

# **Analysis of a one-component sorption in a single adsorbent particle by the orthogonal collocation method**

## **IV. One-point collocation method and linear-driving-force approximation\***

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A generally acceptable mathematical model for a sorption process (Second Fick's law) is studied in this paper. Various solutions of this diffusion equation are compared. A close connection of the one-point collocation method with a linear-driving-force approximation is shown. An attempt has been made to extend the applicability of the one-point collocation method for solving the mathematical model in the first steps of the sorption process.

В работе изучается общепринятая математическая модель для описания процесса сорбции (второй закон Фика). Сравниваются различные решения этого диффузионного уравнения. Показана близкая взаимосвязь метода одноточечной коллокации с приближением линейной движущей силы. Сделана попытка расширить приложимость метода одноточечной коллокации для решения математической модели на первых стадиях процесса сорбции.

In the previous papers we presented an analysis of the mathematical models of a one-component sorption in a single adsorbent particle under the isothermal behaviour assumption [1] and under the nonisothermal behaviour assumption [2]. The transients of average values of dimensionless adsorbate concentration and temperature rise in the particle were solved by the orthogonal collocation method in connection with the integration technique for solving the resulting system of ordinary differential equations. It was mentioned that for the first rapid steps of the adsorption process a greater number of collocation points is needed, but further a smaller number is sufficient for the same accuracy. A one-point collocation method is reported in this paper. A close connection of the one-point collocation with a linear-driving-force (LDF) approximation is shown. It is also explained why

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suitable caution must be exercised in the LDF approximation use in the internal diffusion dominant cases. In the last part of the paper an attempt has been made to extend the applicability of the one-point collocation method for solving the mathematical model in the first rapid steps of the sorption process.

### *Mathematical model*

In the previous paper we presented a rather general mathematical model of a one-component sorption in a single adsorbent particle, in which a particle is regarded as a solid, interspersed with very small pores [3]. Internal diffusion can then occur either by pore, or by surface diffusion or by both simultaneously. In the present investigation the isothermal homogeneous surface diffusion model will be studied. According to this model the adsorption process occurs at the outer surface of a pellet followed by the diffusion of the adsorbate in the adsorbed state. The mass transport in the spherical particle is described by the following unsteady-state equation (Second Fick's law)

$$\frac{\partial a}{\partial t} = D \left( \frac{\partial^2 a}{\partial r^2} + \frac{2}{r} \frac{\partial a}{\partial r} \right) \quad (1)$$

To simplify matters, the diffusivity is assumed to be constant. When the concentration of the adsorptive in the fluid outside a particle is constant and the effect of the external boundary film is negligible, eqn (1) is subject to the following initial and boundary conditions

$$\begin{aligned} a &= 0 & \text{at} & \quad 0 \leq r \leq R & \quad \text{for} & \quad t = 0 \\ \frac{\partial a}{\partial r} &= 0 & \text{at} & \quad r = 0 & \quad \text{for} & \quad t > 0 \\ a &= a^* & \text{at} & \quad r = R & \quad \text{for} & \quad t > 0 \end{aligned} \quad (2)$$

where  $a^*$  is the concentration in equilibrium with the fluid outside the pellet. By introducing dimensionless time parameter  $\tau$ , dimensionless radial coordinate  $x$ , dimensionless concentration  $q$  as

$$\tau = \frac{Dt}{R^2} \quad x = \frac{r}{R} \quad q = \frac{a}{a^*} \quad (3)$$

respectively, eqn (1) may be expressed in the following dimensionless form

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial x^2} + \frac{2}{x} \frac{\partial q}{\partial x} \quad (1a)$$

with the initial and boundary conditions

$$\begin{aligned}
 q &= 0 & \text{at} & \quad 0 \leq x \leq 1 & \quad \text{for} & \quad \tau = 0 \\
 \frac{\partial q}{\partial x} &= 0 & \text{at} & \quad x = 0 & \quad \text{for} & \quad \tau > 0 \\
 q &= 1 & \text{at} & \quad x = 1 & \quad \text{for} & \quad \tau > 0
 \end{aligned}
 \tag{2a}$$

