). F and $(EF)_{slab}$ have the dimension of either a mass fraction or a volume fraction (both on solute basis). Contrary to the non-shrinking case, these equations give rise to considerable deviations from the numerical solutions when applied to desorption with constant reduced diffusion coefficient D_r. *For desorption calculations the shrinking core model can be applied only when $D_r(m_0) << \overline{D}_r$.* Since this will be rarely the case, application of the above equations will practically be restricted to *absorption with swelling*.

From the diffusion equation for shrinking or swelling systems (III.4.12) we can conclude, that shrinkage results apparently in an effective decrease of the diffusion coefficient with decreasing concentration. This leads to the conclusion, that for the same concentration dependence of $D_r(m_r)$ the penetration period is longer for swelling systems (absorption) than for systems with constant volume. These, in turn, show longer penetration periods than shrinking systems (desorption). The equations derived from the shrinking-core approach can be applied when $E_t > .6$. Hence, we can often use these relations for the calculation of absorption rates in the penetration period for swelling systems.

(ii) When the transition to the regular regime takes place at $E_t < .6$, the shrinking core approach may not be applied. This will be generally so in desorption processes where the dispersed phase shrinks upon removal of sorbent. From a large number of computer simulations it appeared, that the value of the flux parameter F during the penetration period differs by an approximately constant term ΔF from the value calculated from slab-penetration rates (with correction for the specific surface area, equation IV.2.70). Hence, F can be calculated according to

$$F = \left\{ \frac{(m_0 - m_i)}{(1+m_0)^{1/(\nu+1)} - (1+\bar{m})^{1/(\nu+1)}} \right\} \cdot (EF)_{slab} - \Delta F \qquad \text{(IV.2.73)}$$

Again ΔF is related to the value of F at the transition point, F_t:

$$\Delta F \simeq \frac{\nu}{2} F_t \qquad \text{(IV.2.74)}$$

Once the combination $(EF)_{slab}$ and the regular regime sorption curve are known we can find ΔF by estimation of the point of transition from the penetration period to the regular regime where equation IV.2.74 applies. We could not find a simple general relation for the penetration period -analogous to systems with constant volume- with which the transition point could be correlated.

A simple and effective way to find the transition point is the following. We assume that the transition between penetration period and regular regime is smooth: $dF/d\bar{m}$ is approximately equal for both regular regime and penetration curve. We plot the curve for

$$F'(\bar{m}) = \frac{\nu+2}{2} F_{RR}(\bar{m}) \qquad \text{(IV.2.75)}$$

in the same figure as the penetration curve without the correction term ΔF. These two curves will intersect at the transition point because of relation IV.2.74 and the fact that the slopes of the curves are different. Also when equation IV.2.74 does not hold exactly this difference in the slopes will assure intersection. Only when the penetration period extends longer than $E_t \approx .6$ the deviation from equations (IV.2.74) and (IV.2.73) become so large that sometimes no intersection point can be found. (e.g. non-shrinking sphere and constant diffusivity). In that case the "shrinking-core"-equations (IV.2.71-72) can be applied. An example of the present calculation method is given in figure IV.2.10 for a shrinking sphere with D_r=m and $m_0 = 10\ m^3/m^3$. Excellent agreement between the results of the numerical calculations and the results of the correlation method can be observed.

The value of $(EF)_{slab}$ can also be obtained directly from the (experimentally determined) regular regime sorption curve of the shrinking or swelling system over a sufficiently large concentration interval. In such a calculation use is made of the effect of shrinkage on the Sherwood number $\overline{Sh}_d$ in the regular regime. By differentiation of the regular regime curve, d ln F/d ln (1-E) can be calculated. From the values obtained the effect of shrinkage or swelling can be subtracted. The relation between these new values and E can then -analogously to systems with constant volume- be used for the calculation of $(EF)_{slab}$.

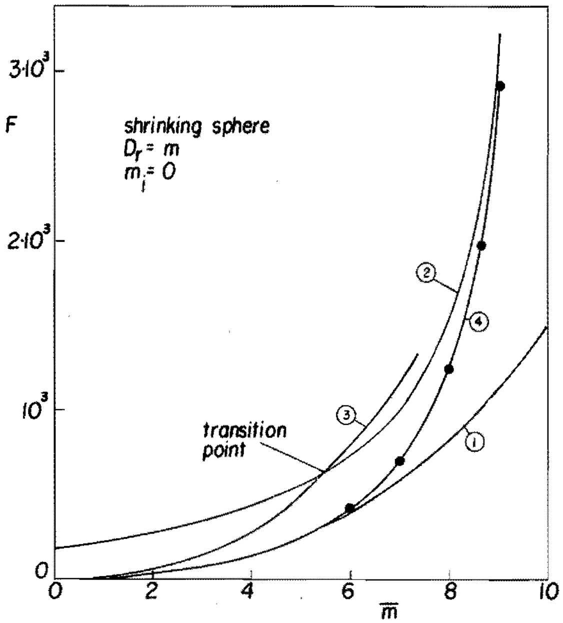


Fig. IV.2.10 Graphical determination of the transition point for a shrinking sphere. $D_r = m$ and $m_i = 10$.

(1) Regular Regime $F_{RR}(\overline{m})$;

(2) Penetration period from slab (equation IV.2.70);

(3) $2 \times F_{RR}(\overline{m})$;

(4) Actual sorption history.

Points indicate the values calculated according to equation (IV.2.73).

IV.3 Constant surface flux

IV.3.1 General

In paragraph III.5, which deals with the regular regime for constant surface flux, the term "critical point" has been introduced for the combination of F and $\bar{m}$ at the end of the constant rate period. The critical point curve is defined as the relation between the flux parameter F during the constant rate period and the average concentration $\bar{m}$ at the end of this period. Since we are generally interested in the duration of the constant rate period, the critical point curve provides important information about the constant rate period. In paragraph III.5 it has been shown, that there is a relation between the critical point curve and the sorption curve with a constant surface concentration equal to the critical concentration, during the regular regime. In this paragraph we will investigate the characteristics of the critical point curve for short constant rate periods, in which the concentration at the centre of the body has not yet changed considerably.

IV.3.2 Slabs

In his work on the calculation of the length of the constant rate period in drying, Kerkhof (1975) has shown, that for short times the length of the constant rate period t_{cr} is inversely proportional to the square of the surface flux during this period:

$$t_{cr} = \frac{\text{constant}}{(n_{m,i})^2} \qquad \text{(IV.3.1)}$$

In reduced coordinates this equation reads:

$$\tau_{cr} = \frac{\text{constant}}{F^2} \qquad \text{(IV.3.2)}$$

where the index cr refers to the critical point.

Analogously to Kerkhof we define a "profile penetration number" N_{pp} by

$$N_{pp} = \frac{m_0 - \bar{m}_{cr}}{m_0 - m_{cr}} \qquad \text{(IV.3.3)}$$

N_{pp} is amount of sorbent (water) desorbed at the end of the constant rate period relative to the amount which would have been (de)sorbed in case of a flat concentration profile at the same surface concentration. N_{pp} is in fact the constant rate-analogon for E in case of a constant surface concentration.

From a mass balance and equations (IV.3.2-3) it follows, that

$$F.N_{pp} = \text{constant} \qquad \text{(IV.3.4)}$$

which relation is analogous to equation (IV.2.8) for constant surface concentration. *The critical point curve in the penetration period can be characterized by a single parameter which is independent of the surface flux during the constant rate period.* This parameter may be the product $F.N_{pp}$ or a constant effective diffusion coefficient.

A method for the calculation of this parameter can be based upon a similar approach as has been used for the calculation of the penetration period in case of constant surface concentration. Also here, we assume that the period of transition from the penetration period to the regular regime can be approximated by a *transition point* and that the transition is smooth. Following the same line of reasoning as for constant surface concentration, we can find the transition point by intersection of the relation between d ln F/d ln $(1-N_{pp})$ and N_{pp} for the critical point curve in the regular regime with the general relation for the penetration period.

$$\frac{d \ln F}{d \ln (1 - N_{pp})} = \frac{1 - N_{pp}}{N_{pp}} \tag{IV.3.5}$$

In the regular regime the ratio between the Sherwood numbers for constant surface concentration, $\overline{Sh}_{d,CSC}$ and for the constant rate period $\overline{Sh}_{d,CRP}$ does not change strongly with the concentration dependence of the diffusion coefficient. Hence, it can by good approximation be assumed, that, *for slabs, the relative average concentration at the point of transition from the penetration period to the regular regime is for the critical point curve* ($N_{pp,t}$) *equal to the transition point for the sorption curve with constant surface concentration* (E_t). $N_{pp,t}$ can therefore be calculated according to the graphical method or the integration method, which makes use of the assumption of a steady-state concentration profile. These methods have been described in paragraph (IV.2.1).

The calculation of the product $F.N_{pp}$ is also analogous to the calculation of the product F.E for sorption with constant surface concentration. Once we know N_{pp} we only have to determine F at the transition point, F_t. At the transition point the relations for the regular regime still hold. For the regular regime, the ratio between the flux parameter belonging to the critical point curve and the flux parameter belonging to the sorption curve with constant surface concentration is equal to the ratio between the two Sherwood numbers, $\overline{Sh}_{d,CRP}$ / $\overline{Sh}_{d,CSC}$, as given in figure III.5.1. Because $N_{pp,t}$ and E_t are equal, the product $F.N_{pp}$ can be calculated from the product F.E. for constant surface concentration by

$$F.N_{pp} = \left|\frac{\overline{Sh}_{d,CRP}}{\overline{Sh}_{d,CSC}}\right|_t \cdot (F.E)_{CSC} \tag{IV.3.6}$$

It is important to notice, that this relation holds for equal surface concentrations only. *The product* $(F.E)_{CSC}$ *in this equation refers therefore to sorption with a constant surface concentration equal to the critical concentration.*

Constant diffusion coefficient

For constant diffusion coefficient the relation between the surface concentration and the time coordinate τ (= Fo) reads for constant surface flux (Luikov (1968)):

$$m_0 - m_i = 2\,F\sqrt{\tau}\sum_{n=1}^{\infty}\left\{\text{ierfc}\,\frac{(2n-1)-1}{2\sqrt{\tau}} + \text{ierfc}\,\frac{(2n-1)+1}{2\sqrt{\tau}}\right\} \tag{IV.3.7}$$

For short times the first term of the series dominates and the equation acquires a simple form:

$$m_0 - m_i = \frac{2}{\sqrt{\pi}}\,F\sqrt{\tau} \tag{IV.3.8}$$

It follows, that

$$F \cdot N_{pp} = \frac{\pi}{4}\,(m_0 - m_i) \tag{IV.3.9}$$

In paragraph IV.2.1 we showed, that

$$(F.E)_{CSC} = \frac{2}{\pi}\,(m_0 - m_i) \tag{IV.3.10}$$

Hence, the ratio between the two products is:

$$\frac{F.N_{pp}}{(FE)_{CSC}} = \frac{\pi^2}{8} \approx 1.23 \tag{IV.3.11}$$

whereas the ratio between the Sherwood numbers at the transition point amounts to

$$\frac{Sh_{d,CRP}}{Sh_{d,CSC}} = \frac{12}{\pi^2} \approx 1.22 \tag{IV.3.12}$$

For constant diffusivity the method can therefore be concluded to be valid.

Concentration dependent diffusivity

For variable diffusion coefficients some results are given in table IV.3.1. Also for these cases, excellent agreement between the two ratio's is observed.

Diffusion coefficient D_r	$\frac{F.N_{pp}}{(m_o-m_i)}$	$\frac{F.N_{pp}}{(EF)_{CSC}}$	$\frac{Sh_{d,CRP}}{Sh_{d,CSC}}{}_t$	D_{eff}	$\bar{D}_r$
1	.7854	1.23	1.22	1	1
m_r	.292	1.30	1.30	.372	.5
m_r^4	.0628	1.38	1.38	.080	.2
$\exp(8m_r)$	92	1.41	1.39	117	373
$\exp(-8m_r)$	.1	1		.13	.125

Table IV.3.1 Some calculated results for the penetration period with constant surface concentration

The table gives also values of the effective diffusion coefficient which is defined by

$$D_{eff} = \frac{\pi}{4} \frac{F\ N_{pp}}{(m_0-m_i)} \qquad \text{(IV.3.13)}$$

The values of this effective diffusivity deviate considerably from the concentration-averaged diffusivity D_r for the concentration dependences under consideration. Also for exponential concentration dependence a strong deviation is observed. Suzuki et.al. (1975) claim, that the critical point curve for high-intensive drying of slabs can be described by an effective diffusion coefficient equal to the concentration averaged diffusion coefficient, among others, in case of an exponential concentration dependence. This statement clearly is contradictory to the results of our calculations.

IV.3.3 Cylinders and spheres

For very small penetration distances the outer shell of a sphere or cylinder behaves like a slab. The relation describing the penetration period in non-shrinking systems then reads:

$$F \cdot N_{pp} = (\nu+1)(F \cdot N_{pp})_{slab} \tag{IV.3.14}$$

Analogously to the case of constant surface concentration, further refinement is required in order to describe the complete penetration period.

Constant diffusivity

For a *cylinder* the relation between the surface concentration and the time variable τ (= Fo) reads for constant surface flux and small values of τ (Luikov (1968)):

$$m_0 - m_i = \frac{2}{\sqrt{\pi}} F\sqrt{\tau} + \frac{1}{2} F\tau \tag{IV.3.15}$$

If we substitute the mass balance

$$2\, F\tau = N_{pp}\, (m_0 - m_i) \tag{IV.3.16}$$

this equation becomes for small values of N_{pp}

$$\frac{F}{(m_0 - m_i)} = \frac{\pi}{2}\frac{1}{N_{pp}} - \frac{\pi}{4} \tag{IV.3.17}$$

The solution of the diffusion equation for *spheres* with constant surface flux reveals for short times (Luikov (1968)):

$$m_0 - m_i = F\left\{\exp(\tau) \times \operatorname{erfc}(-\sqrt{\tau}) - 1\right\} \tag{IV.3.18}$$

This relation acquires a simpler form upon substitution of

$$\operatorname{erfc}(-\sqrt{\tau}) \simeq 1 + \frac{2}{\sqrt{\pi}} \sqrt{\tau} \qquad \text{(IV.3.19)}$$

and the Taylor series expansion for $\exp(\tau)$.

$$m_0 - m_i = \frac{2}{\sqrt{\pi}} F\sqrt{\tau} + F\tau \qquad \text{(IV.3.20)}$$

We substitute the mass balance

$$3F\tau = N_{pp}\,(m_0 - m_i) \qquad \text{(IV.3.21)}$$

The relation between N_{pp} and $F/(m_0 - m_i)$ then reads:

$$\frac{F}{(m_0 - m_i)} = \frac{3\pi}{4}\,\frac{1}{N_{pp}} - \frac{\pi}{2} \qquad \text{(IV.3.22)}$$

Analogously to the penetration period for constant surface concentration we have the following general formulation for the penetration period of non-shrinking cylinders and spheres:

$$F = (\nu+1)\left|\frac{(F.N_{pp})_{slab}}{N_{pp}}\right| - \Delta F \qquad \text{(IV.3.23)}$$

The term ΔF differs only slightly from ΔF for constant surface concentration (ΔF_{CSC}). The ratio between the terms for these two cases is independent of geometry and reads:

$$\frac{(\Delta F)_{CRP}}{(\Delta F)_{CSC}} = \frac{\pi}{3} \simeq 1.05 \qquad \text{(IV.3.24)}$$

Variable diffusion coefficient

From the results of many computer simulations it is concluded, that the equation (IV.3.23) also holds for variable diffusion coefficient, provided that N_{pp} is not too large.