Analytical solution of eqn (1a) and (2a) is well known [4]. Time dependence of mean internal concentration  $\bar{q}$  (see eqn (17)) is

$$\bar{q} = 1 - \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \exp(-k^2 \pi^2 \tau)
 \tag{4}$$

and the corresponding solution for small-time values is [4]

$$\bar{q} = 6 \sqrt{\frac{\tau}{\pi}} - 3\tau
 \tag{5}$$

For large values of  $\tau$  the first term of series (4) dominates the solution

$$\bar{q} = 1 - \frac{6}{\pi^2} \exp(-\pi^2 \tau)
 \tag{6}$$

After some mathematical manipulations we can get from eqns (5) and (6) the rate equations

$$\frac{d\bar{q}}{d\tau} = \frac{3}{\sqrt{\pi\tau}} - 3
 \tag{5a}$$

$$\frac{d\bar{q}}{d\tau} = \pi^2(1 - \bar{q})
 \tag{6a}$$

Eqn (6a) states that for sufficiently large  $\tau$ , the rate of diffusion in the particle becomes proportional to the difference between the amount that can be sorbed and that which has been sorbed. In this expression the rate of mass transfer is approximated as a linear function of the driving force (linear-driving-force (LDF) approximation). *Glueckauf* [5] and *Jury* [6] have shown that LDF approximation in the form

$$\frac{d\bar{q}}{d\tau} = 15(1 - \bar{q}) \quad \text{Glueckauf's LDF approximation}
 \tag{7}$$

provides a good approximation for many boundary conditions and for the linear isotherm. The corresponding expressions for the systems with equilibrium governed by a Langmuir isotherm [7] or by a Freundlich isotherm or for the systems in which the diffusivity is strongly concentration dependent [9] are in the form

$$\frac{d\bar{q}}{d\tau} = \eta_1 15(1 - \bar{q}) \quad (8)$$

where  $\eta_1$  is the correction factor to improve the LDF approximation and it can be found in the cited papers. Factor  $\eta_1$  is obtained by comparing the time slope of the curve of particle uptake vs. time, as in a packed bed [10] with the slope given by eqn (8) at  $\bar{q} = 0.5$ .

It was shown by Vermeulen [11] that eqn (4) is well approximated by the empirical expression

$$\bar{q} = [1 - \exp(-\pi^2\tau)]^{0.5} \quad (9)$$

which is equivalent to the following rate equation

$$\frac{d\bar{q}}{d\tau} = \pi^2 \frac{1 - \bar{q}^2}{2\bar{q}} \quad \text{Vermeulen's QDF approximation} \quad (10)$$

or in its general form

$$\frac{d\bar{q}}{d\tau} = \eta_2 15 \frac{1 - \bar{q}^2}{2\bar{q}} \quad (11)$$

where correction factors  $\eta_2$  for various systems can be found in [7]. Eqns (10) and (11) are the mathematical forms of the quadratic-driving-force (QDF) approximation.

Fig. 1 shows the comparison between  $\log d\bar{q}/d\tau$  computed from eqns (4), (5a), (6a), (7), and (10) which have been plotted against  $\log \tau$  as abscissa. The results

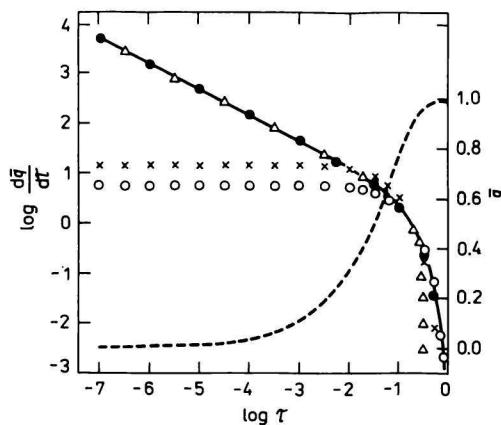


Fig. 1. Comparison of various solutions of "Second Fick's law".

— Exact solution, eqn (4); --- .

$\Delta$  Limiting solution for small  $\tau$  values, eqn (5a);  $\circ$  limiting solution for large  $\tau$  values, eqn (6);  
 $\times$  Glueckauf's LDF approximation, eqn (7);  $\bullet$  Vermeulen's QDF approximation, eqn (10).

indicate that Vermeulen's empirical QDF approximation gives excellent description of the diffusion process. Glueckauf's LDF approximation differs noticeably at the start of an investigated problem. Approximation (5a) is excellent for small  $\tau$ , but quite fails for  $\tau > 0.2$ . On the other hand, approximation (6a) is suitable only for the larger values of  $\tau$ .