In drying, the diffusion coefficient of water does generally not increase strongly with decreasing water concentration and this condition will therefore be satisfied. In table (IV.3.2) a few results of such calculations are given. It appears, that ΔF can be calculated according to (cfr. equation IV.2.49)

$$\Delta F = q \, \overline{D}_r \, (m_o - m_i) \qquad \text{(IV.3.25)}$$

where the coefficient q is related to the coefficient for constant surface concentration by

$$q_{CRP} \simeq 1.05 \, q_{CSC} \qquad \text{(IV.3.26)}$$

		SPHERE		CYLINDER	
D_r	$\frac{F}{m_0 - m_{cr}}$	ΔF	q	ΔF	q
$D_r = m_r$	3	.789	1.58	.395	.79
	2	.808	1.62	.412	.82
	1.5	.822	1.64	.425	.85
	1	.848	1.70	.451	.90
$D_r = m_r^4$	3	.288	1.44	.140	.70
	2	.292	1.46	.140	.70
	1.5	.296	1.48	.152	.76
	1	.301	1.51	.153	.77

Table IV.3.2 Some calculated results for the critical point curve in the penetration period for variable diffusion coefficient.

The value of q_{CSC} in relation to $D_r(m_0)/\overline{D}_r$ is given in figure (IV.2.6). The observations imply also, that the term ΔF, determined by one of the methods described in paragraph IV.2.2 can also be used in the calculation of the critical point curve during the penetration period, after application of equation (IV.2.23).

Shrinking systems

During the constant activity period in a drying process the surface flux increases with progress of drying due to the increasing continuous phase mass transfer coefficient (paragraph III.5). Hence, the value of F for a given N_{pp} is increased by this effect. For constant surface flux a relation for F would be expected, analogous to equation (IV.2.73). From the results presented by Kerkhof (1975) it appears, that the constant term ΔF may be compensated or even overcompensated by the effect of shrinkage. Therefore, the penetration period can effectively be described by the equation, which follows from the penetration period for slabs. The relation for the critical point curve in the penetration period can for high sorbent concentrations therefore be approximated by

$$F \simeq \left\{ \frac{m_0 - m_i}{(1 + m_0)^{1/(\nu+1)} - (1 + \bar{m})^{1/(\nu+1)}} \right\} (F.N_{pp})_{slab} \tag{IV.3.27}$$

IV.4 Conclusions

1. The penetration period is the period which precedes the regular regime in a sorption process with homogeneous initial concentration.
2. For constant surface concentration or constant surface flux this period is characterized by a single parameter (slabs) or at most two parameters (cylinders and spheres)
3. These parameters can be calculated from the regular regime sorption curve with constant surface concentration or from the concentration dependence of the diffusion coefficient.

4. For slabs with constant surface concentration the parameter E.F is calculated from the value of E at the point of transition to the regular regime (E_t) and the value of F in the regular regime at the same average concentration (F_t). The transition point is determined either by a graphical method or by assuming, that the concentration profile at the transition point is close to the profile for stationary mass transfer through the slab.
5. When $D_r(m_0) << \overset{\sqcup}{\overline{D}}_r$ the method under 4 can not be applied. The penetration period can then be calculated by assuming a uniformly retreating front from which mass transfer is quasi-stationary.
6. When $D_r(m_0) \leqq \overset{\sqcup}{\overline{D}}_r$ the penetration period for spheres and cylinders with constant surface concentration can be calculated from the parameter E.F for slab-penetration by relations which are derived from a shrinking core approach. The approach is also applied to swelling systems.
7. When $D_r(m_0) \geqq \overset{\sqcup}{\overline{D}}_r$ a second parameter, ΔF, is required for the calculation of the penetration period, in addition to the parameter E.F for slabs. For non-shrinking systems, ΔF can be calculated from the concentration dependence of the diffusion coefficient. Two graphical methods are described for the determination of ΔF from the regular regime sorption curve. One of these is also applicable to shrinking systems.
8. The critical point curve for the penetration period with constant surface flux is described analogously to the penetration period with constant surface concentration. It can be calculated from the regular regime sorption curve with constant surface concentration or from the concentration dependence of the diffusion coefficient.

V A SHORT-CUT METHOD FOR THE CALCULATION OF DRYING RATES IN CASE OF STRONGLY CONCENTRATION DEPENDENT DIFFUSION COEFFICIENTS

V.1 Introduction

The transfer of water in a drying specimen can for many water transport mechanisms, such as molecular diffusion, capillary transport and evaporation condensation, formally be described by the diffussion equation. Once the concentration dependence of the (apparent) diffusion coefficient is known, the drying rate and moisture distribution can be calculated by solving this diffusion equation with the appropriate initial and boundary conditions simultaneously with the (differential) equations for heat transfer. In general, these solutions have to be obtained numerically. As has been stated before, these calculations are rather cumbersome and data about the concentration dependence of diffusion coefficients in aqueous systems are very scarce.

Several alternative methods have been reported in literature for the approximate calculation of drying times. They generally make use of the characteristic properties of the constant and falling rate period of drying.

For the *constant rate period* a correlation method was recently developed by Kerkhof (1974, 1975). The method has been applied to the drying of food liquids. It requires only a few simple slab drying experiments from which the length of the constant rate period can be calculated for specimen of various geometries under practical conditions.

The first attempt to predict the length of the *falling rate period* has been made by Lewis (1921), who assumed the mass flux to be proportional to the difference between the average moisture content of the drying body and its final equilibrium moisture content. Since this method is only applicable to cases where constant diffusivities prevail, it is of limited practical interest. Broughton and Mickley (1953) have described a method of determining drying time by analogue experimentation. This method consists in the experimental simulation of practical drying conditions on laboratory scale. From a number of such experiments nomographs can be derived, as described by Van Arsdel (1973). Using these nomographs, interpolations can be made, thus limiting the number of experiments. These interpolations, however, still require many experiments and the results are only applicable to the specific geometries used. Under certain circumstances, e.g. when peculiar geometries and time-dependent physical properties are involved, analogue experimentation may be the only way to predict drying times.

Another method is based upon the concept of a characteristic drying curve (Van Meel (1958), Krischer (1963), Keey (1972)). It is assumed that the drying rate can be described by

$$n = n_{\text{const.rate}} \times f$$

where $n_{\text{const.rate}}$ is the mass flux during the constant rate period, n the mass flux and f the ratio between both fluxes, which is supposed to be a function of $(\bar{\omega} - \omega^*)/(\bar{\omega}_{cr} - \omega^*)$ only. In this relation the variable $\bar{\omega}$ represents the average moisture fraction, ω^* the equilibrium moisture fraction and $\bar{\omega}_{cr}$ the average moisture fraction at the end of the constant rate period. This generalization would be valid if all drying curves were geometrically similar, irrespective of temperature, initial concentration, initial mass flux and Biot number for mass transfer. The relation between f and the reduced average concentration $(\bar{\omega} - \omega^*)/(\bar{\omega}_{cr} - \omega^*)$ is referred to as the characteristic drying curve. From the severe assumption of similarity it follows that the method can only be approximate (Keey (1972)). Nevertheless, the method is reported to have some practical value for porous materials. It is however not valid for drying of solutions with strongly variable diffusion coefficient, as follows from the results of the diffusion calculations presented in this thesis. The description of the transport process cannot be generalized for different initial concentrations or initial drying rates by the introduction of a reduced mean weight fraction, since the diffusion coefficient depends on the absolute concentration itself.

This chapter deals with a new short-cut procedure for the calculation of drying rates in case of strongly concentration dependent diffusion coefficients. The procedure is based upon the concept of regular regime and penetration theory as described in the previous chapters. The application to the drying of slabs has been subject of a recent publication (Schoeber & Thijssen (1975)).

The main simplifying assumption in the model description is the absence of temperature gradients in the drying material. This assumption is justifiable when the heat required for water evaporation is supplied at the evaporating surface, in particular when heat is supplied by means of the drying air. From the Chilton-Colburn analogy between heat and mass transfer then follows, that the ratio of the Biot-numbers for heat (Bi_H) and mass transfer (Bi_M) can be expressed as:

$$\frac{Bi_H}{Bi_M} = \frac{\lambda_c}{\lambda_d} \frac{\mathbb{D}_d}{\mathbb{D}_c} \cdot \frac{1}{\alpha_m} \qquad (V.1.1)$$

where λ is the thermal conductivity and $\mathbb{D}$ the diffusivity of water in the continuous (index c) or dispersed phase (index d). α_m represents the partition coefficient of water, defined by

$$\alpha_m = \rho_m'^{*} / \rho_{m,i} \tag{V.1.2}$$

Here $\rho_m'^{*}$ is the water concentration in the gas phase in equilibrium with the surface concentration in the slab $\rho_{m,i}$. Typical values of these parameters in air drying are:

$\lambda_c \approx 0.026 \quad J/m^2\ s\ ^oC; \quad \mathbb{D}_c \approx 2.74\ 10^{-7}\ m^2/s$

$\lambda_d \approx 0.61 \quad J/m^2\ s\ ^oC; \quad \mathbb{D}_d < 10^{-9}\ m^2/s$

$\alpha_m > .02$

With these values equation (V.1.1) becomes

$$\frac{Bi_H}{Bi_M} < .008 \tag{V.1.3}$$

Up to high values of Bi_M, the heat transfer Biot-number is still so low, that temperature gradients in the dispersed phase are negligible. The heat transfer Biot-number is effectively even lower than is indicated by the ratio in equation (V.1.3), since part of the heat transferred to the dispersed phase is directly used for water evaporation at the phase boundary. When both heat and mass transfer are completely dominated by dispersed phase transport ($Bi_M \rightarrow \infty$; $Bi_H \rightarrow \infty$) the heat conduction is relatively fast compared to mass transfer:

$$\frac{\lambda_d}{d_d\ C_{p,d}\ \mathbb{D}_d} > 100 \tag{V.1.4}$$

where d_d and $C_{p,d}$ are the specific density (kg/m^3) and specific heat (J/kg ^oC) of the dispersed phase, respectively. Temperature gradients will therefore have disappeared after a relatively short period in the drying process. *In air drying, a uniform temperature in the drying specimen may generally be assumed.*

V.2 Typical drying histories

The isothermal drying of a slab of an aqueous solution of glucose is taken as an example to illustrate the present approach. Since the slab shrinks upon drying, the appropriate reduced diffusion coefficient D_r reads $D \times \rho_s^2$ (figure III.4.3). The value of $D_0 \times \rho_{s,0}^2$ which can be chosen arbitrarily, is taken here to be 1 kg^2/m^4s, so that D_r is numerically equal to $D \times \rho_s^2$. Figure V.2.1 shows a number of drying curves, presented in terms of the average concentration $\bar{m}$, which reads ρ_m/ρ_s for the shrinking system, and the flux parameter F, having the numerical value of $j_{m,i}^s\ d_s\ R_s$ (kg^2/m^4s).

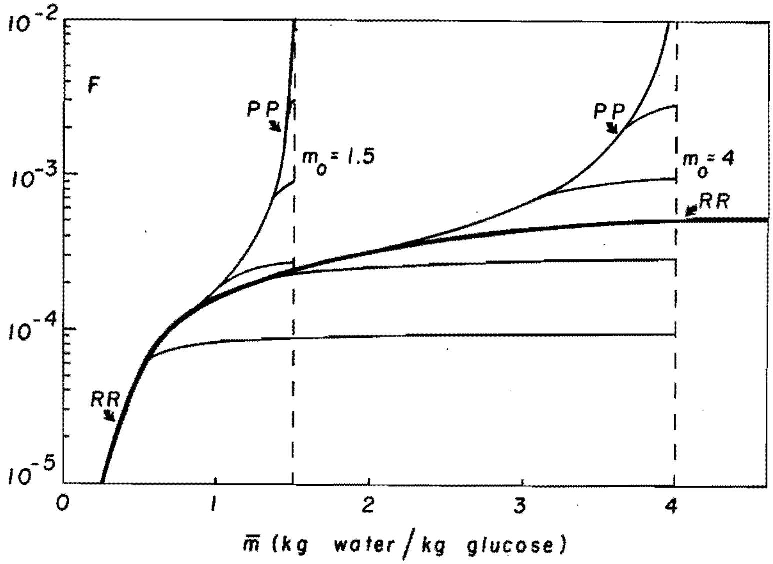


Fig. V.2.1 Isothermal drying curves of glucose slabs at 30 °C. Parameters are the initial water concentration (m_o = 2.5 and m_o = 4 kg water/kg glucose) and the initial value of the flux parameter. The mass transfer coefficient in the gas phase is taken constant during the drying process. PP: penetration period. RR: regular regime.

Two major conclusions can be drawn from this figure:

(i) The curve, which relates the flux parameter with the value of the average concentration at the end of the constant rate period ("critical point curve") coincides with the drying curve for the falling rate period. We call this curve the "*parent curve*". There exists one parent curve for every initial concentration m_0.

(ii) There exists one "*grandparent-curve*", which relates the flux parameter F and the average concentration and into which all parent curves for different values of m_0 eventually merge.

(i) The drying curves, starting at the same initial concentration with different initial drying rates all coincide after a -more or less- constant rate period in a parent curve. Consequently, this parent curve is independent of the initial drying rate and of the gas phase mass transfer coefficient.

Two conditions have to be fulfilled for this phenomenon to occur: First, the sorption isotherm of water should be such, that from the initial concentration down to a certain critical surface concentration the activity is fairly constant (e.g. close to 1). Secondly, the resistance to mass transfer inside the drying specimen should be rate-controlling soon after the surface concentration has dropped below the critical surface concentration. This means, that a further decrease of the surface concentration m_i to the equilibrium concentration m* has no influence on dispersed phase mass transfer. According to paragraph III.6.2 this means, that

$$\int_{m^*}^{m_i} D_r \, dm \ll \int_{m^*}^{\bar{m}} D_r \, dm \qquad (V.2.1)$$

This condition will generally be fulfilled if the effective value of Bi_M is sufficiently high (so that m_i is not too close to $\bar{m}$) and if the diffusion coefficient decreases strongly with decreasing moisture content when $m_i < m_{crit}$.

The two conditions set out above are generally fulfilled in drying aqueous systems where the dissolved solid component(s) are hydrophilic and have a molecular weight higher than about 150. Liquid foods fall very often in this category. The water vapour isotherm of liquid foods is generally such that the water activity does not differ much from unity above a certain critical moisture content m_{cr}. Below m_{cr} the water activity and the water diffusivity fall rapidly with decreasing moisture content, both being influenced by the increasing water binding forces. Upon passing the critical water concentration at the surface and entering the falling rate period of drying, the resistance to mass transfer inside the drying body starts to grow rapidly and soon it controls the mass transfer rate completely. The water concentration at the interface falls rapidly and soon equation V.2.1 will be fulfilled. The drying rate can then be described by the relations for constant surface concentration: *The parent curve reflects in fact the drying history of a slab with homogeneous initial concentration and constant surface concentration.*

If the critical concentration is equal to the equilibrium concentration, the constant rate period extends down to a lower average concentration than would be indicated by the parent curve. This has been stated in the chapters III and IV already. For constant diffusion coefficient this effect may be considerable (see figure V.2.2).
However, if the diffusion coefficient decreases sharply with concentration, this difference in terms of $\bar{m}$ is less (figure V.2.3). In practice, this effect is reinforced by the decrease in surface activity that occurs before equation (V.2.1) is fulfilled. Another effect has already been mentioned in paragraph III.5. Due to the increase in air humidity with progress of drying in a practical drying process, the drying rate will often decrease during the

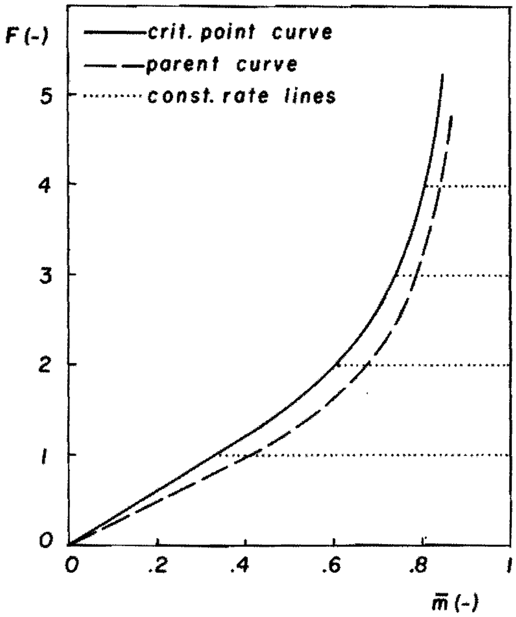


Fig. V.2.2

Critical point curve for a critical concentration equal to zero and constant diffusion coefficient ($D_r=1$). Initial concentration $m_o=1$. The broken line represents the parent curve for constant surface concentration $m_i=0$. Dotted lines represent some constant rate periods for various values of F.

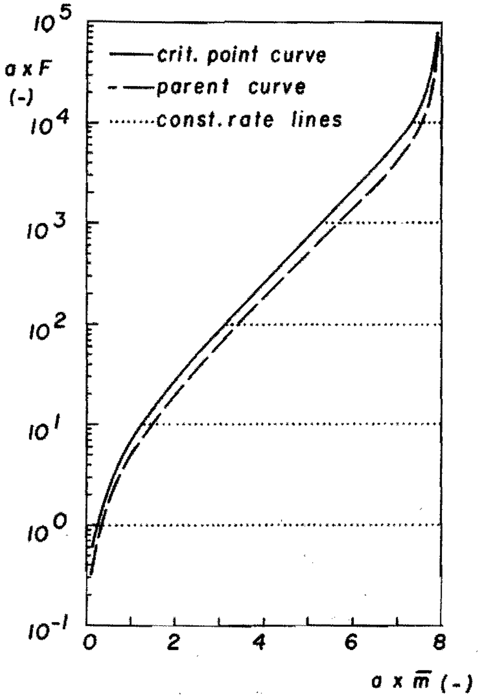


Fig. V.2.3

Critical point curve for a critical concentration equal to zero and exponentional concentration dependence of the diffusion coefficient (D_r=exp (am)). Initial concentration $am_o=8$. The broken line represents the parent curve for constant surface concentration $m_i=0$. Dotted lines represent some constant rate periods for various values of F.

"constant activity period". This also brings the critical point curve closer to the parent curve. *The parent curve is indeed a good approximation of the critical point curve in case of strongly concentration dependent diffusion coefficients.*

(ii) The parent curves of different initial concentrations merge after some drying time has elapsed into a "grand-parent" curve. The concentration distribution inside the drying body becomes virtually independent of the initial distribution: the regular regime of drying with constant surface concentration is reached. *This regular regime drying curve is characteristic for the material to be dried and its position in the flux parameter-average concentration diagram depends on temperature and equilibrium concentration only.* It contains all the information needed to calculate isothermal drying histories for any initial concentration and any initial drying rate.

The present short-cut method consists in the calculation of complete drying histories of slabs, cylinders and spheres from an experimentally determined regular regime curve. For non-isothermal drying or isothermal drying at different temperature levels a second regular regime curve at a different temperature has to be determined experimentally.

V.3 Isothermal slab drying

V.3.1 Determination of the regular regime drying curve

In the calculation of drying histories the regular regime drying curve plays a very important role: it is the drying history which is followed after a certain amount of water has been evaporated. In addition, the penetration period can be calculated from the regular regime (chapter IV). The regular regime drying curve of a material for a given temperature and surface (equilibrium) concentration can be obtained in several ways: (i) direct experimental determination, (ii) calculation from regular regimes for different temperatures, (iii) calculation from regular regimes for different surface concentrations and (iv) calculation from the relation between the diffusion coefficient and concentration.

(i) *Experimental determination of the regular regime drying curve in the concentration interval of interest*

This can be achieved by drying a slab with an initial concentration that is higher than or equal to the upper limit of this concentration interval. The initial value of the flux parameter F (to be influenced by slab thickness, gas phase mass transfer coefficient and slab temperature) should be so high, that the constant rate period is clearly followed by a penetration period with constant surface concentration. This can be checked by plotting the average concentration $\bar{m}$ versus the square root of time, which yields a straight line for the penetration period.

(ii) *Calculation of the regular regime curve from the regular regimes at two different temperatures*

It is well known, that the temperature dependence of the diffusion coefficient can be described by the Arrhenius equation

$$D = D_\infty \exp(E_D/RT) \qquad (V.3.1)$$

where D_∞ is the diffusion coefficient in the limit $T \to \infty$, E_D the activation energy of diffusion, R the gas constant and T the absolute temperature. It is clear, that if this activation-energy is independent of concentration, the shape of the concentration profiles is not influenced by the temperature because this temperature effect can be accounted for in the time parameter: the relative change of F is equal to the relative change in D_r with temperature, so that

$$E_F = E_D \tag{V.3.2}$$

However, in case of variable diffusivity also the activation energy is generally concentration dependent. Nevertheless it was found, that the temperature dependence of the flux parameter F in the regular regime can by good approximation be described by the Arrhenius equation:

$$F = F_\infty \exp(-E_F/RT) \tag{V.3.3}$$

where F_∞ is the value of F in the limit $T \to \infty$ and E_F the concentration dependent activation energy. This is illustrated in figure V.3.1, which shows an Arrhenius plot of ln F versus 1/T for the drying of a slab of an aqueous solution of glucose.

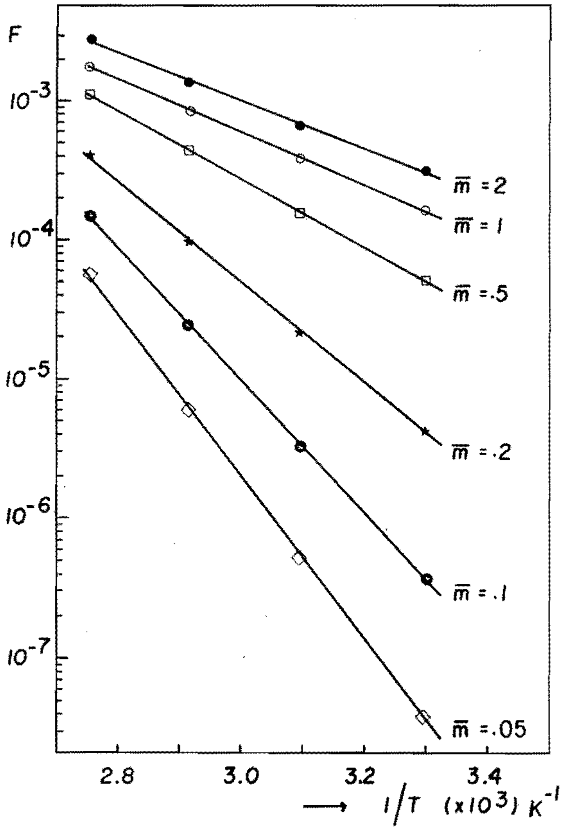


Fig. V.3.1

Arrhenius plot showing the temperature dependence of the flux parameter F in the regular regime for isothermal diffusion of water in a glucose slab. Parameter: the average water concentration in the slab (kg water/kg glucose). The surface concentration m_i=0.

By first approximation this activation energy is equal to the activation energy of the concentration averaged diffusion coefficient $\overline{D}_r$ (see figure V.3.2).

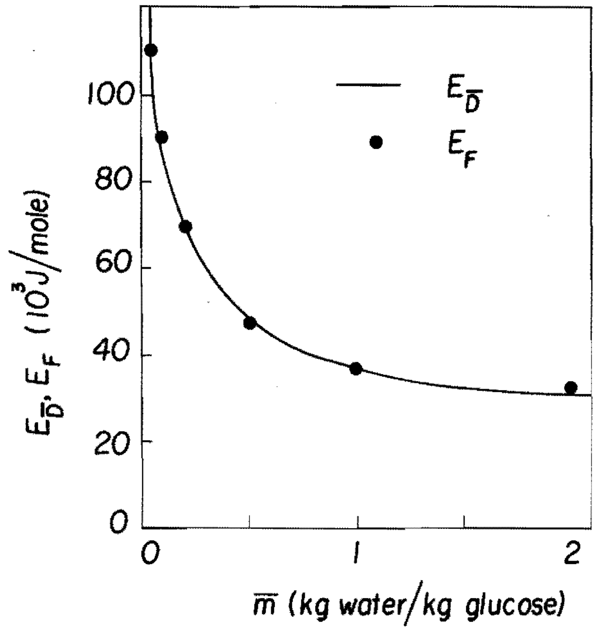


Fig. V.3.2.

Activation energy of the concentration averaged diffusion coefficient ($E_{\overline{D}}$) and of the flux parameter (E_F) in relation to the average concentration $\overline{m}$. Regular regime of drying of a slab of an aqueous glucose solution with zero surface concentration.

It can be concluded, that the experimental determination of the regular regime drying curve at two different temperatures provides sufficient information to allow the calculation of regular regimes at any temperature by means of the Arrhenius equation with concentration dependent activation energy.

(iii) *Calculation from an experimentally determined regular regime drying curve with different surface concentration e.g. surface concentration zero.*

If the diffusion coefficient is strongly dependent on the concentration, in particular if D_r is low in the region down from m_i, the flux parameter F is hardly influenced by the value of m_i (see paragraph III.6.2). Only if m_i is relatively high or the average concentration approaches the equilibrium concentration closely the following procedure is necessary to apply. We differentiate the regular regime curve in order to obtain d ln F/d ln $(\bar{m}-m_i)$. From figure III.4.6a we can obtain the Sherwood number $\overline{Sh}_d$ in relation to the average concentration $\bar{m}$. With this Sherwood number the integrated diffusion coefficient is calculated:

$$\int_{m_i}^{\bar{m}} D_r \, dm = 2F/\overline{Sh}_d \qquad (V.3.4)$$

From the observation, that d ln F/d ln $(\bar{m}-m_i)$ is approximately equal to $D_r(\bar{m})/\bar{D}_r$ the following approximate relation is derived:

$$\left\{\frac{d \ln F}{d \ln (1-E)}\right\}_2 = \frac{(\bar{m}-m_2)}{(\bar{m}-m_1)} \left\{\frac{\int_{m_1}^{\bar{m}} D_r \, dm}{\int_{m_2}^{\bar{m}} D_r \, dm}\right\} \left\{\frac{d \ln F}{d \ln (1-E)}\right\}_1 \qquad (V.3.5)$$

The index 1 refers to the "old" regular regime curve with surface concentration m_1 and the index 2 refers to the regular regime curve to be calculated with surface concentration m_2. After application of this relation we can find the relation between $\overline{Sh}_d$ and $\bar{m}$ for the new regular regime curve from figure III.4.6a. The value of the flux parameter at every concentration follows then from the equation

$$F_2 = \frac{1}{2} \, Sh_{d,2} \left\{ \int_{m_1}^{\bar{m}} D_r \, dm - \int_{m_1}^{m_2} D_r \, dm \right\} \qquad (V.3.6)$$

Also when the surface concentration changes with progress of drying the same procedure can be applied, provided that this change of surface concentration is not so fast that it has considerable influence on the Sherwood number.

(iv) *Calculation from the relation between diffusion coefficient and concentration*

We integrate the diffusion coefficient between the surface concentration and the average concentration for various average concentrations:

$$\int_{m_i}^{\bar{m}} D_r \, dm$$

For the estimation of the Sherwood number $\overline{Sh}_d$ we use the parameter

$$\frac{D_r(\bar{m})}{\bar{D}_r} = \frac{(\bar{m}-m_i)\ D_r\ (\bar{m})}{\int_{m_i}^{\bar{m}} D_r \, dm} \qquad (V.3.8)$$

and figure III.4.5a. The flux parameter for every average concentration is calculated by

$$F = \frac{1}{2}\ \overline{Sh}_d \int_{m_i}^{\bar{m}} D_r \, dm \qquad (V.3.9)$$

The regular regime drying curve obtained in one of these ways serves as a basis for the calculation of the complete drying history.

V.3.2 Calculation of the parent curve and the length of the constant rate period

Since the parent curve represents the drying from a certain homogeneous initial concentration with a constant surface (equilibrium) concentration it can be divided into a regular regime and a penetration period. The penetration period is calculated from the regular regime by one of the methods described in chapter IV.

The evaporation rate during the constant rate period is determined by gas phase mass transfer. For non-shrinking systems this can be formulated as

$$n'_{m,i} = k'_g\ (A_i\ \rho'^{*}_{water} - \rho'_{m,bulk}) \qquad (V.3.9)$$

where $n'_{m,i}$ is the mass flux through the phase boundary in the gas phase, k'_g the mass transfer coefficient in the gas phase and A_i the relative humidity at the surface. ρ'^{*}_{water} is the water concentration in the gas phase in equilibrium with pure water at the slab temperature and $\rho'_{m,bulk}$ is the water vapor concentration in the bulk of the gas phase.
For shrinking or swelling systems $j^{s}_{m,i}$ has to be substituted for $n'_{m,i}$ in equation (V.3.9). The value of F during the constant rate period is the product of this mass flux and the slab thickness in the appropriate coordinates (R or $d_s\ R_s$). The end of the constant rate period ("critical point") is the intersection point between the constant rate line (parallel to the $\bar{m}$-axis) and the parent curve (cfr. figure V.2.1). The duration of the constant rate period in terms of the time parameter then reads:

$$\tau_{cr} = (m_0 - m_{cr}) \; / \; F \qquad \text{(V.3.10)}$$

where the index cr refers to the critical point.
Although this approximation of the length of the constant rate period may be accurate enough for the calculation of drying times, more accuracy may be required for other purposes, e.g. the calculation of aroma retention (Kerkhof (1975)). In that case the critical point curve may be calculated from the regular regime curve with a constant surface concentration equal to the critical concentration. We apply the ratio between the values of F of the critical point curve and the regular regime as presented in figure III.5.1. For the penetration period the value at the transition point is used (cfr. paragraph IV.3). If the diffusion coefficient in relation to the concentration is unknown the value of $D_r(\bar{m})/\bar{D}_r$ can be approximated by the differential quotient d ln F/d ln $(\bar{m}-m_i)$ of the regular regime curve.