The use of LDF approximation, eqns (6a), (7) or (8), is a familiar concept to represent the transport of mass and/or energy. It is another means of lumping parameters. Transport in a spatial direction down a gradient is replaced by the coefficient multiplied by the driving force. The point-to-point variation is neglected. When used in dynamic models the LDF approximation permits the process with spatial gradient, eqn (1a), to be described by an ordinary differential equation (eqns (6a) or (7)) with time as the only independent variable. However, in some cases we have assumed that empirical quantities such as the mass transfer coefficient can be used to represent transport processes even during periods of dynamic operation. LDF approximation is such an ingrained engineering concept that it is used quite naturally in dynamic models. However, it is strictly a steady state concept. In general it is not applicable in the unsteady state. Fortunately, in many dynamic applications it is a good approximation. From Fig. 1 it is apparent that the assumption that a distributed parameter system, eqn (1a), can be approximated by a lumped parameter model, eqns (6a) or (7), will be valid only if there is a much larger capacitance elsewhere in the system, so that the time needed for the mass transfer coefficient to decay to its steady state value is negligible in comparison with the response time of the remainder of the adsorption system. In other words, it means that the internal diffusion is not limiting the response time of the adsorption process.

### *Standard one-point collocation*

Orthogonal collocation is another means of "lumping parameters" The one-point collocation method (orthogonal collocation method with single internal collocation point) has been mentioned in numerous papers in recent years [12]. The main objective of this part is to show that one-point collocation is a means of obtaining typical LDF relations such as those in eqn (7). The derivation of the solution follows most conveniently if (1a) and (2) are rewritten in terms of  $u = x^2$  for  $0 \leq x \leq 1$

$$\frac{\partial q}{\partial x} = \frac{\partial q}{\partial u} \cdot 2 \sqrt{u} \quad \text{for } u \geq 0$$

$$\frac{\partial^2 q}{\partial x^2} = 2 \frac{\partial q}{\partial u} + 4u \frac{\partial^2 q}{\partial u^2}$$
(12)

Eqn (1a) is reformulated to

$$4u \frac{\partial^2 q}{\partial u^2} + 6 \frac{\partial q}{\partial u} = \frac{\partial q}{\partial \tau} \quad (13)$$

The boundary condition  $\partial q/\partial x = 0$  at  $x = 0$  is automatically satisfied in eqn (12). The boundary and initial conditions (2a) are consequently given as

$$\begin{aligned} q = 0 & \quad \text{at} \quad 0 \leq u \leq 1 & \quad \text{for} \quad \tau = 0. \\ q = 1 & \quad \text{at} \quad u = 1 & \quad \text{for} \quad \tau > 0 \end{aligned} \quad (14)$$

The one-point collocation version of eqn (13) is [1]

$$\frac{dq_1}{d\tau} = B_{11}q_1 + B_{12}q_2 = B_{12}(1 - q_1) \quad (15)$$

where

$$B_{12} = -B_{11} = \frac{6}{1 - u_1} \quad (16)$$

and  $q_1$  is the value of  $q$  at  $u_1 = x_1^2$ . Inserting  $u_1 = 0.6$  leads precisely to the choice of  $B_{12} = 15$ . The average concentration is found by the Gauss—Legendre quadrature

$$\bar{q} = 3 \int_0^1 qx^2 dx = \frac{3}{2} \int_0^1 q \sqrt{u} du = q(u = u_1) = q_1 \quad (17)$$

Then from eqns (15) and (17) we get

$$\frac{d\bar{q}}{d\tau} = 15(1 - \bar{q}) \quad (7)$$

which is the known Glueckauf's LDF approximation.

### *Improved one-point collocation*

Fig. 2 shows the typical concentration profiles at some selected values of  $\tau$  in a sphere [4]. From the figure it is evident that the position of the collocation point is quite disadvantageous in the first steps of the sorption process, when concentration at the collocation point is zero or nearly zero.