V.4 Isothermal drying of spheres and cylinders

V.4.1 Regular regime drying curve with constant surface concentration

The regular regime drying curve with constant surface concentration can be calculated for a desired temperature and surface concentration according to several methods. All except one are analogous to the methods for slabs as described above. They follow directly from the analysis presented in the chapters III and IV of this thesis. An additional possibility is the calculation from a regular regime curve of a slab. This procedure is as follows:
By differentiation of the regular regime curve of a slab we find d ln F/d ln $(\overline{m}-m_i)$ in relation to the average concentration $\overline{m}$. $\overline{Sh}_d$ is then obtained from figure III.4.6a. The "non-shrinking" $\overline{Sh}_d$ for the sphere or cylinder then follows from figure III.7.1. For shrinking systems $\Delta\overline{Sh}_d$ has to be added, which can be read from figure III.4.8 in relation to the average concentration (volume fraction). The value of F for the sphere or cylinder is then calculated from the equation

$$F = \frac{\overline{Sh}_d}{\overline{Sh}_{d,slab}} F_{slab} \qquad (V.4.1)$$

The "translation" of a regular regime curve to a different geometry is analogous for other transitions (e.g. cylinder → sphere). The ratio between the sorption rates for different geometries, θ, is equal to the ratio between the values of the Sherwood number:

$$\theta = \frac{F_1}{F_2} = \frac{\overline{Sh}_{d1}}{\overline{Sh}_{d2}} \qquad (V.4.2)$$

where the indices 1 and 2 refer to different geometries. An error in the estimation of $\overline{Sh}_d$ for the basic geometry causes an error in the value of θ calculated according to the above method. The error propagation can be calculated analytically by differentiation of the equations (III.7.1-3). Three examples are *slab → sphere:*

$$\frac{d \ln \theta}{d \ln \overline{Sh}_{d,slab}} = \frac{9.13}{\overline{Sh}_{d,sphere}} \tag{V.4.3}$$

slab → cylinder:

$$\frac{d \ln \theta}{d \ln \overline{Sh}_{d,slab}} = \frac{4.45}{\overline{Sh}_{d,cylinder}} \tag{V.4.4}$$

sphere → slab:

$$\frac{d \ln \theta}{d \ln \overline{Sh}_{d,sphere}} = - \frac{2.87}{\overline{Sh}_{d,slab}} \tag{V.4.5}$$

It can be concluded, that for the values of the Sherwood number under consideration, the error in the ratio θ is of the same order of magnitude as the error in $\overline{Sh}_d$. From the figures (III.4.6a-c) it follows that $\overline{Sh}_d$ can generally be estimated with the highest accuracy for slabs, compared with the other geometries. However, the error propagation is slightly larger when the slab is used as basic geometry for the calculation of regular regime curves. Therefore, *the relative error in θ is practically independent of the basic geometry used.* It will generally be less than 5%.

V.4.2 Penetration period and constant activity period

The penetration period with constant surface concentration can be calculated from the regular regime by one of the methods described in chapter IV. Also the calculation of the length of the constant activity period is analogous to the calculation for slabs. Only for shrinking systems has the effect of shrinkage on the gas phase mass transfer coefficient to be taken into account.

V.5 Non-isothermal drying

It has been stated before, that in case of a concentration independent activation-energy of the diffusion coefficient the shape of the concentration profile is *not influenced* by a changing temperature. This implies, that the value of the flux parameter at a given average concentration lies on the isothermal parent curve belonging to the actual slab temperature.

If the diffusion coefficient decreases strongly with decreasing concentration,the concentration profile inside the drying specimen tends to a rectangular shape. Despite a strongly variable activation-energy a varying temperature does not effect the shape of the profile very much. Therefore, the value of F at a given average concentration still lies in good approximation on the isothermal drying curve belonging to the actual slab temperature. If the temperature of the drying body is known in relation to the surface flux-parameter F and/or the average moisture content, the non-isothermal drying curve can be obtained from the isothermal parent curves at different temperatures. This is illustrated in figure V.5.1, which shows the non-isothermal drying curve for a slab of an aqueous glucose solution. We assumed heat and mass transfer to take place by convection only and in addition the Chilton-Colburn analogy is assumed to apply. The effect of possible changes in the heat content of the slab is neglected. The slab is dried with air of 90 ^{o}C and the moisture content of the air is taken to be zero. For any surface water activity the temperature of the slab and the surface water concentration in the gas phase can be derived from a psychrometric chart. The adiabatic cooling line, corresponding to the air temperature and -humidity involved, is used in this calculation. Thus, at any temperature between the wet and dry bulb values we can calculate the ratio between the actual driving force during the constant activity period. With this ratio and the value of the flux parameter F during the constant activity period

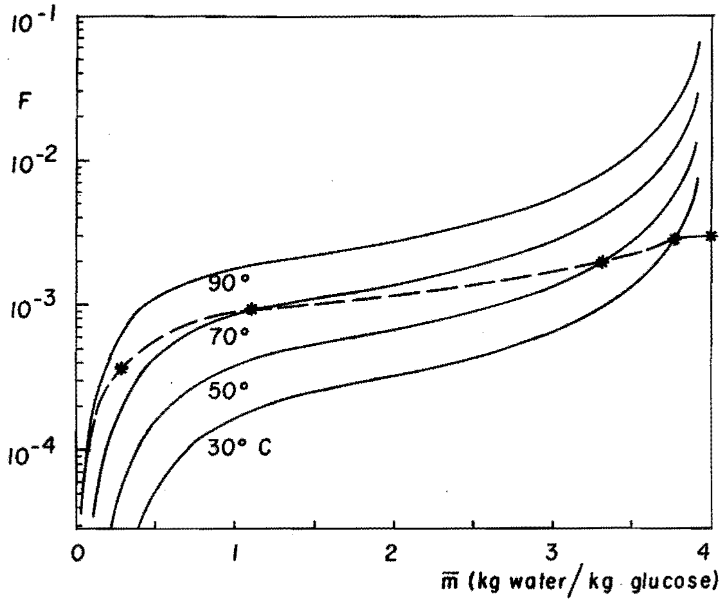


Fig. V.5.1 Non-isothermal drying of a slab of an aqueous solution of glucose. The solid curves are isothermal parent curves for various temperatures. The broken curve is the non-isothermal drying curve with air temperature 90 °C and air humidity 0 kg water/m^3. The mass transfer coefficient in the gas phase is taken constant. The asterisks indicate the points calculated using the present method.

we calculated the relation between F and the slab temperature. For a given temperature the value of F is related to the average concentration by the isothermal parent curve. The point on this parent curve where the value of F is equal to the value of the flux parameter calculated for the same temperature from the psychrometric chart belongs then to the non-isothermal drying curve. The asterisks in figure V.5.1 represent the points calculated in this way. It can be concluded, that *the mass transfer rate inside the drying slab is virtually independent of the temperature history: only the actual slab temperature is of relevance.* Mass transfer coefficients inside a non-isothermally drying specimen are by good approximation equal to mass transfer coefficients for isothermal drying at the same temperature.

A more severe testing of the influence of a change in temperature on the value of F and on the time needed to reach the isothermal parent curves is illustrated in figure V.5.2.

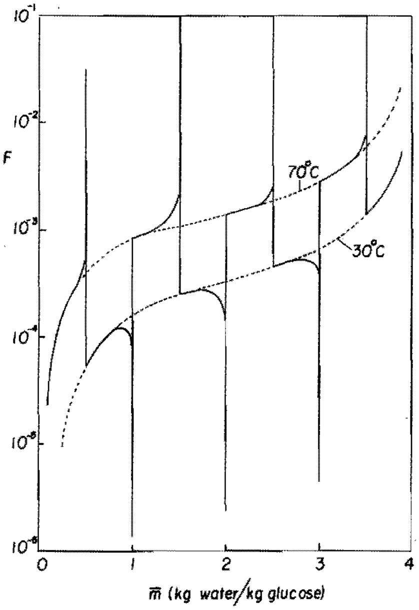


Fig. V.5.2 Drying history of a slab of an aqueous glucose solution with zero surface concentration. When $\bar{m}$ is a multiple of .5 the temperature is forced from 30 to 70 °C and vice versa. The broken curves represent the isothermal parent curves of 30 and 70 °C respectively.

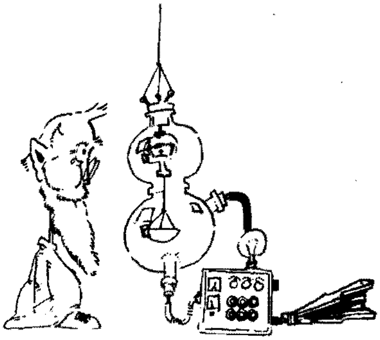
In this figure a temperature-game is played of the following nature: a sudden change in temperature from 30 to 70 °C and vice versa is forced every time $\bar{m}$ is a multiple of

.5 kg water/kg glucose. The surface concentration m_i is taken to be zero. Directly upon the change of temperature, the value of F changes in correspondence with the activation-energy of the diffusion coefficient at the surface concentration. (E_D = 139 kJ/mole). However, soon after this change the value of F in relation to $\bar{m}$ follows the isothermal parent curve of the actual temperature already.

V.6 Conclusions

1. When the diffusion coefficient decreases strongly with decreasing water concentration the critical point curve (F in relation to $\bar{m}$ at the end of the constant rate period) can generally be assumed to coincide with the isothermal drying curve for the falling rate period ("parent curve").
2. The isothermal regular regime drying curve can be obtained by direct experimental measurement or can be calculated from the regular regime curve under different conditions (temperature, surface concentration) or from a regular regime curve for a different geometry.
3. The mass transfer rate inside a non-isothermally drying specimen is virtually independent of the temperature history; only the actual temperature is of relevance. Dispersed phase mass transfer coefficients during the regular regime are therefore determined only by average concentration, surface concentration and actual temperature.

VI DETERMINATION OF CONCENTRATION DEPENDENT DIFFUSION COEFFICIENTS



VI.1 Introduction

The determination of diffusion coefficients has been subject to a vast number of publications. Methods of measurement have been reviewed, among others, by Johnson & Babb (1956), Crank (1956) and Crank & Park (1968). The many methods described can be subdivided into various classes according to different criteria.

1. Some methods deal with physical phenomena which are - just like diffusion - related to the mobility of certain molecules: transverse or spin-spin relaxation in nuclear magnetic resonance (Torrey (1956), Crank & Park (1968)) and quasi-elastic light scattering (Gulari et al. (1973)). These techniques have, up to now, only been applied to a very few compounds. It is questionable whether these methods can be applied to more complex aqueous systems, such as liquid foods. Furthermore, these determinations require highly sophisticated instrumentation.

2. The vast majority of the methods for the determination of diffusion coefficients consists in the comparison of the results of a diffusion experiment (in terms of concentration profiles, sorption rates, etc.) with the solution of the diffusion equation for this particular case. The (concentration dependence of the) diffusion coefficient is then adjusted so that the model description fits the experimental result. In fact, this is a parameter-estimation problem.

The properties of the system in which the diffusion coefficient is to be measured sets constraints to the experimental method of measurement. Measurements may be *internal* or *external*.

2.1 *Internal measurement* of concentration gradients can be performed by non-destructive techniques which require a certain (natural) labeling of the migrating components and by destructive techniques where the body is sliced and the average concentration in every slice can be determined. The non-destructive techniques include optical methods (optical density, refractive index, gradient in refractive index) and other radiation methods (radiation absorption, radio-tracer methods). Optical methods have been widely used for the determination of liquid diffusivities and the diffusion coefficients of sugar solutions (e.g. Gosting & Morris (1949), Longsworth (1953), English & Dole (1950), Gladden & Dole (1953), v.d. Lijn (1976)). For natural systems, such as fruit juices, extracts etc. these methods can not be applied due to the presence of a mixture of compounds, coloured components and (coloidal) dispersed materials. Since the other internal methods are technically rather cumbersome (radioactivity) or laborious (micro-slicing), external measurements are to be preferred for such systems.

2.2 *External measurement* of global variables such as average concentration and surface flux or surface concentration is often the most attractive or the only possible way to follow a diffusion process. This process can be stationary or unstationary:

2.2.1 *Steady state.* The interpretation of the results from steady state measurements is relatively simple, since the diffusion equation goes over into an ordinary differential equation. A disadvantage, however, is the long period of time that may be required to reach the steady state, in particular when the diffusion coefficient is very low. Another disadvantage is of experimental origin. Since the steady state in a sorption process corresponds with the trivial solution of the diffusion equation $m(\phi,\tau) = m_i$, the only relevant stationary method is permeation through a membrane. It is clear, that this technique may give rise to some experimental problems when the diffusion coefficient in a liquid is to be measured.

2.2.2 *Unsteady state.* A (de)sorption process is very often used for the determination of diffusion coefficients. When the diffusion coefficient depends on concentration, however, the interpretation of such experiments is relatively complicated. This will in more detail be discussed below.

Interpretation of sorption experiments with concentration dependent diffusivity

1. The diffusion process takes place over such a small concentration interval, that the diffusivity can be assumed to be constant. In that case a large number of experiments is required to determine the whole concentration dependence of the diffusion coefficient. Also when a greater interval is involved, the relations for constant diffusivity can be applied in order to obtain an "effective" diffusion coefficient. By iteration a relation can be obtained between a concentration-averaged diffusion coefficient and this effective diffusion coefficient (Crank & Park (1949)). The method requires a number of experiments to obtain the concentration dependence of the concentration averaged diffusion coefficient. The diffusivity in relation to concentration can then be calculated by differentiation. Some other, analogous methods have been reviewed by Crank (1956).

2. A trial and error method has been presented by Huang (1952), which has also been used by Verstegen (1968). The whole concentration dependence of the diffusion coefficient over the concentration range of interest is calculated from

a single sorption curve. A certain relation has to be postulated for the concentration dependence of the diffusion coefficient. By trial and error the parameters in this equation are estimated in such a way that the numerically calculated curve fits the experimental curve. Disadvantages of this method are the number of (much time-consuming) computer simulations required and the fact that the type of concentration dependence of the diffusion coefficient, which is unknown, has to be postulated beforehand.

In this thesis, we present two new methods of calculating the concentration dependence of the diffusion coefficient from a single sorption experiment:

3. The concentration dependence of the coefficient is approximated by a step function. This step function can be calculated step-by-step when the surface concentration moves (slowly) from the initial to the equilibrium concentration during the sorption process. The method is described in appendix D.

4. Another method is based upon the properties of the regular regime of sorption with constant surface concentration, which has been analyzed in chapter III of this thesis. The method is described in the following paragraph. It is applied to an experimentally determined isothermal drying curve of a slab of an aqueous glucose solution.

VI.2 Calculation of the concentration dependence of the diffusion coefficient from the Regular Regime Sorption Curve.

In chapter III the influence of the variation of the diffusion coefficient on the sorption rate was analyzed for the case of constant surface concentration. The results of this analysis offer a procedure to calculate the complete concentration dependence of the diffusion coefficient over the concentration interval over which the regular regime (de)sorption curve has been determined experimentally. The procedure can be applied to all of the geometries treated in chapter III. We take the drying curve of a *slab* as an example. The use of the slab geometry has two advantages: (i) it is relatively easy to create a flat layer of uniform thickness and (ii) the relative variation of $\overline{Sh}_d$ with d ln F/d ln (1-E) is for slabs less than for the other geometries (figures III.4.6a-c).

The calculation procedure consists of the following steps:

1. Differentiation of the regular regime curve in order to obtain the quantity d ln F/d ln $(\bar{m}-m_i)$ in relation to the average concentration $\bar{m}$. The Sherwood number $\overline{Sh}_d$ is correlated with this quantity.
2. From figure III.4.6a we can read $\overline{Sh}_d$ for every average concentration. A good "average" curve in this figure is the relation for $D_r = m^a$. If d ln F/d ln $(\bar{m}-m_i)$ *decreases* with progress of the sorption process, $\overline{Sh}_d$ will generally be slightly *higher* than is indicated by this curve (e.g. exponential dependence). If this parameter *increases* with progress of time, $\overline{Sh}_d$ will generally be *lower* than is indicated by the curve for $D_r = m^a$ (e.g. water-glucose). For the interpretation of the regular regime sorption curve of a certain system we will preferentially use the relation between d ln F/d ln (1-E) for a system for which the concentration dependence of the diffusion coefficient can be expected to be similar to the diffusivity of the system under consideration. For instance, the relation for water-glucose at 30°C can be expected to be close to the relation for water-glucose at other temperatures. It will even be a reason-

able approximation for the relation for other aqueous carbohydrate solutions.

3. The diffusion coefficient integrated over the concentration interval $m_i < m < \overline{m}$ is then calculated according to:

$$\int_{m_i}^{\overline{m}} D_r \, dm = \frac{2F}{\overline{Sh}_d} \qquad (VI.2.1)$$

4. The concentration dependence of the diffusion coefficient is finally obtained by differentiation of the integrated diffusivity with respect to $\overline{m}$:

$$D_r \; (\overline{m}) \; = \frac{d}{d\overline{m}} \int_{m_i}^{\overline{m}} D_r \, dm \qquad (VI.2.2)$$

Accuracy

The relative error in the integrated diffusivity is smaller than or equal to the sum of the relative errors in F (experimental error) and in $\overline{Sh}_d$ ("theoretical error"). The relative error in $\overline{Sh}_d$ can be expected to be smaller than about 5%, if a reasonable approximation to the relation between d ln F/d ln (1-E) and $\overline{Sh}_d$ is used in the interpretation. If a better accuracy is required an iteration may be applied by calculation of the relation between $\overline{Sh}_d$ and d ln F/d ln (1-E) for the concentration dependence calculated in the first approximation. One iteration will generally be sufficient since this relation is not very sensitive to the kind of concentration dependence of the diffusion coefficient. The relative error in the integrated diffusion coefficient is then equal to the relative error in the experimentally determined F. From the analysis presented in this thesis it can be concluded that the concentration-averaged diffusion coefficient determines the sorption rate mainly. Hence, the relative error in F will result in approximately the same relative error in the sorption rate calculated with the concentration dependence of the diffusion coefficient obtained by using the present method.

The error in the diffusivity itself may be higher due to the differentiation. However, so many "points" of this concentration dependence are obtained, that the noise can effectively be eliminated. Only at the end of the experimentally measured curve this may be difficult and a slightly higher error may result.

VI.3 Experimental

VI.3.1 Drying apparatus

For the determination of the regular regime drying curve it is required, that the constant rate period is clearly followed by a penetration period which effectively behaves as if the surface concentration were constant ($Bi_{eff} \rightarrow \infty$). A high value of Bi_{eff} can be realized by taking thick slabs and/or by creating a high mass transfer coefficient in the gas phase. Since the thickness of the slab also influences the time-scale of the drying process, the gas phase mass transfer coefficient should be maximized anyhow. This is the reason why we have chosen vacuum-drying in the experimental set up to establish the regular regime drying curves. In this pressure range, gas phase diffusion coefficients are approximately inversely proportional to the absolute pressure (Bird et al (1960)).

The drier is diagrammatically shown in figure VI.3.1. It consisted of two horizontal cylindrical vessels, one on top of the other and connected with each other by means of a tube. The diameter of each vessel was 60 cm. and the depth 70 cm. At the front the cylindrical vessels were closed by covers provided with "O"-rings. The sample holder in the lower cylinder was connected to a precision Mettler balance in the upper cylinder by a wire. During the drying

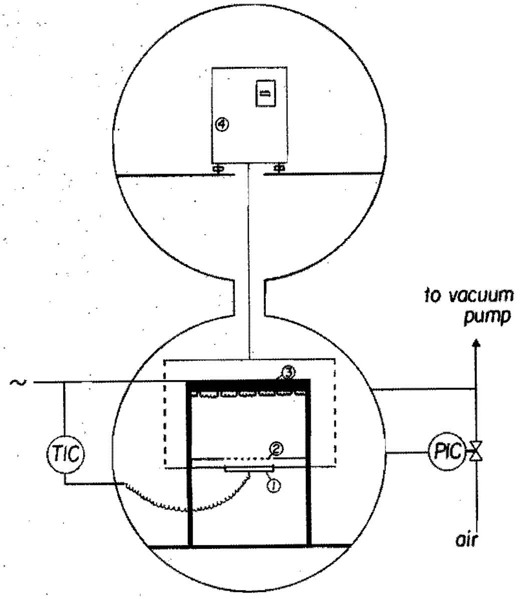


Fig. VI.3.1. Vacuum drying apparatus. (1) sample holder; (2) sieve plate; (3) radiation plate; (4) precision balance. A constant air stream is blown between the sieve plate (2) and the radiation plate (3).

process the weight of the sample and sample-holder could be read from the balance through a "perspex" window in the center of the cover of the upper vessel.

The energy necessary for the evaporation of water was supplied to the drying sample by an electrically heated radiation plate, placed 10 cm. above the sample holder. Between the sample holder and the radiation plate air was blown, approximately evenly distributed over the surface area of the sample. In order to avoid uneven drying of the slab a sieve plate had been placed between the sample holder and the air stream, at 1 cm. above the sample holder.

The stainless steel sieve plate had an open surface area of 32.5%, round openings of .19 mm diameter and was .04 mm thick. The aim of this set-up was to create a diffusional resistance between the sample and the sieve plate, which would be constant over the slab surface. Above the sieve plate convective transport of the water evaporated could take place. Introductory experiments showed that the presence of this sieve-plate effectively avoided the influence of wall effects etc. in case of a direct air stream over the sample and that even drying was created.
The energy input to the electric heater was controlled automatically in such a way, that the temperature of the bottom of the drying sample was kept constant within 0.3°C during the drying process. A constant air flow over the sample was taken from the laboratory low pressure circuit and amounted to $.6 \times 10^{-3}$ Nm^3/s. The total chamber pressure was kept constant within 1 mm Hg by adjusting the air flow through an air inlet just before the vacuum pump.

The sample holder consisted of a PTFE ring with an inner diameter of 111 mm and an outer diameter of 118.5 mm. This material was chosen because it is hydrophobic and therefore the wall would have a negligible effect on the distribution of the slab thickness over the sample holder. The ring, with a height of 10 mm had been attached to a red copper bottom plate of 2 mm thickness and 118.5 mm diameter. In the centre of the bottom plate a thermocouple was fixed through the plate with its junction .5 mm above the plate.

VI.3.2 Experimental procedure

In order to test the present method experimentally the drying of a slab of an aqueous solution of glucose was chosen. This, because the water diffusion coefficient in such solutions has been determined over a wide range of concentrations by Gladden and Dole (1953). This diffusion coefficient depends strongly on the water concentration. Furthermore, glucose has a low tendency to crystallize in supersaturated solutions because of the high viscosity of these solutions.

The experiments were carried out on gelled slabs in order to avoid convective transport inside the slab. The addition of agar-agar in small amounts to aqueous solutions appears to have a negligible effect on the diffusion rate of water (Kamenka (1966), Ermolaev & Levchenko (1968)).

A mixture of about 100 grams of water and glucose in the desired ratio and 1 gram of agar-agar was heated until a clear solution was obtained. The sample was then prepared by injecting the desired amount of the warm solution into the sample holder, which was placed on a flat, horizontal heat exchanger, thermostated slightly above the desired drying temperature. The empty sample holder had been weighed beforehand. After injection of the liquid, the sample holder was closed by means of a brass cover plate, which was kept at a temperature higher than the temperature of the solution to avoid condensation. After cooling for about one hour the sample holder was placed in the drying apparatus and attached to the balance. The apparatus was evacuated down to a pressure of about 5 mm Hg above the equilibrium vapor pressure of pure water at the slab temperature.
The weight of the sample and sample holder was then read from the balance at time intervals which increased with progress of the drying process. Typical duration of one experiment was three days.

VI.4 Results and discussion

Introductory experiments with gelled slabs of aqueous solutions of 1% agar-agar showed, that the gas phase mass transfer was indeed determined by the diffusional resistance over the distance between the slab surface and the sieve plate. For instance, at a slab temperature of 50°C the gas phase mass transfer coefficient amounted to $1.32\ 10^{-2}$ m/s at a chamber pressure of 150 mm Hg. Since the diffusion coefficient of water vapor in air is approximately $1.56\ 10^{-4}\ m^2/s$ at this pressure, this mass transfer coefficient corresponds with a diffusion distance of .012 m. This is by good approximation equal to the distance between slab surface and sieve plate. Thus, it was expected, that the drying rate could be assumed to be constant over the slab surface. This was confirmed by measurement of the thickness over a cross-section of a gelled slab after evaporation of approximately half of the initial amount of water present.

The presence or absence of considerable temperature gradients inside the slab was another important factor which had to be checked beforehand. If the heat necessary for evaporation is supplied at the bottom of the slab only, maximum temperature differences of 9 and 34°C over the slab can be calculated for slab temperatures of 30 and 50°C (slab thickness 0.01 m, surface water activity = 1 and $k_c = 0.01$ m/s). However, heat is supplied by radiation to the evaporating surface. Depending on the relative penetration depth of this thermal radiation the temperature differences will be smaller. We estimated the absorption coefficient for the long-wave infra-red radiation from our radiation plate (maximum temperature 1000°K) by extrapolation from values for radiant black bodies of higher temperature (Int.Crit. Tables (1933)). A conservative estimate of the absorption coefficient is 600 $[m^{-1}]$. This means, that 80% of the radiation is absorbed within 2.7 mm from the surface and

50% within 1.1 mm. Hence, the temperature differences over the slab thickness will be lower than the above calculated differences by at least a factor 10. Furthermore, the differences will also decrease proportionally to the decrease of the surface water activity (water flux). Hence, *the assumption of a homogeneous slab temperature is justifiable*. This was confirmed experimentally. In some experiments we added approximately 0.1 ml of black drawing ink to 100 ml of agar solution. The drying rate of these black slabs in the constant rate period appeared to be equal to the drying rate for non-coloured slabs: The improved radiation absorption did for equal bottom temperature not result in a detectable increase in surface temperature.

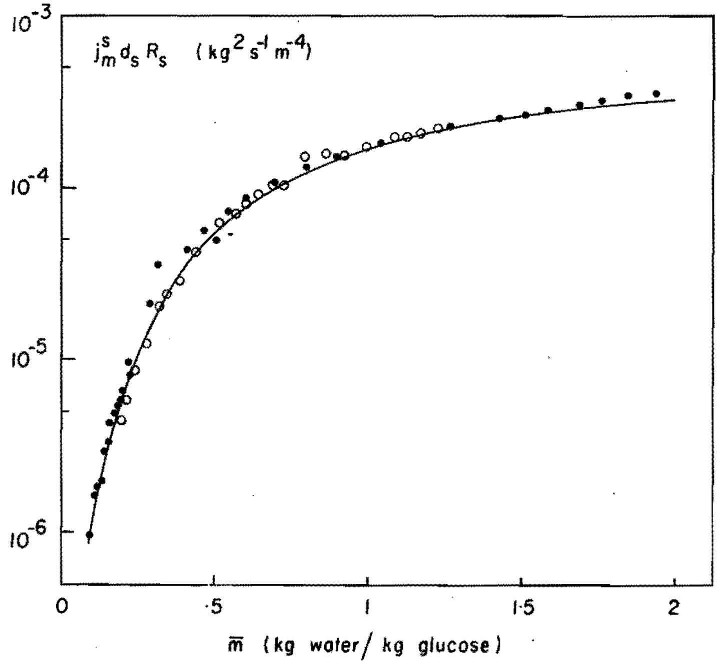


Fig.VI.4.1 Isothermal drying curves of gelled slabs of an aqueous glucose solution at 30 °C. The solid line represents the numerically calculated regular regime drying curve. ○ experiment 1 ● experiment 4. The experimental points are calculated by direct differentiation of the measured weight versus time, without smoothing (appendix E).

Isothermal drying curves have been measured at 30 and 50 °C. The tabulated results of three experiments are given in appendix E. Figure VI.4.1 shows two experimentally determined drying curves at 30 °C and the numerically calculated regular regime curve for this temperature at zero surface concentration. In this calculation we used equation (III.4.8) for the concentration dependence of the diffusion coefficient. Good agreement between the experimental and theoretical results can be claimed.

From the experimental curves we calculated the concentration dependence of the diffusion coefficient at 30 and 50 °C according to the method described in paragraph VI.2. We used in these calculations the relations between $\overline{Sh}_d$ and d ln F/ d ln $(\bar{m}-m_i)$ as given in figure III.4.6a for the concentration dependences $D_r = m^a$ ("average curve") and water-glucose in a shrinking coordinate system (after Gladden & Dole (1953)). The results for 30 °C are presented in figure (VI.4.2). It appears that there is no considerable difference between the values calculated with the different relations between $\overline{Sh}_d$ and d ln F/d ln $(\bar{m}-m_i)$.

Good agreement can be observed between the present results and the values interpolated to 30 °C from the measurements by Gladden & Dole. Only at 20 % water by weight (x_s = 0.29) their result deviates considerably from our experimental data. This difference can be explained by the fact, that the authors used an optical method for the measurement of concentration profiles near a boundary between two solutions of slightly different water concentration. They state, that at the low water concentration "the high viscosity of the solution, approximately 21 poises (...), made the formation of a sharp clean boundary difficult". Therefore, they expect a relatively high experimental error in the value of the diffusion coefficient at this low water concentration. The results of a second experiment at 30 °C appear to differ less than 20 % from the first measurement,

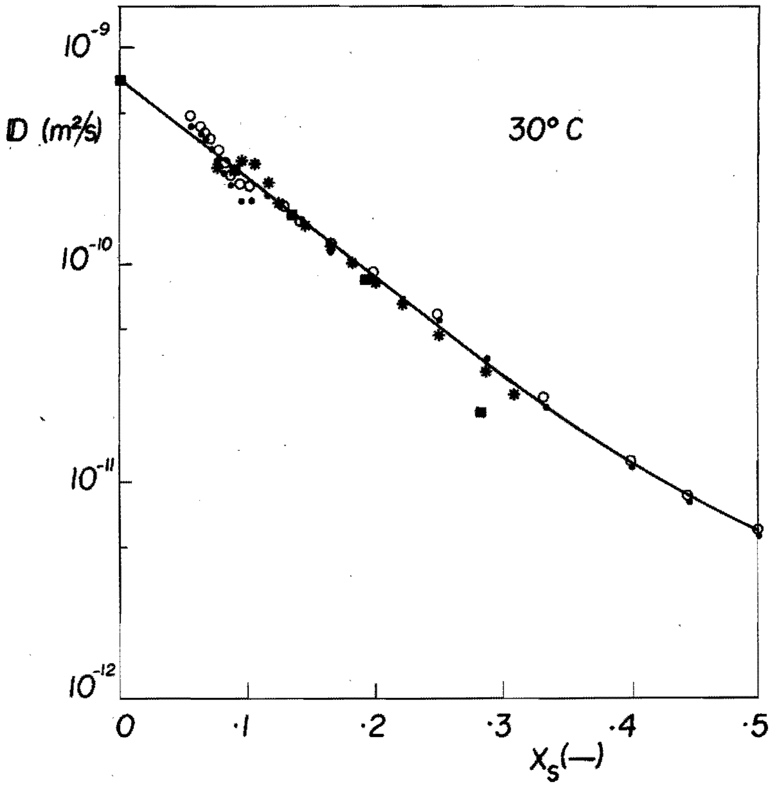


Fig. VI.4.2 The diffusion coefficient of water-glucose versus the mole fraction glucose (x_s) in the (supersaturated) solution at 30 °C.

- ● experiment 4; interpretation with the relation for $D_r = m^a$.
- ○ experiment 4; interpretation with the relation for water-glucose at 30 °C.
- ✱ experiment 1; interpretation with the relation for water-glucose at 30 °C.
- ■ results by Gladden & Dole (1953); interpolated between 25 and 35 °C to 30 °C.

the average difference being approximately 10%.

The diffusion coefficient of water-glucose as calculated from the sorption experiment at 50 °C is given in figure (VI.4.3). It is compared with the linearized relation between ln D and x_s after the measurements of Gladden &

Dole (Van der Lijn (1971)). These linearized values are extrapolated from 25 and 35 °C to 50 °C using an Arrhenius temperature dependence. Also at this temperature good agreement can be observed.