Now let us show how a one-point collocation can be used to obtain a solution that is accurate for small  $\tau$  values. The main purpose of this paper is to make an extension of the applicability of the one-point collocation method in eqn (1a) to small values of  $\tau$  following the *Paterson* and *Cresswell's* concept of a "burnt-out" and a "reaction" zone of the catalyst pellet problem with large Thiele modulus

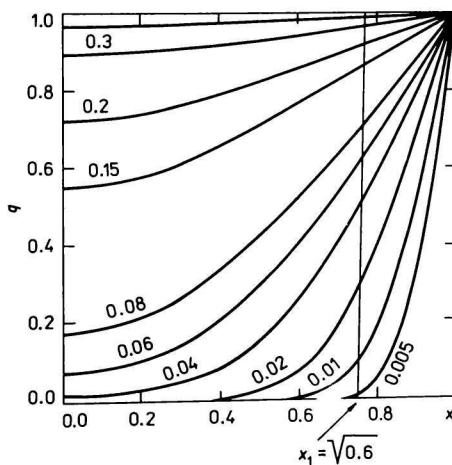


Fig. 2. Concentration distribution at various times in a sphere and position of a single standard collocation point  $x_1$ . Numbers on curves are values of dimensionless time  $\tau$ .

values [13]. This concept is a model approximation in which the dependent variable has been equated to zero in part of the range of independent variable  $x$  to treat steep profiles in catalyst pellets. We shall now formalize this procedure and point out to its application to our sorption (diffusion) problem. We shall introduce the following model simplification

$$q \quad \text{given by (1a)} \quad \text{for} \quad x \geq x_s \quad (18)$$

$$\frac{\partial q}{\partial x} = 0 \quad \text{for} \quad x \leq x_s$$

A new variable

$$v = \frac{x - x_s}{1 - x_s}$$

is introduced in the mass balance (1a)

$$\frac{1}{(1 - x_s)^2} \frac{\partial^2 q}{\partial v^2} + \frac{1}{(1 - x_s)} \frac{2}{x_s + v(1 - x_s)} \frac{\partial q}{\partial v} = \frac{\partial q}{\partial \tau} \quad (19)$$

The boundary conditions are

$$q = 1 \quad \text{at} \quad v = 1 \quad \text{for} \quad \tau > 0 \quad (20)$$

$$\frac{\partial q}{\partial v} = 0 \quad \text{at} \quad v \leq 0 \quad \text{for} \quad \tau > 0$$

If eqns (19) and (20) are again rewritten in terms of  $u = v^2$ , we get

$$\frac{\partial q}{\partial \tau} = \frac{4u}{(1-x_s)^2} \frac{\partial^2 q}{\partial u^2} + \left[ \frac{2}{(1-x_s)^2} + \frac{4\sqrt{u}}{(1-x_s)[x_s + \sqrt{u}(1-x_s)]} \right] \frac{\partial q}{\partial u} \quad (21)$$

The one-point collocation version of eqn (21) is

$$\frac{dq_1}{d\tau} = \left[ \frac{2}{(1-x_s)^2} + \frac{4\sqrt{u_1}}{(1-x_s)[x_s + \sqrt{u_1}(1-x_s)]} \right] \frac{1}{1-u_1} (1-q_1) \quad (22)$$

or

$$\frac{dq_1}{d\tau} = K(x_s) \cdot (1-q_1) \quad (23)$$

Inserting  $u_1 = 0.6$  leads to

$$K(x_s) = \left[ \frac{2}{(1-x_s)^2} + \frac{4\sqrt{0.6}}{(1-x_s)[x_s + \sqrt{0.6}(1-x_s)]} \right] 2.5 \quad (24)$$

where  $K(x_s)$  is the  $x_s$ -dependent mass transfer coefficient. Obviously, for  $x_s = 0$  we get  $K(x_s) = 15$ . It is simple to show that from eqn (1a)

$$\frac{\partial \bar{q}}{\partial \tau} = 3 \left( \frac{\partial q}{\partial x} \right)_{x=1}$$

or

$$\frac{\partial \bar{q}}{\partial \tau} = \frac{3}{1-x_s} \left( \frac{\partial q}{\partial v} \right)_{v=1} = \frac{6}{1-x_s} \left( \frac{\partial q}{\partial u} \right)_{u=1} \quad (25)$$

and the collocation version is

$$\frac{d\bar{q}}{d\tau} = \frac{6}{1-x_s} (A_{21}q_1 + A_{22} - 1) = \frac{6}{1-x_s} \frac{1}{1-u_1} (1-q_1) \quad (26)$$

The solution of eqn (23) is

$$q_1 = 1 - \exp[-K(x_s) \cdot \tau] \quad (27)$$

and after substituting of 0.6 for  $u_1$  in (26) we get

$$\frac{d\bar{q}}{d\tau} = \frac{15}{(1-x_s)} \exp[-K(x_s) \cdot \tau] \quad (28)$$



From eqns (28) and (5) it is possible to find the exact values of  $x_s$  and  $K(x_s)$  for any  $\tau$ , or in other words, the exact value of mass transfer coefficient  $K(x_s)$ . The results are presented in Table 1.