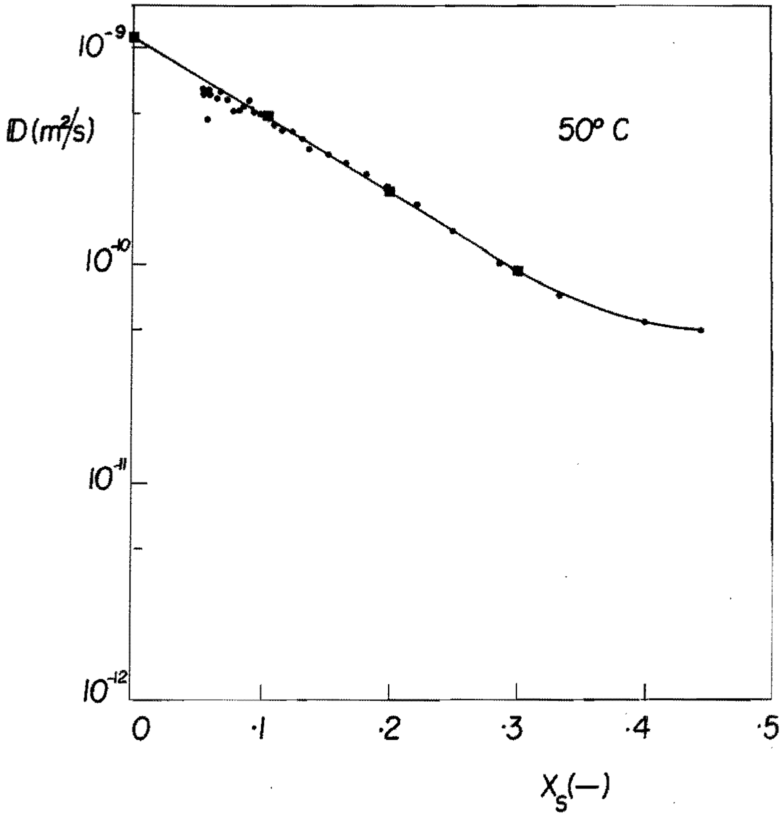


Fig. VI.4.3 The diffusion coefficient of water-glucose versus the mole-fraction glucose x_s in the (supersaturated) solution at 50 °C.

- ● experiment 7; interpretation with the relation for water-glucose at 30 °C.
- ■ linearized relation between ln D and x_s after the results by Gladden & Dole, extrapolated to 50 °C.

The activation energy of the diffusion coefficient in relation to the mole fraction glucose, x_s, is presented in figure (VI.4.4) and compared with the values by Gladden &

Dole. Again a deviation is observed at high glucose concentrations. The reason of this deviation has already been discussed above.

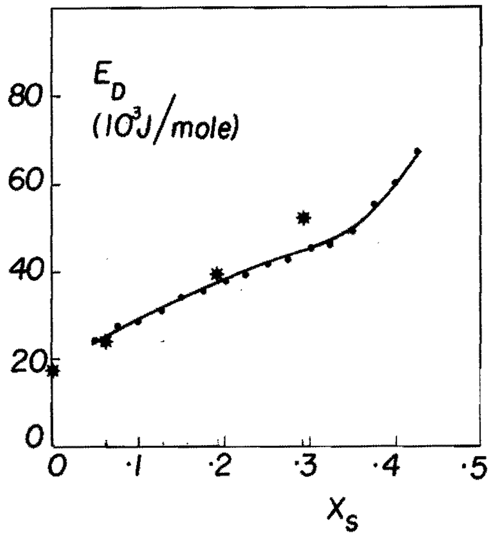


Fig. VI.4.4 Activation-energy of diffusion coefficient of water-glucose versus the mole fraction x_s in the (supersaturated) glucose solution.

✱ Gladden & Dole (1953)

● present work

VI.5 Conclusions

1. Based upon the properties of the regular regime of sorption with constant surface concentration we developed a method for the calculation of the concentration dependence of the diffusion coefficient from a single sorption experiment.
2. Isothermal drying curves of a slab of an aqueous solution of glucose have been determined experimentally at 30 and 50 °C. These drying curves are in good agreement with theoretical curves calculated with literature values for the concentration dependence of the diffusion coefficient.

3. The concentration- and temperature dependence of the diffusion coefficient have been calculated from the experimentally determined drying curves by application of the new method. The results are in good agreement with literature data, obtained from successive measurements over small concentration intervals (Gladden & Dole (1953)). Only at low water concentrations deviations are observed, which can be explained by inaccuracy in the experimental method applied by Gladden & Dole.

APPENDIX A

Solution of the diffusion equation for the regular regime with geometrically similar profiles ($D_r = m^a$)

In paragraph III.3 the diffusion equation for the regular regime with $D_r = m^a$ and surface concentration $m_i = 0$ has been transformed to the equation:

$$\frac{d}{d\phi}\left\{ (g')^a \, \phi^{\frac{\nu}{\nu+1}} \, \frac{dg'}{d\phi} \right\} = -P\, g' \tag{A.1}$$

with the boundary conditions

$$\phi^{\frac{\nu}{\nu+1}} \, \frac{dg'}{d\phi} = 0 \qquad \text{at } \phi = 0 \tag{A.2}$$

$$g' = 0 \qquad \text{at } \phi = 1 \tag{A.3}$$

and the norm

$$g' = 1 \qquad \text{at } \phi = 0 \tag{A.4}$$

Substitution of a new variable y, defined by

$$y = (g')^{a+1} \tag{A.5}$$

yields for the differential equation

$$\frac{d}{d\phi}\left\{ \phi^{\frac{2\nu}{\nu+1}} \, \frac{dy}{d\phi} \right\} = -P\,(a+1)\, y^{\frac{1}{a+1}} \tag{A.6}$$

and for the boundary conditions

$$\phi = 1 \qquad y = 0 \tag{A.7}$$

$$\phi = 0 \qquad y = 1 \tag{A.8}$$

$$\phi^{\frac{\nu}{\nu+1}} \, \frac{dy}{d\phi} = 0 \tag{A.9}$$

For *slabs* ($\nu=0$) the differential equation reads:

$$\frac{d^2y}{d\phi^2} = -(a+1)\ P\ y^{\frac{1}{a+1}} \tag{A.10}$$

This equation can be solved analytically. We introduce

$$s = \frac{dy}{d\phi}\ ,\ \text{so that}\ \frac{d^2y}{d\phi^2} = s\ \frac{ds}{dy}$$

Equation (A.10) goes over into

$$s\ \frac{ds}{dy} = -(a+1)\ P\ y^{\frac{1}{a+1}} \tag{A.11}$$

with the boundary condition

$$s = 0 \text{ at } y = 1 \tag{A.12}$$

The differential equation can be integrated after separation of variables. Resubstitution of $dy/d\phi$ for s gives:

$$\frac{dy}{d\phi} = -A\ (1-y^{\alpha})^{\frac{1}{2}} \tag{A.13}$$

where

$$A = \left|\frac{2(a+1)^2\ P}{(a+2)}\right|^{\frac{1}{2}} \tag{A.14}$$

and

$$\alpha = (a+2)/(a+1) \tag{A.15}$$

We use the series development (Bronstein & Semendjajew (1974)).

$$(1-y^{\alpha})^{-\frac{1}{2}} = \sum_{n=0}^{\infty} \frac{2n!}{2^{2n}\ n!n!}\ y^{n\alpha} \tag{A.16}$$

This series is convergent for $|y^{\alpha}| < 1$. Hence $\alpha > 1$ and $a > -1$. This condition is fulfilled, since the left-hand side of equation (A.10) is negative:

$$\frac{d^2y}{d\phi^2} = -\frac{d}{d\phi}\left(-D_r\ \frac{d(g')}{d\phi}\right) \tag{A.17}$$

This represents the negative increase of the sorption flux with increasing ϕ. Therefore, *a regular regime of sorption does not exist for* $a \leq -1$.

Substitution of (A.16) in equation (A.13) and subsequent integration yields

$$A\ (1-\phi) = \sum_{n=0}^{\infty} \left\{ \frac{2n!}{2^{2n}\ n!n!} \cdot \frac{1}{(n\alpha+1)} \cdot y^{n\alpha+1} \right\} \qquad (A.18)$$

The value of the parameter A follows then from substitution of $\phi = 0$ and $y = 1$:

$$A = \sum_{n=0}^{\infty} \left\{ \frac{2n!}{2^{2n}\ n!n!} \quad \frac{1}{(n\alpha+1)} \right\} \qquad (A.19)$$

The parameter P can then be calculated from equation (A.14). The average normalized concentration $\bar{g}'$ is found by integration of (A.18) over $0 \leqq \phi \leqq 1$

$$\bar{g}' = 1 - \frac{1}{A} \sum_{n=0}^{\infty} \left\{ \frac{2n!}{2^{2n}\ n!n!} \quad \frac{1}{(n\alpha+a)\,(1+(a+1)\,(n\alpha+1))} \right\} \qquad (A.20)$$

Substitution of the values of P and $\bar{g}'$ in equation (III.3.46) yields the Sherwood number $\overline{Sh}_d$.

Analogously to slabs, the equation for *non-shrinking cylinders* (ν=1) reads:

$$\frac{d^2y}{d\phi^2} + \frac{dy}{d\phi} + P(a+1)\ y^{\frac{1}{a+1}} = 0 \qquad (A.21)$$

and for *non-shrinking spheres* (ν=2):

$$\phi^{4/3}\,\frac{d^2y}{d\phi^2} + \frac{4}{3}\ \phi^{1/3}\,\frac{dy}{d\phi} + P(a+1)\ y^{\frac{1}{a+1}} = 0 \qquad (A.22)$$

These equations can not be solved in a simple analytical way. Hence, we solved the boundary-value problem numerically. Since boundary condition (A.2) gives rise to some problems in the programming, the equation is described in a new distance coordinate x, defined by

$$x = \frac{r}{R} = \phi^{\frac{1}{\nu+1}} \tag{A.23}$$

Equation (A.1) then becomes:

$$\frac{d^2y}{dx^2} + \frac{\nu}{x}\frac{dy}{dx} + (\nu+1)^2.(a+1).P\ y^{\frac{1}{a+1}} = 0 \tag{A.24}$$

with boundary conditions

$$x = 0 : y = 1 \tag{A.25}$$

$$\frac{dy}{dx} = 0 \tag{A.26}$$

$$x = 1 : y = 0 \tag{A.27}$$

The equation is solved numerically using a fifth order Runge Kutta procedure. The step size was chosen such, that the relative error in y and dy/dx did not exceed 10^{-6}. This accuracy was necessary because of the error propagation in the calculation of $\overline{Sh}_d$ from P and $\bar{g}'$. The value of P is evaluated by using a Regula Falsi procedure.

Solutions for high values of a.

For high values of a the factor $y^{\frac{1}{a+1}}$ approaches 1 except for y=0. We solve equation (A.1) with the boundary condition $y=\varepsilon$ at $\phi=1$ and take the limit of this solution for $\varepsilon \downarrow 0$. Equation (A.1) goes over into

$$\frac{d}{d\phi}\left\{\phi^{\frac{2\nu}{\nu+1}}\frac{dy}{d\phi}\right\} = -P\ (a+1) \tag{A.28}$$

Integration yields

$$y = -\tfrac{1}{2}P.(a+1)(\nu+1).\phi^{\frac{2}{\nu+1}} + C_1\phi + C_2 \tag{A.29}$$

From the boundary conditions at $\phi = 0$ then follows, that the integration constants C_1 and C_2 are equal to

$$C_1 = 0 \quad \text{and} \quad C_2 = 1 \tag{A.30}$$

Substitution of these constants and the value $y = \varepsilon$ at $\phi = 0$ then yields:

$$1 - \varepsilon = + \frac{1}{2} P(a+1)(\nu+1) \tag{A.31}$$

We take the limit for $\varepsilon \downarrow 0$:

$$P = \frac{2}{(a+1)(\nu+1)} \tag{A.32}$$

The solution of equation (A.28) then reads:

$$y = 1 - \phi^{\frac{2}{\nu+1}} \tag{A.33}$$

For the calculation of $\overline{Sh}_d$ we need the value of $\bar{g}'$:

$$\bar{g}' = \int_0^1 y^{\frac{1}{a+1}} d\phi = \int_0^1 \left\{1 - \phi^{\frac{2}{\nu+1}}\right\}^{\frac{1}{a+1}} d\phi \tag{A.34}$$

We introduce an auxiliary variable q defined by

$$q = 1 - \phi^{\frac{2}{\nu+1}} \tag{A.35}$$

Substitution of q in equation (A.34) yields

$$\bar{g}' = \frac{\nu+1}{2} \left| \int_0^1 q^{\frac{1}{a+1}} (1-q)^{\frac{\nu-1}{2}} dq \right| \tag{A.36}$$

Hence, we can write

$$\bar{g}' = \frac{(\nu+1)}{2} B\left\{\frac{a+2}{a+1}, \frac{\nu+1}{2}\right\} \tag{A.37}$$

where B represents the Beta function (Abramowitz & Stegun (1970), p. 258). Thus, it follows for the Sherwood number $\overline{Sh}_d$ at high values of a, that

$$\overline{Sh}_d = 4 \left[\frac{(\nu+1)}{2} \cdot B\left\{\frac{a+2}{a+1}, \frac{\nu+1}{2}\right\} \right]^{-a} \tag{A.38}$$

In order to calculate the limit for a → ∞, we write the Beta function as

$$B\left\{\frac{a+2}{a+1}, \frac{\nu+1}{2}\right\} = \frac{\Gamma\left\{\frac{a+2}{a+1}\right\} \cdot \Gamma\left\{\frac{\nu+1}{2}\right\}}{\Gamma\left\{\frac{1}{a+1} + \frac{\nu+3}{2}\right\}} \tag{A.39}$$

where Γ represents the gamma function. We expand the gamma-functions according to Euler's Infinite Product into (Abramowitz & Stegun (1970), p. 255)

$$\frac{1}{\Gamma(z)} = z e^{\gamma z} \prod_{n=1}^{\infty} \left\{ \left(1 + \frac{z}{n}\right) e^{-z/n} \right\} \tag{A.40}$$

where γ is Euler's constant. After some algebraic manipulation then follows, that

$$\lim_{a\to\infty} \overline{Sh}_d = 4 \exp\left\{ (\nu+1) \sum_{n=1}^{\infty} \frac{1}{n(2n + \nu + 1)} \right\} \tag{A.41}$$

The sum of the infinite series in the exponent can then be calculated by means of Polygamma Functions (Abramowitz & Stegun (1970), p. 264):

$$\sum_{n=1}^{\infty} \frac{1}{n(2n + \nu + 1)} = \sum_{n=1}^{\infty} \left\{ \frac{1}{(\nu+1)n} - \frac{2}{(\nu+1)(2n + \nu + 1)} \right\} \tag{A.42}$$

Then,

$$\sum_{n=1}^{\infty} \frac{1}{n(2n + \nu + 1)} = - \frac{1}{(\nu+1)} \psi(1) + \frac{1}{\nu+1} \psi\left(\frac{\nu+3}{2}\right) \tag{A.43}$$

where ψ is the Psi- or digamma function. Evaluation of these functions and substitution in equation (A.41) yields the Sherwood number for a → ∞:

slab: $$\overline{\mathrm{Sh}}_d = 4\ \exp(-2\ \ln 2 + 2) = \exp(2) \qquad \text{(A.44)}$$

cylinder: $$\overline{\mathrm{Sh}}_d = 4\ \exp(1) = 4e \qquad \text{(A.45)}$$

sphere: $$\overline{\mathrm{Sh}}_d = 4\ \exp(-2\ \ln 2 + \tfrac{8}{3}) = \exp\left(\tfrac{8}{3}\right) \qquad \text{(A.46)}$$

APPENDIX B

The Regular Regime for exponential concentration dependence of the diffusion coefficient and constant surface concentration, at high values of the exponent.

The diffusion equation reads:

$$\frac{\partial m}{\partial \tau} = \frac{\partial}{\partial \phi} \left(\exp\ (am)\ X^2\ \frac{\partial m}{\partial \phi}\right) \tag{B.1}$$

with the initial and boundary conditions:

$$\tau = 0 \quad 0 \leqq \phi \leqq 1 \qquad m = m_0 \tag{B.2}$$

$$\tau > 0 \qquad \phi = 0 \qquad X\,\frac{\partial m}{\partial \phi} = 0 \tag{B.3}$$

$$\phi = 1 \qquad m = 0 \tag{B.4}$$

Substitution of $u = \exp(am-am_0)$ in the diffusion equation yields:

$$\frac{1}{u}\,\frac{\partial u}{\partial \tau} = \frac{\partial}{\partial \phi}\ (\exp(am_0)\ X^2\ \frac{\partial u}{\partial \phi}) \tag{B.5}$$

We account for the constant $\exp(am_0)$ by the introduction of $\tau' = \tau\ \exp(am_0)$.

$$\frac{\partial u}{\partial \tau'} = u\,\frac{\partial}{\partial \phi}\ (X^2\ \frac{\partial u}{\partial \phi}) \tag{B.6}$$

with initial and boundary conditions

$$\tau' = 0 \quad 0 \leq \phi \leq 1 \qquad u = 1 \tag{B.7}$$

$$\tau' > 0 \qquad \phi = 0 \qquad X\,\frac{\partial u}{\partial \phi} = 0 \tag{B.8}$$

$$\phi = 1 \qquad u = \exp(-am_0) \tag{B.9}$$

For high values of am_0 boundary condition (B.9) goes over into

$$\phi = 1 \qquad u = 0 \tag{B.10}$$

It should be noted, however, that the solution of the equation does not give relevant information about the concentration profile if the average concentration is small compared with the initial concentration. Therefore, the homogeneous boundary condition (B.10) can be applied in the regular regime only if

$$\exp(a\bar{m}) \gg \exp(am_i) \tag{B.11}$$

Equation (B.6) is solved by separation of variables:

$$u = f(\tau') \,.\, g(\phi) \tag{B.12}$$

$$\frac{1}{f^2} \frac{df}{d\tau'} = \frac{d}{d\phi} (X^2 \frac{dg}{d\phi}) = \lambda \tag{B.13}$$

with the boundary conditions for the ϕ-dependent part:

$$\phi = 0 \qquad X \frac{dg}{d\phi} = 0 \tag{B.14}$$

$$\phi = 1 \qquad g = 0 \tag{B.15}$$

For the calculation of λ we take a normalized function $g(\phi)$ with the norm

$$\phi = 0 \qquad g = 1 \tag{B.16}$$

This is allowable because we can account for any factor in the function $f(\tau')$. The equation (B.15) with boundary conditions is then similar to equation (A.28). Hence,

$$\lambda = 2(\nu+1) \tag{B.17}$$

and the solution reads

$$g = 1 - \phi^{\frac{2}{\nu+1}} \tag{B.18}$$

We derive the relation for $\overline{Sh}_d$:

$$\overline{Sh}_d = \frac{2F}{\int_0^{\bar{m}} D_r \, dm} = \frac{2a}{(\nu+1)} \exp(-a\bar{m}) \frac{d\bar{m}}{d\tau} \tag{B.19}$$

and calculate the factors occurring in this equation. With

$$am = am_0 + \ln u = am_0 + \ln f + \ln g \tag{B.20}$$

it follows, that

$$a\bar{m} = am_0 + \ln f + \int_0^1 \ln g \, d\phi \tag{B.21}$$

Differentiation with respect to τ and substitution of equation (B.13) yields:

$$\frac{d\ a\bar{m}}{d\tau} = \frac{d \ln f}{d\tau} = f.\lambda \exp(am_0) \tag{B.22}$$

Substitution of (B.22) and (B.21) in equation (B.19) then gives:

$$\overline{Sh}_d = \frac{2\lambda}{(\nu+1)} \cdot \exp\left\{ - \int_0^1 \ln g \, d\phi \right\} \tag{B.23}$$

With the solution for $g(\phi)$ (B.18) and the value of λ (B.17) it follows then, that

$$\overline{Sh}_d = 4 \exp\left\{ - \int_0^1 \ln(1-\phi^{\frac{2}{\nu+1}}) \, d\phi \right\} \tag{B.24}$$

We expand the logarithm in an infinite series:

$$\ln(1-\phi^{\frac{2}{\nu+1}}) = - \sum_{n=1}^{\infty} \left\{ \frac{1}{n} \cdot \phi^{\frac{2n}{\nu+1}} \right\} \tag{B.25}$$

and integrate this series with respect to ϕ:

$$\overline{Sh}_d = 4 \exp \left\{ \sum_{n=1}^{\infty} \frac{(\nu+1)}{n(2n+\nu+1)} \right\} \qquad (B.26)$$

This relation for $\overline{Sh}_d$ is identical with equation (A.41), which holds for the concentration dependence $D_r = m^a$; $a \rightarrow \infty$. In both cases the surface concentration is constant ($m_i = 0$).

APPENDIX C

The "shrinking-core" model for systems which shrink or swell upon (de)sorption.

For ease of notation we describe the process in *reference component volume centered coordinates*. The differential equation for the steady state then reads:

$$\frac{d}{d\phi}\left\{D_r(\nu+1)^2\left\{\int_0^{\phi}(1+m)\,d\phi\right\}^{\frac{2\nu}{\nu+1}}\frac{dm}{d\phi}\right\} = 0 \tag{C.1}$$

We assume, that the concentration in a "core" $0 < \phi < \phi_c$ is equal to the initial concentration m_o. In the annular space $\phi_c < \phi < 1$ the concentration is equal to m_i. Hence,

$$\int_0^{\phi}(1+m)\,d\phi = \phi_c\,(1+m_o) + (\phi-\phi_c)(1+m_i) \tag{C.2}$$

Integration of equation (C.1) yields after substitution of (C.2):

$$D_r(\nu+1)^2\left\{\phi_c(m_o-m_i) + \phi(1+m_i)\right\}^{\frac{2\nu}{\nu+1}}\frac{dm}{d\phi} = -FX_i \tag{C.3}$$

Integration between the limits $\phi_c < \phi < 1$ then yields the flux parameter F as a function of ϕ_c:

slab :
$$F = \frac{\overline{D}_r\,(m_o-m_i)}{1-\phi_c} \tag{C.4}$$

cylinder :
$$F = \frac{(m_o-m_i)(1+m_i)\,\overline{D}_r}{Q_c} \tag{C.5}$$

where
$$Q_c = \frac{1}{2}\left\{(1+m_i) + \phi_c(m_o-m_i)\right\}^{1/2}\ln\left\{\frac{\phi_c(m_o-m_i)+(1+m_i)}{\phi_c(1+m_o)}\right\} \tag{C.6}$$

sphere : $$F = \frac{(m_o - m_i)(1+m_i)\,\overline{D}_r}{Q_s} \tag{C.7}$$

where

$$Q_s = \left[\frac{(1+m_i) + \phi_c(m_o - m_i)}{\phi_c(1+m_o)} \right]^{1/3} - 1 \tag{C.8}$$

In these equations ϕ_c can also be read as (1-E). For low values of m_o and m_i the equations reduce to the relations derived for systems with constant volume.

APPENDIX D

A step-by-step method for the calculation of the concentration dependence of the diffusion coefficient from a single sorption experiment.

Prager (1951) has presented a method for the calculation of the concentration dependence of the diffusion coefficient. The concentration interval of interest is divided into a number of intervals and for each interval the diffusion coefficient is assumed to be constant (figure D.1).

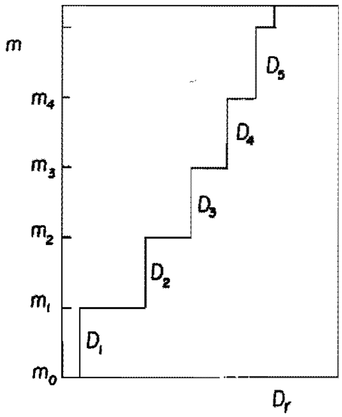


Fig. D.1. A step-function approximation to the diffusion coefficient

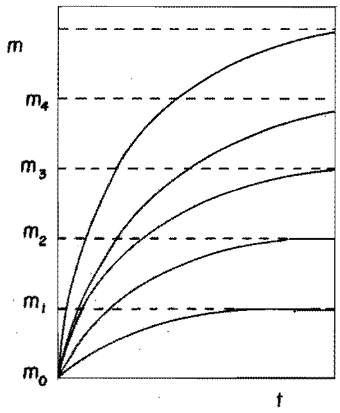


Fig. D.2. Increasing concentration intervals as covered by successive sorption experiments

For the first interval $m_0 < m < m_1$ a sorption experiment reveals the diffusivity D_1. The diffusion coefficient for the second interval D_2 is then calculated from a sorption experiment over both intervals: $m_0 < m < m_2$. The (analytical) solution of the diffusion equation contains D_2 as the only parameter that has to be determined. Once D_1 and D_2 are known, D_3 is determined similarly by interpretation of a sorption experiment between $m_0 < m < m_3$ (see figure D.2). In this way the whole concentration interval of interest is covered. It is clear, that for diffusivities which depend strongly on the concentration this method requires a large number of experiments to permit the assumption of a constant diffusivity per concentration interval.

A similar approach can also be applied to a single sorption or desorption experiment with variable surface concentration. The concentration profiles during such a process are drawn schematically in figure D.3.

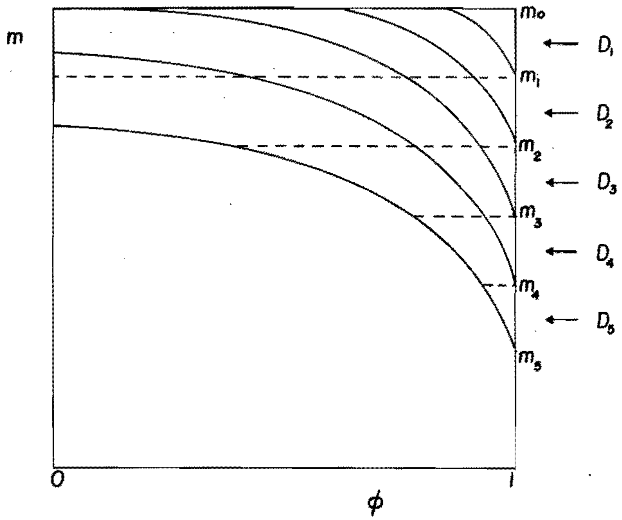


Fig. D.3. Schematic representation of the change of concentration profiles during a desorption process.

If the surface flux and the surface concentration are measured as a function of time, the concentration dependence of the diffusion coefficient is obtained in the following way.
The diffusion coefficient is assumed to be constant in the concentration interval $m_1 < m < m_0$. Its value D_1 is calculated by trial and error, using the numerical program for the solution of the diffusion equation (cfr. chapter

II). After time τ_2 the surface concentration has reached the value m_2. This corresponds with a certain value of D_2 in the region $m_2 < m < m_1$. For the calculation the known diffusivity D_1 is used at concentrations between $m_1 < m < m_0$. Once the diffusivities D_1 and D_2 are known, they are applied in the appropriate concentration interval and D_3 can again be calculated by trial and error. Thus, subsequent values of the diffusion coefficient are obtained. By choosing the concentration intervals small enough the concentration dependence is approximated closely.

The implementation of this calculation method is relatively easy when the diffusion equation is solved by a finite difference method. For the solution of the diffusion equation with known concentration dependence of the diffusion coefficient the diffusion equation is descretized into a difference-equation. The space-parameter ϕ is then divided into a number of intervals (n). Initially, the concentration at every "grid-point" is known from the initial condition of the differential equation. By application of the difference equation, (n-2) relations are found to calculate the concentration at every grid-point after some time $\Delta\tau$. Together with 2 relations for the boundary conditions the concentrations at the "new" value of τ can be calculated by solving the complete set of n equations with n unknown concentrations. By taking small steps $\Delta\tau$ the sorption process can be calculated in this way.

In a similar way we can calculate the concentration dependence of the diffusion coefficient from a sorption experiment. Again the initial condition gives the concentration at $\tau=0$ at every grid-point. Again (n-2) relations are found by application of the difference-equation and 2 relations come from the boundary conditions. However, only (n-1) concentrations at time τ_1 are unknown, since the surface concentration is given by the experimental measurement. Therefore, the parameter D_1, the diffusion coefficient in the concentration interval $m_0 < m < m_1$, can be calculated by solving the complete set of n equations with (n-1) unknown concentrations and 1 unknown diffusion coefficient. In the next step again n equations are found from the difference equation with boundary conditions. Now the parameter D_2, the diffusion coefficient in the interval $m_1 < m < m_2$ can be solved. In this calculation D_1 is used as the diffusion coefficient in the interval $m_0 < m < m_1$. In this way the whole concentration dependence of the diffusion coefficient can in principle be calculated by moving step-by-step through the sorption history.

Problems

It can be understood, that this method of calculation is very sensitive to inaccuracies in the measurements. Experimental noise on the relation between surface concentration and time may have drastic influence on the concentration dependence of the diffusivity calculated in this way. The unstability can be illustrated as follows: if D_1 is estimated too low, this must be compensated by D_2 which is therefore estimated too high: D in relation to m tends to oscillate. This oscillation can be effectively suppressed by smoothing D(m) during the calculation process. However, somewhat larger errors in the experimental $m_i(\tau)$ may cause serious problems. For instance, a local increase of m_i with time is "impossible" in a desorption process and results in a negative value of the local diffusion coefficient. Therefore, also the input curve $m_i(\tau)$ has to be effectively smoothed.

Another problem stems from the fact that for a highly concentration dependent diffusion coefficient the surface concentration hardly influences the sorption rate, unless the average concentration is close to the surface concentration. In order to have this latter condition in the experiment, the mass transfer coefficient in the continuous phase must be so low that the concentration profile inside the body remains rather flat. However, if mass transfer is completely dominated by continuous phase mass transfer, the process becomes very insensitive to the value of the diffusion coefficient inside the body. For strongly concentration dependent diffusion coefficients a constant value of the gas phase mass transfer coefficient can never fulfill both requirements during the complete sorption history. Therefore, only part of the process can be used for the calculation or the mass transfer coefficient in the continuous phase has to be varied during the experiment.

The third problem encountered in this method deals with the determination of the surface concentration inside the dispersed phase. It is calculated from the equation describing the sorption flux in the continuous phase (cfr. chapter V):

$$n'_{m,i} = k'_c \ (A_i \ \rho'^{*}_{m,pure} - \rho'_{m,bulk}) \tag{D.1}$$

where $n'_{m,i}$ is the mass flux through the phase boundary in the continuous phase, k'_c the mass transfer coefficient in the continuous phase and A_i the activity of the sorbent at the surface. $\rho'^{*}_{m,pure}$ is the sorbent concentration in the continuous phase in equilibrium with pure sorbent and $\rho'_{m,bulk}$ is the sorbent concentration in the bulk of the continuous phase. In an experimental situation all variables can be measured except A_i, which can therefore be calculated from this equation. The sorption isotherm, i.e. the relation between A_i en m_i, then reveals the value of m_i: the surface concentration in the dispersed phase. However, if the activity is constant or varies only slightly with varying m_i ($dA_i/dm_i << 1$) a small experimental error in the value of A_i causes a large error in the calculated value of m_i. In drying, for instance, the water activity is approximately constant with varying m_i if $m_i > m_{cr}$ and m_i can not be calculated with sufficient accuracy from the measured surface activity. Therefore, the present method can only be applied to concentrations below m_{cr}.