Table 1

Values of  $q_1$  and  $K(x_s)$  for small  $\tau$  values

$x_s$	$\tau$	$K(x_s)$	$q_1$
0.999	$3.231 \times 10^{-7}$	5 007 748	0.8017
0.990	$3.192 \times 10^{-5}$	50 776	0.8023
0.900	$2.857 \times 10^{-3}$	579	0.8089
0.800	$1.027 \times 10^{-2}$	166	0.8173
0.700	$2.106 \times 10^{-2}$	83	0.8267

From the tabulated results the following conclusion is apparent: The value of  $q_1$  is almost constant in the first steps of the sorption process. It is convenient to use this fact for the numerical solution of eqn (22). The results presented here can easily be organized into an algorithm for solving eqn (22) in the first steps of the sorption process. Spline point  $x_{s1}$  is chosen. The length of a suitable interval  $(1 - x_{s1})$  can be arbitrarily chosen as, for example  $(1 - x_s) = 0.001$  at the start of the computation. Next we integrate eqn (22) and check the condition  $q_1 > 0.8$ . If it is so the length of new interval  $(1 - x_{s2})$  is estimated as  $10 \cdot (1 - x_{s1})$  and the next integration can run in the same way. Computational results are shown in Fig. 3.

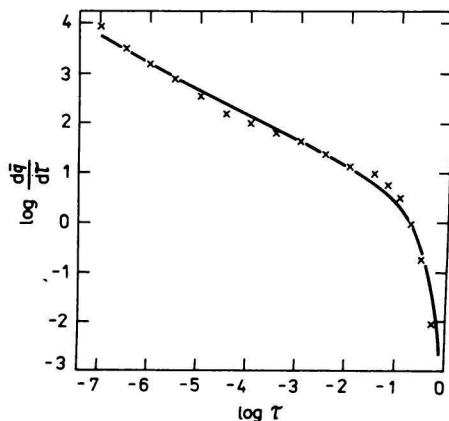


Fig. 3. Improved one-point collocation method.

Starting spline point  $x_{s1} = 0.999$ .

— Exact solution, eqn (4).

× Improved one-point collocation, eqn (28).

## Conclusion

The results presented in this paper can be divided into three parts:

1. Glueckauf's LDF approximation gives unsatisfactory description of the sorption (diffusion) process for small-time values. Vermeulen's empirical QDF approximation, on the other hand, is excellent for the whole range of  $\tau$ .

2. Glueckauf's LDF approximation can be derived when the one-point collocation method with  $u_1 = 0.6$  as the position of the collocation point, combined with the Gauss—Legendre quadrature, is applied in the diffusion equation (Second Fick's law).

3. A simple algorithm is suggested to solve the diffusion equation, based on the Cresswell and Paterson's concept. Dividing the particle into two parts — “sorption” and “nonactive” zones — and applying the one-point collocation procedure in the sorption zone we can obtain fairly accurate results for small-time values as well.

## Symbols

$a$	adsorbate concentration in particle	$\text{mol m}^{-3}$
$a^*$	equilibrium adsorbate concentration	$\text{mol m}^{-3}$
$B_{11}, B_{12}$	differentiation weights	1
$D$	diffusivity	$\text{m}^2 \text{s}^{-1}$
$K(x_s)$	$x_s$ — dependent mass transfer coefficient	1
$q$	dimensionless adsorbate concentration	1
$q_1, q_2$	dimensionless concentrations at the collocation points	1
$\bar{q}$	average dimensionless adsorbate concentration	1
$R$	radius particle	m
$t$	time	s
$u$	dimensionless radial coordinate $u = x^2$	1
$u_1$	position of the collocation point	1
$v$	dimensionless variable	1
$x$	dimensionless radial coordinate	1
$x_1$	position of the collocation point	1
$x_s$	position of the spline point	1
$\eta_1$	correction factor defined by eqn (8)	1
$\eta_2$	correction factor defined by eqn (11)	1
$\tau$	dimensionless time	1

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