Testing of the method

The method has successfully been applied to a desorption curve, which was obtained by simulating the drying of a slab on a computer. The result of the calculation is presented in figure D.4. This figure also shows the concentration dependence of the diffusion coefficient which was used for the simulation.

The method has not been tested yet on an experimentally determined (de)sorption history.

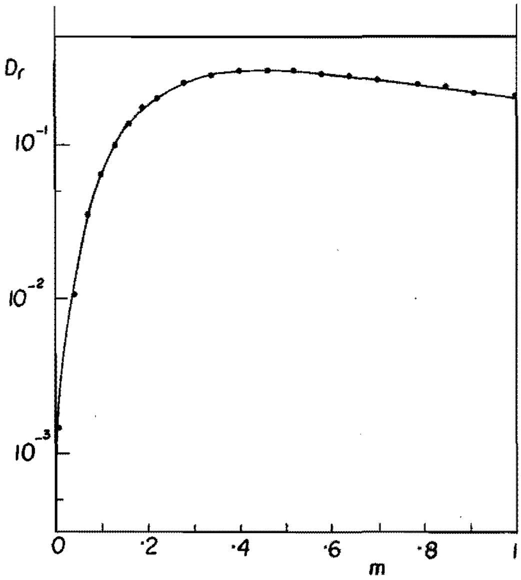


Fig. D.4. Concentration dependence of the diffusion coefficient as used for testing the present method. The solid line represents the dependence used in the simulation. Points indicate values of the diffusion coefficient calculated from the simulated desorption curve by the present method

APPENDIX E

Experimental results

Experiment nr. : 1
Temperature : 30 °C
Pressure : 100 mm Hg
$\bar{m}_o$: 2.418 kg water/kg glucose
d_s R_s : 1.565 kg glucose/m^2

time (min)	$\bar{m}$	time (min)	$\bar{m}$	time (min)	$\bar{m}$
0	2.418	60	1.628	240	0.745
1	2.408	69	1.563	255	0.706
3	2.370	81	1.482	270	0.668
5	2.328	90	1.426	293	0.616
7	2.283	103	1.349	308	0.586
9	2.238	118	1.263	328	0.552
11	2.186	131	1.194	383	0.467
13	2.121	141	1.143	438	0.412
20	2.022	148	1.111	518	0.356
23	1.981	158	1.063	563	0.330
28	1.918	168	1.019	603	0.310
31	1.884	181	0.965	813	0.248
36	1.832	203	0.883	888	0.232
43	1.767	213	0.844	1122	0.199
52	1.689	220	0.805	1168	0.194

Experiment nr. : 4
Temperature : 30 °C
Pressure : 100 mm Hg
$\bar{m}_o$: 3.865 kg water/kg glucose
$d_s\ R_s$: 1.944 kg glucose/m^2

time (min)	$\bar{m}$	time (min)	$\bar{m}$	time (min)	$\bar{m}$
0	3.865	138	2.354	1537	0.199
2	3.861	156	2.235	1571	0.196
4	3.817	168	2.159	1688	0.184
6	3.774	173	2.128	1746	0.179
8	3.731	180	2.087	1797	0.176
10	3.690	191	2.024	1847	0.172
12	3.650	201	1.966	1966	0.163
15	3.593	210	1.915	2047	0.157
16	3.574	232	1.793	2097	0.154
18	3.538	246	1.719	2171	0.149
20	3.506	261	1.646	2269	0.145
24	3.441	279	1.564	2757	0.128
28	3.378	299	1.478	2797	0.127
30	3.347	321	1.391	2867	0.125
34	3.288	392	1.143	2917	0.123
36	3.260	462	0.941	3032	0.120
43	3.167	501	0.847	3072	0.119
49	3.095	554	0.735	3118	0.117
55	3.028	607	0.644	3171	0.116
61	2.965	664	0.563	3274	0.114
67	2.907	703	0.518	3382	0.110
71	2.870	737	0.492	3465	0.108
78	2.808	808	0.427	3619	0.105
84	2.757	863	0.389	3707	0.104
91	2.700	957	0.336	4442	0.093
96	2.661	1269	0.234	4502	0.092
101	2.621	1287	0.234	4562	0.092
110	2.552	1367	0.221	4622	0.091
126	2.435	1412	0.214		

Experiment nr. : 7
Temperature : 50 ^{o}C
Pressure : 150 mm Hg
$\bar{m}_o$: 3.852 kg water/kg glucose
$d_s R_s$: 1.821 kg glucose/m^2

time (min)	$\bar{m}$	time (min)	$\bar{m}$	time (min)	$\bar{m}$
2	3.773	124	1.764	327	0.491
4	3.705	130	1.707	337	0.464
6	3.636	135	1.661	343	0.449
8	3.567	139	1.625	349	0.434
10	3.498	144	1.580	359	0.412
12	3.425	150	1.528	366	0.398
14	3.355	157	1.468	370	0.390
16	3.290	162	1.426	377	0.377
18	3.232	167	1.384	387	0.360
20	3.178	173	1.334	393	0.351
22	3.128	180	1.278	400	0.340
24	3.082	186	1.231	405	0.333
26	3.038	192	1.185	413	0.323
28	2.997	197	1.148	420	0.315
30	2.957	203	1.105	426	0.309
34	2.882	210	1.055	435	0.301
38	2.811	216	1.013	479	0.266
42	2.743	223	0.966	608	0.195
46	2.681	229	0.928	695	0.166
52	2.588	236	0.884	800	0.140
59	2.488	240	0.860	833	0.136
62	2.448	246	0.827	900	0.128
67	2.382	252	0.794	1000	0.117
76	2.271	261	0.746	1100	0.110
81	2.213	267	0.718	1165	0.106
84	2.179	274	0.686	1200	0.104
89	2.124	282	0.651	1300	0.099
93	2.080	289	0.621	1350	0.097
99	2.016	295	0.598		
106	1.943	302	0.572		
112	1.881	308	0.551		
117	1.832	322	0.505		

LIST OF SYMBOLS

a	: activity	
	: constant	
A_i	: surface activity	
Bi_m, Bi_M	: mass transfer Biot-number	
Bi_H	: heat transfer Biot-number	
d	: specific density	kg/m^3
D	: (apparent) diffusion coefficient	m^2/s
$\mathbb{D}$	: molecular diffusion coefficient	m^2/s
$\bar{D}_r$	: $\int_{m_i}^{\bar{m}} D_r \, dm$	
$\overset{\sqcap}{D}_r$	: $\int_{m_i}^{m_c} D_r \, dm$ or $\int_{m_i}^{m_0} D_r \, dm$	
E	: efficiency $(m_0-\bar{m})/(m_0-m_i)$	
	: activation energy	J/kmole
f, f_1	: function	
F	: flux parameter (see table III.4.1)	
F_{ext}	: external forces	
g, g_1, g'	: function	
j^s	: mass flux with respect to reference component mass centered coordinates	kg/m^{2}s
k	: mass transfer coefficient	m/s
k'	: mass transfer coefficient based on concentration difference (m_0-m_i) or (m_c-m_i) in stationary	

	coordinates	m/s
k''	: idem in reference component centered coordinates	kg/m^2s
K	: dimensionless mass transfer coefficient	
L_m	: phenomenological coefficient	Kmole s/kg
m	: general formulation of concentrattion (see table II.4.1)	
m^*	: equilibrium concentration	
$\bar{m}_\rho$	: average concentration in the volume $0<\phi<\phi$	
n	: mass flux (stationary coordinates)	kg/m^2s
N_{pp}	: profile penetration number (variable m_i): $(m_0-\bar{m})/(m_0-m_i)$	
p	: auxilary parameter	
P	: auxiliary parameter	
	: pressure	N/m^2
q	: constant in the relations for the penetration period for cylinders and spheres	
r	: distance coordinate	(m)
R	: characteristic dimension (radius)	(m)
	: gas constant	J/Kmole K
R_s	: radius of the massive body which has a volume, equal to the volume of the shell (systems with constant total volume) or equal to the volume of the reference component	

(shrinking or swelling systems) m

Sh : Sherwood number $2\ kR/D$

$\overline{Sh}_d$: Sherwood number $2\ F/(\bar{D}_r(\bar{m}-m_i))$

t : time s

T : temperature K

u : mass fraction ρ_m/ρ_s

v : volume fraction $d_s\rho_m/d_m\rho_s$

x : mole fraction (total basis)

X : geometric quantity (see table II.4.2)

y : reference component mass centered coordinate $\int_0^r \rho_s\ r^\nu\ dr$ kg $m^{\nu-2}$

Y : value of y at r=R kg $m^{\nu-2}$

z : reduced space coordinate $(r/R)^{\nu+1}$

Greek symbols

α : partition coefficient

: constant

β : constant

Δ : difference

ε : constant

η : variable in Boltzmann transformation $(1-\phi)/2\sqrt{\tau}$

θ : argument of periodic function,

: ratio between Sherwood numbers for two different geometries

λ : constant (eigen-value)

λ : thermal conductivity $J/m^2 s\ K$

μ : eigen-value

ν : geometric factor (slab:0; cylinder:1; sphere:2)

ξ : dimensionless space coordinate y/Y

ρ : mass concentration kg/m^3

τ : general formulation of the time coordinate (see table II.4.1)

τ^* : time coordinate $D_0 t/R^2$

τ^{**} : time coordinate $\frac{\mathbb{D}_0 \rho_{s,0}^2 t}{d_{s,p}^2 R_s^2}$

ϕ : general formulation of the space coordinate (see table II.4.1)

ω : mass fraction (total basis)

Subscripts

c : refers to hollow core or centre ($\phi=0$)

: continuous phase

cr : critical (end of constant rate period)

crp, CRP : constant rate period

csc, CSC : constant surface concentration

d : dispersed phase

: discontinuity

eff : effective

g : gas phase

i : at the phase boundary (interface)($\phi=1$)

m : migrating component

n : n-th eigen-function

p : pure

PP : penetration period

r : reduced

res : residence

RR : regular regime

s : dissolved solids, sorbate

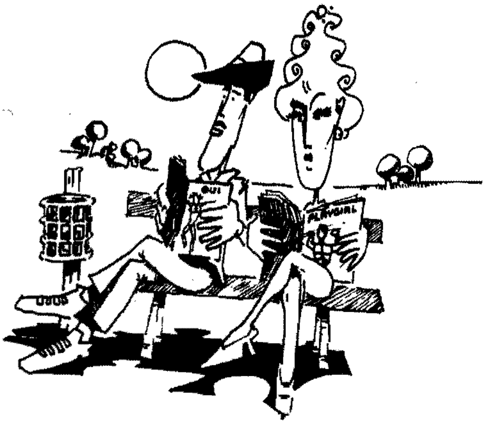
t : at the point of transition from the penetration period to the regular regime

0 : arbitrary value

1,2 : referring to different surface concentrations

: referring to different geometries

∞ : in the limit $T\to\infty$



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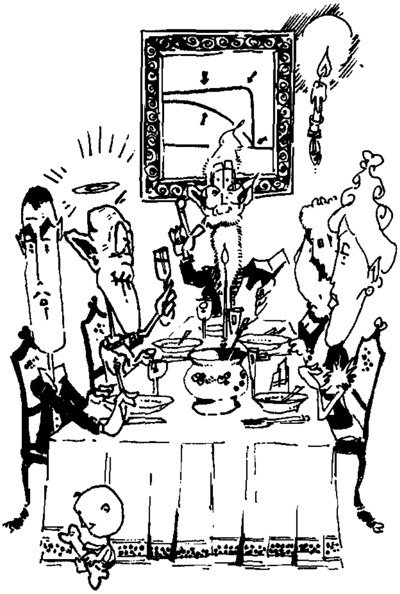

STELLINGEN

1. Bij een sorptie-proces wordt het instationaire stoftransport in de disperse fase na verloop van tijd praktisch onafhankelijk van het begin-concentratieprofiel. In het bijzonder wanneer de diffusiecoëfficiënt afneemt met afnemende (toenemende) concentratie bij desorptie (absorptie), geldt dit al in een vroeg stadium van het instationaire proces.

2. De stoftransportcoëfficiënt in drogend materiaal is, bij afwezigheid van een temperatuurgradiënt, praktisch onafhankelijk van de temperatuurgeschiedenis. Bij konstante oppervlakte-concentratie is deze transportcoëfficiënt gedurende het reguliere droogregime alleen een funktie van de aktuele temperatuur, de gemiddelde waterconcentratie en de oppervlakte waterconcentratie.

3. Bij het drogen van vlakke lagen met relatief hoge droogsnelheden kan de lengte van de periode van konstante droogsnelheid worden berekend met behulp van een konstante effektieve waarde van de diffusiecoëfficiënt, die onafhankelijk is van de droogsnelheid. Suzuki et al. beweren ten onrechte, dat deze effektieve diffusiecoëfficiënt, onder meer voor exponentiële concentratie-afhankelijkheid van de diffusiecoëfficiënt, gelijk kan worden gesteld aan de concentratie-gemiddelde diffusiecoëfficiënt.

   Suzuki, M. , Keey, R.B. & Maeda, S.
   Paper presented at the 80th National Meeting of the American Institute of Chemical Engineers, Boston (Mass.), September 7 - 10 (1975)

4. Door een ongelijkmatige verdeling van fluïdisatiegassen over de bodemplaat van een gefluïdiseerd bed kan segregatie van een heterogeen mengsel in het bed worden voorkomen (bijvoorbeeld: "spout-fluid" bed). Van dit verschijnsel kan gebruik gemaakt worden bij het pyrolyseren van huisvuil in een gefluïdiseerd heet zand-bed.

   Kox, W.M.A. , Afstudeerverslag Afdeling Scheikundige Technologie, T. H. Eindhoven (1975)

5. De beschrijving van de pyrolyse van hout met het "Unreacted Core Shrinking"- model, zoals voorgesteld door Maa, is onjuist. Met name de door deze auteur uitgevoerde extrapolatie van de benodigde reaktietijd naar kleine deeltjes-afmetingen, waar reaktiesnelheidslimitering optreedt, is niet geoorloofd.

   Maa, P.S. , Ph.D. Thesis, West Virginia University (1971)

6. Bij de extraktie van Zirconium-complexen, zoals disulfato-zirconyl ionen, uit een sterk zwavelzure oplossing (pH<1) met een oplossing van zware tertiaire aminen (bijvoorbeeld tri-n-octylamine) kan de co-extraktie van Niobium worden voorkomen door toevoeging van geringe hoeveelheden waterstofperoxide bij de bereiding van de moederoplossing. Deze toevoeging leidt tevens tot enige vergroting van de extraktie-snelheid van Zirconium.

   Schoeber, W.J.A.H. , Internal Report, Atomic Energy Commission, Research Establishment Risö, Roskilde, Denmark (1971)

7. De aanname van Massoth en Scarpiello, dat bij de reduktie van Bi_2O_3 met propeen de aselektieve reaktie tot CO_2 verwaarloosd mag worden, is aanvechtbaar.

   Massoth, F.E. & Scarpiello, D.A.
   J. Catal. 21, 225 - 238 (1971)

8. De ontwikkeling van de recycling in Nederland zou gediend zijn met minder overkoepelende instanties voor meer onderzoek.

9. Het ruwe imago, dat de waterpolosport bij velen heeft, wordt meer veroorzaakt door het feit, dat een aantal gebeurtenissen door het water aan een goede waarneming wordt onttrokken, dan door de gebeurtenissen, die werkelijk plaatsvinden.

28-5-1976 W.J.A.H.Schoeber